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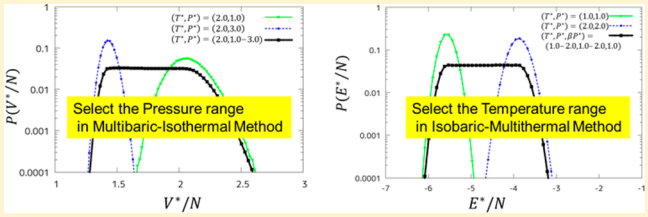
Approaches for Controlling the Temperature and Pressure Range in Generalized NPT Ensembles

Hideo Doi* and Kenji Yasuoka

Department of Mechanical Engineering, Keio University, Yokohama 223-8522, Japan

Supporting Information

ABSTRACT: Isobaric−multithermal and multibaric−isothermal methods are powerful methods for sampling in a wide energy and/or volume space. A finite temperature or pressure is required to study phase diagrams and many properties of many types of systems. However, it is difficult to control the temperature or pressure range because these systems move randomly in energy or volume space. Here, we develop a method to control the temperature range in the isobaric−multithermal ensemble and a method to control the pressure range in the multibaric−isothermal ensemble. These methods have the advantage of adequately determining the weight factor to create the multicanonical ensemble and can be applied to study thermodynamic properties.



1. INTRODUCTION

Computer simulations are powerful tools in many fields of science and technology because high-performance computers are now available. In the field of computational chemistry, the ab initio molecular orbital (MO) method can calculate the energy and geometry of a midsized molecule with a fairly large basis set taking into account the electron correlation effect at 0 K. However, it is still difficult to calculate a distribution of molecular structures at finite temperature and pressure.

In the past few decades, many methods have been developed to generate an ensemble at finite temperature and pressure. Molecular dynamics (MD) simulations[1] can generate the ensemble by solving Newton's equations of motion for a system of interacting particles. In Monte Carlo (MC) simulations, a new configuration is generated by randomly selecting a molecule and then translating and rotating the molecule. Whether a new configuration is accepted is determined by the Metropolis−Hastings algorithm.[2,3] Average structures or thermodynamic quantities in an equilibrium state are calculated after creating a sufficient number of configurations. With the MC method in the canonical ensemble,[2,3] an equilibrium state can be obtained at finite temperature with a constant volume.

The isobaric−isothermal (ISOBATH) MC method was developed by McDonald.[4] In the ISOBATH ensemble, the temperature and pressure are constant. It is difficult to simulate some phenomena, such as the multiple-minima problem (e.g., protein folding) and the large energy gap problem (e.g., first-order phase transitions), with the ISOBATH method. Therefore, we need a generalized ensemble method.

In generalized ensemble methods, the simulations are performed with an artificial non-Boltzmann probability weight factor to overcome the multiple-minima problem. There are two main characteristics of generalized ensemble methods. One is that the simulations are performed with a switching thermodynamic condition, such as temperature or pressure. Methods of this type are replica-exchange[5] (also known as parallel tempering[6]) and simulated-tempering methods.[7−9] By switching the thermodynamic condition, these methods prevent trapping in local-minima states. These methods have three features: (1) The users need to decide the thermodynamic conditions in the simulation. (2) The ensemble at each thermodynamic condition is the Boltzmann distribution. (3) It is easy to develop simulation codes. However, multicanonical simulations are performed with a non-Boltzmann weight factor. Methods of this type are the multicanonical method,[10] Wang−Landau sampling,[11] metadynamics,[12] the generalized simulated tempering method,[13] and the generalized replica exchange method.[14] The aim of using a non-Boltzmann weight factor is to sample in metastable or unstable energy states. These energy states exist between humps in bimodal or multimodal distributions. These energy states often appear in first-order phase transition or protein folding simulations. In these simulations, the probability distribution in energy space often becomes a bimodal or multimodal distribution. In particular, in first-order phase transition simulations, the probability distribution is a bimodal distribution consisting of two phases around the phase transition point. Thus, methods that use a non-Boltzmann weight factor are suitable for first-order phase transition and protein folding simulations. Here, we focus on the multicanonical method.

The multicanonical MC method, which is the multithermal ensemble with constant volume, was developed by Berg and Neuhaus.[10] They applied this method to simulate first-order phase transitions. The canonical-ensemble averages are

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obtained as functions of temperature by single-histogram[15] and/or multiple-histogram[16,17] reweighting techniques. An extension of the multiple-histogram method is the weighted histogram analysis method.[17] The multicanonical method is widely used,[18] especially for biological and chemical systems such as the protein folding problem[19,20] and phase transition phenomena.[21−25] We are motivated to explore wide temperature or pressure ranges in these phenