Fluctuation formulas in molecular-dynamics simulations with the weak coupling heat bath

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The statistical mechanical ensemble associated with molecular-dynamics (MD) simulations with the weak coupling (WC) thermostat proposed by Berendsen *et al.* [J. Chem. Phys. **81**, 3684 (1984)] is analyzed. Using a generalized Liouville equation, an approximate equilibrium distribution function in the configurational space for the WC thermostat is obtained. From this distribution function, fluctuation formulas associated with the constant volume specific heat C_v, pressure coefficient γ_v, and isothermal compressibility β_T are obtained. The validity of the derived distribution function and the fluctuation formulas were examined in a Lennard-Jones fluid. C_v and γ_v calculated from the formulas for the WC thermostat agree very well with those obtained in the canonical or microcanonical MD. © *2000 American Institute of Physics.* [S0021-9606(00)51932-1]

I. INTRODUCTION

Molecular dynamics (MD) simulations have been carried out in various fields and significant understanding has been achieved for many physical and chemical problems. To apply MD simulations to various situations, several extensions of MD method have been proposed. The constant temperature or pressure methods are typical extensions, which realize MD simulations under constant temperature or pressure conditions.

The velocity scaling scheme by Woodcock[1] is the first attempt to realize constant temperature MD. Schneider and Stoll[2] employed another strategy in which a Langevin equation (a stochastic coupling with a heat bath) was used instead of Newton's equation for particles. In 1980, Andersen[3] introduced a similar constant temperature method which is a hybrid of MD and Monte Carlo simulations. Particles suffer the stochastic collisions with a Poisson process and their velocities are chosen at random from a Maxwellian distribution after each collision. However, in the method with random force, the trajectory in the phase space is discontinuous by the fictitious collisions, although they can realize the canonical ensemble (C.E.) in the phase space. From the formulations in the nonequilibrium MD simulations, Hoover *et al.*[4] and Evans[5] proposed the Gaussian thermostat. This is based on Gauss' principle of least constraint and momentum $\mathbf{p}_i$ is forced to keep kinetic energy $K(=\Sigma \mathbf{p}_i^2/2m_i)$ to a constant. This method yields the C.E. in the configurational space $(\mathbf{q}_i)$. In addition, it is proved[6] that Woodcock's velocity scaling scheme in the Verlet (leapfrog) algorithm is close to the Gaussian thermostat; the difference in the equation of motion (EOM) is $O(\Delta t)$ (Δt is a time step in MD simulations). Haile and Gupta[7] showed that the velocity scaling scheme and the Gaussian thermostat are obtained from a generalized potential and a generalized force attached to Newton's EOM, respectively. However, the reformulated velocity scaling scheme in Ref. 7 [the Haile–Gupta (HG) thermostat] does not generate the same trajectory in the phase space as the velocity scaling in the leapfrog algorithm (see the Appendix). Nosé proposed the method which produces the rigorous C.E. in 1984.[8,9] The extended system method first introduced in Andersen's constant pressure MD[3] is incorporated in this method. Hoover[10] modified its formulation (the Nosé–Hoover thermostat), and it is the most widely used method at present. Recently, its modifications were also reported.[11,12]

In the same year, Berendsen and co-workers introduced another type of the constant temperature method.[13] This is derived by eliminating local disturbance from random noise in a Langevin equation. Only the global coupling with a heat bath remains, so that it results in relatively modest temperature controlling. This method is called ''weak coupling (WC) thermostat'' or ''Berendsen thermostat.'' This thermostat is easily employed in the leapfrog algorithm. Although integrations are not under the accuracy of the Verlet algorithm [the difference is $O(\Delta t)$ in the EOM], the velocity scaling with the following factor realize the weak coupling with a heat bath

$$S_{\mathrm{WC}}=\sqrt{1+\frac{\Delta t}{\tau}\left(\frac{T_0}{T}-1\right)}, \tag{1.1}$$

where T_0 is the pre-set temperature, T is the instantaneous temperature associated with kinetic energy K, and τ is a coupling parameter which determines the strength of coupling with a heat bath. Due to its simplicity, the WC thermostat is often used in MD for biological systems such as protein. Unfortunately, a corresponding statistical mechanical ensemble for this thermostat is unknown so far. In previous studies employing the WC thermostat,[14,15] it is reported that fluctuations of thermodynamic properties are coincident with neither those in the C.E. nor microcanonical ensemble (M.E.). Generally, ensemble averages are identical in differ-

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ent ensembles (e.g., C.E. and M.E.). However, fluctuations of thermodynamic properties are different[16,17] and fluctuation formulas associated with thermodynamic derivatives such as $C_v(=\partial E/\partial T)$ are also dependent on the statistical ensemble.[16–18] Therefore, it is clear that the statistical ensemble associated with the WC thermostat is neither the C.E. nor M.E.

In this study, an approximate expression of the equilibrium distribution function in the configurational space for the WC thermostat is presented. It is obtained from an assumed relation, $\delta K=-\alpha(\tau)\delta\Phi$, where δK and $\delta\Phi$ are fluctuations of kinetic and potential energy, respectively and α only depends on τ. This distribution function is dependent on the parameter τ and a corresponding statistical ensemble can change from the C.E. to M.E. according to τ. The fluctuation formulas for various thermodynamic properties are derived by the distribution function. From these formulas, expressions for the constant volume specific heat C_v, thermal pressure coefficient $\gamma_v(=\partial P/\partial T)$, and the isothermal compressibility $\beta_T(=-V^{-1}(\partial V/\partial P)_T)$ are obtained.

These formulas were examined in a Lennard-Jones (12-6) fluid. In the MD simulations with the WC thermostat, C_v and γ_v were calculated by formulas for the WC thermostat, and they are in good agreement with those calculated in the C.E. and M.E.

In Sec. II, a brief review of the WC thermostat is described. The approximate distribution function and fluctuation formulas for the WC thermostat are shown in Sec. III. The validity of these analyses are examined in Sec. IV. Finally, our conclusion is drawn in Sec. V. It is also found that the HG thermostat corresponds to the special case of the WC thermostat (with $\alpha=1/2$). The relation will be described in the Appendix.

II. WEAK COUPLING THERMOSTAT

Berendsen and co-workers introduced a constant temperature technique by the modification of a Langevin equation.[13] This method mimics the global energy exchange between an ionic system and an external heat bath in a Langevin equation, while local coupling by random noise is eliminated. Comparing other constant temperature methods, it is a relatively modest scheme for temperature controlling. The equations of motion (EOM) with the weak coupling thermostat are

$$\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m_i}, \tag{2.1}$$

$$\dot{\mathbf{p}}_i=-\frac{\partial\Phi}{\partial\mathbf{q}_i}+\eta\mathbf{p}_i, \tag{2.2}$$

where

$$\eta=\frac{1}{2\tau}\left(\frac{T_0}{T}-1\right). \tag{2.3}$$

The quantity Φ is potential energy, T_0 is the pre-set temperature, T is the instantaneous temperature associated with kinetic energy K, and τ is a coupling parameter which controls the strength of coupling with a heat bath. τ relates the decay time of energy fluctuations. Using Eq. (2.2) and the following relations:

$$\sum_i \dot{\mathbf{p}}_i\cdot\frac{\mathbf{p}_i}{m_i}=\frac{dK}{dt}, \tag{2.4}$$

$$\sum_i \dot{\mathbf{q}}_i\cdot\frac{\partial\Phi}{\partial\mathbf{q}_i}=\frac{d\Phi}{dt}, \tag{2.5}$$

we can rewrite η as

$$\eta=\frac{1}{2K}\left(\frac{dK}{dt}+\frac{d\Phi}{dt}\right)=\frac{1}{2K}\frac{dE}{dt}. \tag{2.6}$$

These equations are solved in MD simulations with the velocity scaling in the leapfrog algorithm as described in Sec. I. Ignoring terms of $O(\Delta t)$ in the EOM, this scaling is consistent with Eqs. (2.1) and (2.2). However, this is not performed under accuracy in the Verlet algorithm, where $O(\Delta t^2)$ is ignored. With the ''modified'' velocity scaling scheme recently proposed by the author,[19] integrations can be performed within the Verlet's accuracy unless τ is $O(\Delta t)$.

In the WC thermostat, τ is a key factor which determines the behavior of an ionic system and a heat bath. It is easily recognized that with large τ, η approaches 0 and Eq. (2.2) becomes Newton's EOM (i.e., the M.E. is realized). On the contrary, energy exchange between an ionic system and a heat bath becomes large with small τ. In particular, when τ equals Δt, S_{WC} becomes $\sqrt{T_0/T}$ and this is the same scaling factor as Woodcock's original one.[1] In this situation, the fluctuation of kinetic energy ΔK is suppressed entirely and the WC thermostat becomes close to the Gaussian thermostat,[4,5] which corresponds to the canonical ensemble in the configurational space.

Unfortunately, except these limiting cases, a statistical ensemble corresponding to the WC thermostat is unknown so far. In the following sections, an approximate equilibrium distribution function in the configurational space for ''WC ensemble (W.E.)'' is presented. Fluctuation formulas for thermodynamic properties in the W.E. are also presented, and their validity is examined in MD simulations of Lennard-Jones (LJ) fluid (Sec. IV).

III. ANALYSIS OF THE WC THERMOSTAT

A. Equilibrium distribution function for the WC ensemble

A generalized Liouville equation in the phase space $\mathbf{\Gamma}(\mathbf{q},\mathbf{p})$ is described,[6,20] as

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial\mathbf{\Gamma}}\cdot(\dot{\mathbf{\Gamma}}f)=0, \tag{3.1}$$

where $f(\mathbf{q},\mathbf{p})$ is an equilibrium distribution function. This equation is easily re-expressed as

$$\frac{df}{dt}=-\left(\frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}\right)f. \tag{3.2}$$

To obtain the right-hand side of Eq. (3.2) for the W.E., we employ the following relation:

$$\frac{1}{2K} \simeq \frac{1}{3NkT_0}\left(1-\frac{2\delta K}{3NkT_0}+\frac{4(\delta K)^2}{(3NkT_0)^2}+O(N^{-3/2})\right), \quad (3.3)$$

where k is Boltzmann's constant, and N is the number of particles. We assume an equilibrium state with the thermostat in Eq. (3.3). Consequently, η can be re-expressed as

$$\eta=\frac{1}{2K}\frac{dE}{dt}\simeq\frac{1}{3NkT_0}\frac{dE}{dt}-\frac{2\delta K}{(3NkT_0)^2}\frac{dE}{dt} + \frac{4(\delta K)^2}{(3NkT_0)^3}\frac{dE}{dt}+O(N^{-2}). \quad (3.4)$$

From this relation and Eqs. (2.1) and (2.2), we can obtain the following:

$$\frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}=\sum_i\frac{\partial(\eta\mathbf{p}_i)}{\partial\mathbf{p}_i} =3N\eta+\sum_i\mathbf{p}_i\cdot\frac{\partial\eta}{\partial\mathbf{p}_i} =\left(\frac{1}{kT}-\frac{2\delta K}{3N(kT)^2}+O(N^{-1})\right)\frac{dE}{dt}+Q(\mathbf{p}), \quad (3.5)$$

where $Q(\mathbf{p})$ is a quantity which only depends on the momentum space. T_0 is replaced by T. Hereafter, we focus on the configurational space, and omit $Q(\mathbf{p})$ which does not contribute to $f(\mathbf{q})$. As a result, Eq. (3.2) for the WC thermostat is given as

$$\frac{df}{dt}=-\left[\frac{1}{kT}-\frac{2\delta K}{3N(kT)^2}+O(N^{-1})\right]\frac{d\Phi}{dt}f. \quad (3.6)$$

We can, here, obtain $f(\mathbf{q})$ for the W.E. when τ approaches very small or infinity. The fluctuation of kinetic energy δK tends to 0 when τ is very small $[\sim O(\Delta t)]$. In this case, ignoring terms of $O(N^{-1})$, above equation becomes

$$\frac{1}{f}\frac{df}{dt}=-\frac{1}{kT}\frac{d\Phi}{dt}. \quad (3.7)$$

This is easily solved and the solution is

$$f(\mathbf{q})=\exp[-\Phi(\mathbf{q})/kT]. \quad (3.8)$$

This is the same distribution function as that in the C.E. On the contrary, δK becomes $-\delta\Phi(\delta E=0)$ when τ approaches infinity. In this case, Eq. (3.6) becomes

$$\frac{1}{f}\frac{df}{dt}=-\left(\frac{1}{kT}\frac{d\Phi}{dt}+\frac{2\delta\Phi}{3N(kT)^2}\frac{d\Phi}{dt}\right). \quad (3.9)$$

The solution is

$$f(\mathbf{q})=\exp\left[-\frac{\Phi(\mathbf{q})}{kT}-\frac{1}{3N}\left(\frac{\delta\Phi(\mathbf{q})}{kT}\right)^2\right]. \quad (3.10)$$

This is the same distribution function as that in the M.E.[21] Above results confirm that the statistical ensemble is dependent on the coupling parameter τ as described in Sec. II.

The fluctuation of kinetic energy δK changes according to τ. It is formally expressed as

$$\delta K=-\left(1-\frac{\delta E}{\delta\Phi}\right)\delta\Phi. \quad (3.11)$$

Now, we assume that the inside of the bracket in Eq. (3.11) is replaced by a constant in equilibrium

$$\delta K\simeq-\alpha\delta\Phi, \quad (3.12)$$

where α is a constant but dependent on τ. The parameter $\alpha(\tau)$ is considered as a ratio of averaged $|\delta K|$ and $|\delta\Phi|$. Upon this assumption, Eq. (3.6) becomes

$$\frac{1}{f}\frac{df}{dt}=-\left(\frac{1}{kT}+\frac{2\alpha\delta\Phi}{3N(kT)^2}+O(N^{-1})\right)\frac{d\Phi}{dt}, \quad (3.13)$$

and the solution is given as

$$f(\mathbf{q})=\exp\left[-\frac{\Phi(\mathbf{q})}{kT}-\frac{\alpha}{3N}\left(\frac{\delta\Phi(\mathbf{q})}{kT}\right)^2\right]. \quad (3.14)$$

Within this assumption, this is the equilibrium distribution function in the configurational space for the WC ensemble.

During MD runs of a LJ system, it is observed that K or E roughly follows the behavior of Φ. In particular, this is evident when large or small τ is employed. This behavior was also reported in liquid water in the original paper by Berendsen *et al.* From these results, the assumption of Eq. (3.12) seems to be reasonable. In simulations, α is determined from the ratio of standard deviations of Φ and K

$$\alpha=\sqrt{\langle(\delta K)^2\rangle/\langle(\delta\Phi)^2\rangle}, \quad (3.15)$$

where $\langle\,\rangle$ denotes time average.

The full part of $f(\mathbf{q},\mathbf{p})$ for the W.E. is still unknown. It seems to be difficult to obtain the exact $f(\mathbf{q},\mathbf{p})$ because the phase space trajectory in the momentum space is confined to some region according to τ. Some constraint in the momentum space is imposed under the WC thermostat. However, most of thermodynamic properties we are interested in are only dependent on the configurational space, and the kinetic part of thermodynamic derivatives such as C_v can be obtained analytically. Therefore, $f(\mathbf{q})$ in the configurational space is sufficient to study thermodynamic properties. The full part of $f(\mathbf{q},\mathbf{p})$ in constant temperature MD is available only for Nosé's type heat bath unless random forces are used.

B. Fluctuation formulas

From the distribution function for the WC thermostat, we can obtain fluctuation formulas associated with the constant volume specific heat C_v, thermal pressure coefficient γ_v, and isothermal compressibility β_T.

The expressions for C_v, γ_v, and β_T are different in each statistical ensemble. However, the ideal gas parts of C_v and γ_v are already known as

$$C_v^K=\frac{3}{2}Nk, \quad (3.16)$$

$$\gamma_v^K=\frac{N}{V}k, \quad (3.17)$$

where $C_v=C_v^K+C_v^\Phi$ and $\gamma_v=\gamma_v^K+\gamma_v^\Phi$. Thus, only the residual parts, C_v^Φ and γ_v^Φ, are calculated in MD simulations. In the C.E., their expressions are well known and given[17,18] as

$$C_v^{\Phi}=\frac{k\langle(\delta\Phi)^2\rangle_{\text{C.E.}}}{(kT)^2}, \tag{3.18}$$

$$\gamma_v^{\Phi}=\frac{1}{V}\frac{\partial\langle W\rangle_{\text{C.E.}}}{\partial T}=\frac{\langle\delta W\delta\Phi\rangle_{\text{C.E.}}}{VkT^2}, \tag{3.19}$$

$$\beta_T^{-1}=\left[\langle\Theta\rangle_{\text{C.E.}}+P-\frac{\langle(\delta W)^2\rangle_{\text{C.E.}}}{kTV}\right], \tag{3.20}$$

where

$$\Theta=\frac{1}{9V}\sum_i\sum_{j>i}\sum_k\sum_{l>k}\left(\mathbf{R_{ij}}\cdot\frac{\partial}{\partial\mathbf{R_{ij}}}\right)\left(\mathbf{R_{k1}}\cdot\frac{\partial}{\partial\mathbf{R_{k1}}}\right)\Phi, \tag{3.21}$$

and $\mathbf{R_{ij}}=\mathbf{q_i}-\mathbf{q_j}$. W is the internal virial and P is the internal pressure expressed by

$$P=\frac{N}{V}kT+\frac{\langle W\rangle}{V}. \tag{3.22}$$

Ensemble averages in the C.E. are denoted as $\langle\Theta\rangle_{\text{C.E.}}$. In the M.E., Lebowitz *et al.* and Cheung derived the following expressions by the transformation formula from the C.E. to M.E.:[16,18]

$$C_v^{\Phi}=\frac{k\langle(\delta\Phi)^2\rangle_{\text{M.E.}}}{(kT)^2-2\langle(\delta\Phi)^2\rangle_{\text{M.E.}}/3N}, \tag{3.23}$$

$$\gamma_v^{\Phi}=\frac{\langle\delta W\delta\Phi\rangle_{\text{M.E.}}}{VkT^2}\left(1+\frac{2C_v^{\Phi}}{3Nk}\right), \tag{3.24}$$

$$\beta_S^{-1}=\left[\langle\Theta\rangle_{\text{M.E.}}+P-\frac{\langle(\delta W)^2\rangle_{\text{M.E.}}}{kTV}+\frac{TV}{C_v}(\gamma_v^2-\gamma_v^{\Phi 2})\right], \tag{3.25}$$

where β_S is the adiabatic compressibility: $\beta_S^{-1}=\beta_T^{-1}+TV\gamma_v^2/C_v$.

Considering that the WC ensemble has the intermediate property between the C.E. and M.E., the following fluctuation formulas for the W.E. are obtained by the similar procedure described in Ref. 16:

$$\langle(\delta\Phi)^2\rangle_{\text{W.E.}}=(kT)^2\Big/\left(\frac{k}{C_v^{\Phi}}+\frac{2\alpha}{3N}\right), \tag{3.26}$$

$$\langle\delta W\delta\Phi\rangle_{\text{W.E.}}=VkT^2\gamma_v^{\Phi}\Big/\left(1+\frac{2\alpha C_v^{\Phi}}{3Nk}\right), \tag{3.27}$$

$$\langle(\delta W)^2\rangle_{\text{W.E.}}=kTV\left[-\beta_T^{-1}+\langle\Theta\rangle_{\text{W.E.}}+P-\frac{2\alpha TV\gamma_v^{\Phi 2}}{3Nk+2\alpha C_v^{\Phi}}\right], \tag{3.28}$$

where α is given in Eq. (3.15). As a result, expressions for C_v, γ_v, and β_T are the following:

$$C_v^{\Phi}=\frac{k\langle(\delta\Phi)^2\rangle_{\text{W.E.}}}{(kT)^2-2\alpha\langle(\delta\Phi)^2\rangle_{\text{W.E.}}/3N}, \tag{3.29}$$

$$\gamma_v^{\Phi}==\frac{\langle\delta W\delta\Phi\rangle_{\text{W.E.}}}{VkT^2}\left(1+\frac{2\alpha C_v^{\Phi}}{3Nk}\right), \tag{3.30}$$

$$\beta_T^{-1}=\left[\langle\Theta\rangle_{\text{W.E.}}+P-\frac{\langle(\delta W)^2\rangle_{\text{W.E.}}}{kTV}-\frac{2\alpha TV\gamma_v^{\Phi 2}}{3Nk+2\alpha C_v^{\Phi}}\right]. \tag{3.31}$$

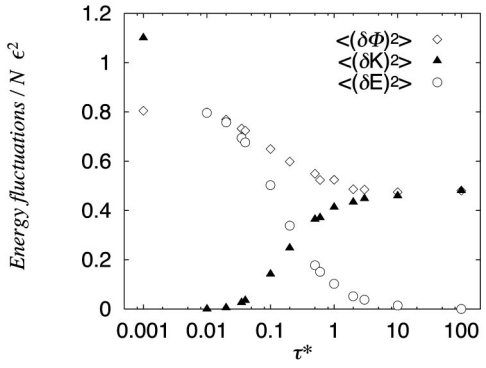


FIG. 1. Fluctuations of Φ, K, and E obtained in four MD runs. Results in the run1 are plotted at $\tau^*=100$ and those in the run2 are at $\tau^*=0.001$. In the run4, results were obtained at various $\tau^*(0.01\sim10)$ but at $\tau^*=0.01$, the run4 is coincident with the run3. In the run2 ($\tau^*=0.001$), $(\delta E)^2$ is so large (~1.91) and not plotted. ϵ is the unit for energy in LJ systems.

These expressions are identical with those in the C.E. or M.E. when α approaches 0 or 1, respectively. The quantities C_v, γ_v, and β_T are independent of the statistical ensemble and hence, are the same values in each ensemble. Therefore, comparing the same quantities calculated by fluctuation formulas in different ensembles, we can verify these fluctuation formulas and new derived distribution function for the W.E.

In the next section, applications of above results to LJ fluid are presented. In each MD simulation for the C.E., M.E., and W.E., C_v^{Φ} and γ_v^{Φ} were calculated by the formulas described in this section. It is found that they are in good agreement with each other.

IV. APPLICATIONS

The results in Sec. III were applied to LJ (12-6) fluid. A cubic MD cell containing 864 particles were employed and periodic boundary conditions were imposed. The reduced number density ρ^* was set to 0.85 and reduced temperature was to 0.870 344, which was the obtained temperature in the microcanonical MD. Cutoff range R_c^* of LJ interaction was 3σ. Time evolution was performed by the leapfrog algorithm with a time step $\Delta t^*=0.01$. Time averages for fluctuations were obtained over 500 000 steps (~3 ns).

Four separate runs were carried out. They are the microcanonical MD (run1), Nosé–Hoover MD (run2), MD with the velocity scaling (run3), and with the WC thermostat (run4). In the run3, the velocity scaling with the factor $\sqrt{T_o/T}$ was performed at every time step: this is nearly the Gaussian thermostat.[6] All runs were started with the same initial conditions prepared in a microcanonical MD of 7000 steps.

In Fig. 1, energy fluctuations, $(\delta\Phi)^2$, $(\delta K)^2$, and $(\delta E)^2$, are shown. In the run4, they were obtained at several τ^* and plotted in the region from $\tau^*=0.01$ to $\tau^*=10$. At $\tau^*=0.01$, the run4 is coincident with the run3. Clearly, fluctuations change according to τ. Fluctuations in the run1 are plotted at $\tau^*=100$ and those in the run2 were at $\tau^*=0.001$. They do not relate with τ at all and plotted just for showing their tendency (i.e., larger τ leads to the M.E. and smaller τ, the C.E.). In the run2, $(\delta E)^2$ is larger than those in

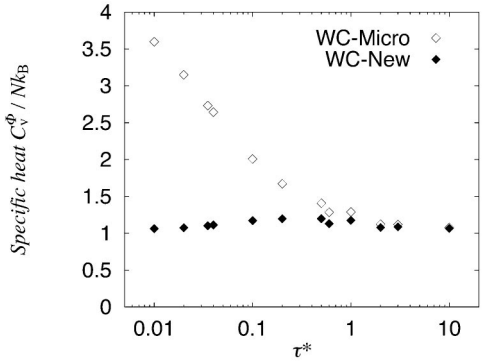


FIG. 2. The residual part of the specific heat (C_v^Φ) obtained in the run4. They were calculated by the two formulas (see text). The values of C_v^Φ in the run1 and run2 are 1.092 and 1.062, respectively.

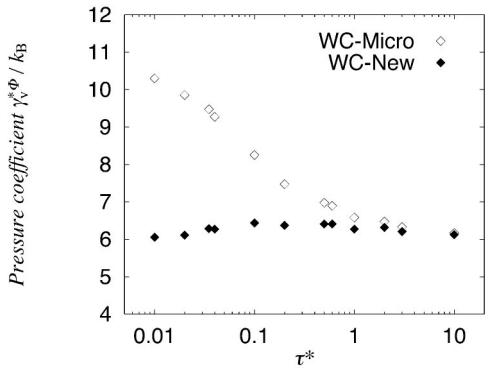


FIG. 3. The residual part of the pressure coefficient (γ_v^Φ) obtained in the run4, but shown in terms of $\gamma_v^{*\Phi}(=\gamma_v^\Phi/\rho)$. They were calculated by the two formulas (see text). The values of $\gamma_v^{*\Phi}$ in the run1 and run2 are 6.068 and 6.037, respectively.

other runs ($\sim$1.91) and not plotted in Fig. 1. In the run1 ($\tau=100$), $(\delta\Phi)^2$ and $(\delta K)^2$ are almost the same, while in the run3 ($\tau^*=0.01$), $(\delta\Phi)^2$ and $(\delta E)^2$ are hard to distinguish.

The relations between fluctuations and τ in the run4 are clear and simple. At small τ^*, $(\delta\Phi)^2$ in the run4 is close to that in the run2 ($\tau^*=0.001$) and run3 ($\tau^*=0.01$). On the contrary, it is nearly the same as that in the run1 ($\tau^*=100$) with large τ^*. In the intermediate region, $(\delta\Phi)^2$ in the run4 is larger than that in the run1 but smaller than those in the run2 and run3. The similar results were reported in Ref. 13–15. The tendency in the W.E. mentioned before is clearly confirmed. It is also found that $(\delta\Phi)^2$ in the run3 is nearly the same as that in the run2. This confirms that both of the Nosé–Hoover and Gaussian (velocity scaling) thermostats produce the same statistical ensemble in the configurational space (i.e., the canonical ensemble).

Figure 2 shows the constant volume specific heat (C_v^Φ/N) in the run4 obtained by the fluctuation formulas. Results labeled by ''WC-Micro'' were obtained by Eq. (3.23), while those labeled by ''WC-New'' were by Eq. (3.29). The specific heat was also calculated in the run1 and run2. They were calculated by Eqs. (3.23) and (3.18), respectively, and obtained values are 1.092 and 1.062. They are in quite good agreement with each other. The results of ''WC-Micro'' in Fig. 2 deviate from the correct value ($\sim$1.1) with decreasing τ^*, although they are close to 1.1 with large τ^*. On the contrary, ''WC-New'' approximately give the correct values at any τ^*. Deviations from the correct value are within only 7%. This means that the formula of Eq. (3.29) and the derived distribution function in Sec. III are remarkably valid.

The constant volume pressure coefficient (γ_v^Φ) was also calculated in a similar way. In Fig. 3, $\gamma_v^{*\Phi}(=\gamma_v^\Phi/\rho)$ obtained in the run4 are shown. Calculated values in the run1 and run2 are 6.068 and 6.037, respectively. The results of ''WC-New'' are all close to 6.1 within the error of 7%, while ''WC-Micro'' fails to give the correct value at small τ^*. The behavior of $\gamma_v^{*\Phi}$ is the same as C_v^Φ. In both calculations, the formulas for C_v^Φ and $\gamma_v^{*\Phi}$ in the W.E. give correct values at any τ. They are in good agreement with the previous MD results in the LJ system[16] and the present results in the canonical and microcanonical MD. Slight deviations are found at middle τ^* ($\sim$0.2) in both C_v^Φ and $\gamma_v^{*\Phi}$. This indicates that the approximation of Eq. (3.12) is not so valid as in other τ^* region. However, even at $\tau^*\simeq 0.2$, the errors are within 7%.

From above results, we can confirm that the derived distribution function for the W.E. is available not only for statistical ensemble averages, but also for fluctuations associated with C_v, γ_v, and so on.

V. CONCLUSION

An approximate expression for the equilibrium distribution function in the configurational space for the WC thermostat was presented. This was derived under the simple approximation and fluctuation formulas in the W.E. were also obtained. In the MD simulation of LJ fluid with the WC thermostat, C_v^Φ and γ_v^Φ were calculated at various τ by the derived formulas and they are all in good agreement with the correct values, which were obtained in the canonical and microcanonical MD. This result shows that the simple relation, $\delta K=-\alpha(\tau)\delta\Phi$, is roughly held at any τ and the derived distribution function represents the characteristic feature of the WC thermostat. Even at middle τ ($\tau^*\simeq 0.2$ in LJ fluid), at which the relation may be weakened, the errors in C_v^Φ and γ_v^Φ are within 7% in LJ fluid. The similar behavior of energy fluctuations with the WC thermostat was observed in previous studies. It is considered that the presented distribution function is available in other systems. It should be noted that thermal equilibration over all degrees of freedom is necessary to obtain thermodynamic properties correctly, but it is sometimes difficult in complex systems such as proteins.

The statistical mechanical ensemble for the WC thermostat has the intermediate property between C.E. and M.E. The similar ensemble was reported in Ref. 9: This is associated with the constant temperature scheme presented by Haile and Gupta (the HG thermostat).[7] This ensemble corresponds to the W.E. with $\alpha=1/2$ in the configurational space. In the Appendix, the derivation of the equilibrium distribution function for the HG thermostat is described.

The present study shows that the WC thermostat does not produce the canonical ensemble but another ensemble. Eliminating random forces in a Langevin equation fails to

produce the C.E. However, the global (weak) coupling with a heat bath produces the WC ensemble presented in this study. This ensemble can be changed from the C.E. to M.E. according to coupling strength of a heat bath (τ). This is the unique feature of the WC ensemble. It approaches the canonical ensemble with small τ, at which the global coupling works as nearly the local disturbance (e.g., random forces) and energy exchange between an ionic system and a heat bath becomes large. With large τ, on the contrary, energy exchange are suppressed and it approaches to the microcanonical ensemble. Since the WC thermostat can change the behavior of the system only by controlling parameter τ, we can use this thermostat in various situations without any changes in the algorithm.

More accurate integrations (under the Verlet's accuracy) with the velocity scaling in the leapfrog algorithm for the WC thermostat can be also implemented. This scaling scheme will be presented with applications to other constant temperature or/and pressure methods in a forthcoming paper.[19]

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APPENDIX: THE STATISTICAL ENSEMBLE FOR THE HG THERMOSTAT

It is found that the Haile–Gupta (HG) thermostat[7] is a special case of the WC thermostat with respect to the equilibrium distribution function in the configurational space. Nosé has already shown the distribution function for the HG thermostat.[9] In this Appendix, we show another derivation for the distribution function (from a generalized Liouville equation).

The EOM for particles with the HG thermostat are

$$\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{Sm_i}=\frac{\mathbf{p}_i'}{m_i}, \tag{A1}$$

$$\dot{\mathbf{p}}_i=-\frac{\partial\Phi}{\partial\mathbf{q}_i}, \tag{A2}$$

or

$$\dot{\mathbf{p}}_i'=\frac{1}{S}\left[-\frac{\partial\Phi}{\partial\mathbf{q}_i}-\zeta_g\mathbf{p}_i'\right], \tag{A3}$$

where

$$S=\sqrt{\frac{\Sigma\mathbf{p}_i^2/m_i}{3NkT_0}} \tag{A4}$$

and

$$\zeta_g=\sum_i\frac{\mathbf{p}_i'}{m_i3NkT_0}\cdot\left(-\frac{\partial\Phi}{\partial\mathbf{q}_i}\right). \tag{A5}$$

We consider $\mathbf{q}$ and $\mathbf{p}'$ are variables in the phase space $\mathbf{\Gamma}(\mathbf{q},\mathbf{p}')$:$\mathbf{p}'$ is the real momentum and $\mathbf{p}$ is regarded as the ''virtual'' momentum just as Nosé's original dynamics.[8,9] Using Eqs. (A1) and (A2), the HG thermostat corresponds to the velocity scaling scheme so that kinetic energy K is kept to a constant $(3NkT_0/2)$ and its fluctuation is suppressed. However, this does not generate the same statistical ensemble as that associated with the velocity scaling in the leapfrog algorithm (i.e., the canonical ensemble). It is noted that Eq. (A3) coincides with the Gaussian thermostat if $S=1$.

We can obtain the following relation with respect to the time derivative of S:

$$\begin{aligned}\frac{dS}{dt}&=\left(\frac{\Sigma\mathbf{p}_i^2/m_i}{3NkT_0}\right)^{-1/2}\sum_i\frac{\mathbf{p}_i}{m_i3NkT_0}\cdot\left(-\frac{\partial\Phi}{\partial\mathbf{q}_i}\right)\\&=\sum_i\frac{\mathbf{p}_i}{m_iS3NkT_0}\cdot\left(-\frac{\partial\Phi}{\partial\mathbf{q}_i}\right)\\&=-\frac{1}{3NkT_0}\frac{d\Phi}{dt}=\zeta_g.\end{aligned} \tag{A6}$$

Here, we assume an equilibrium state and employ the following relation:

$$\begin{aligned}\frac{1}{S}&=\sqrt{\frac{3NkT_0/2}{3NkT_0/2+\Delta K}}\\&\simeq1-\frac{\Delta K}{3NkT_0}+\frac{3}{2}\frac{\Delta K^2}{(3NkT_0)^2}+O(N^{-3/2}),\end{aligned} \tag{A7}$$

where $\Delta K\equiv\Sigma\mathbf{p}_i^2/2m_i-3NkT_0/2$. We should note that kinetic energy K is $\Sigma\mathbf{p}_i'^2/2m_i$. Using this relation, we can also obtain the following relation:

$$\begin{aligned}\frac{d}{dt}\left(\sum_i\frac{\mathbf{p}_i^2}{2m_i}\right)&=\frac{d\Delta K}{dt}\\&=\sum_i\frac{\mathbf{p}_i}{m_i}\cdot\dot{\mathbf{p}}_i\\&=3NkT_0\zeta_gS\\&=3NkT_0\zeta_g+\Delta K\zeta_g+O(N^{-1/2}).\end{aligned} \tag{A8}$$

From this relation and Eq. (A6)

$$\Delta K=-\delta\Phi-\frac{(\delta\Phi)^2}{6NkT_0}+O(N^{-1/2}). \tag{A9}$$

The similar relation introduced in Sec. III is obtained. From Eq. (A7), Eq. (A3) becomes

$$\dot{\mathbf{p}}_i'=-\frac{\partial\Phi}{\partial\mathbf{q}_i}-\zeta_g\mathbf{p}_i'-\frac{\Delta K}{3NkT_0}\left(-\frac{\partial\Phi}{\partial\mathbf{q}_i}-\zeta_g\mathbf{p}_i'\right)+O(N^{-1}). \tag{A10}$$

Therefore, Eq. (3.2) for the HG thermostat can be calculated by Eqs. (A1) and (A10):

$$\begin{aligned}\frac{1}{f}\frac{df}{dt}&=-\left(\frac{\partial}{\partial\mathbf{\Gamma}}\cdot\dot{\mathbf{\Gamma}}\right)\\&=(3N-1)\zeta_g-\left(\frac{\Delta K}{3NkT}\right)3N\zeta_g+O(N^{-1/2})+Q(\mathbf{p}_i')\\&=-\left(\frac{1}{kT}-\frac{\Delta K}{3N(kT)^2}+O(N^{-1})\right)\frac{d\Phi}{dt}+Q(\mathbf{p}_i'),\end{aligned} \tag{A11}$$

where T_0 is replaced by T. With Eq. (A9), the equilibrium distribution function in the configurational space $f(\mathbf{q})$ is obtained in the similar way in Sec. III.

$$f(\mathbf{q}) = \exp\left[-\frac{\Phi(\mathbf{q})}{kT} - \frac{1}{6N}\left(\frac{\delta\Phi(\mathbf{q})}{kT} \right)^2 \right]. \tag{A12}$$

This is the distribution function in the configurational space for the HG thermostat. The equivalent formula of this distribution function is shown in Ref. 9.

It is clear that this is coincident with the distribution function for the WC thermostat with $\alpha = 1/2$ [see Eq. (3.14)]. Therefore, the HG thermostat corresponds to the special case of the WC thermostat. Fluctuation formulas for the HG thermostat corresponds to Eqs. (3.26), (3.27), and (3.28) with $\alpha = 1/2$. The same expression for C_v^{Φ} as Eq. (3.29) ($\alpha = 1/2$) is also presented in Ref. 9. However, it is noted that the behavior in the momentum space is absolutely different because fluctuation of kinetic energy is fully suppressed in the HG thermostat.

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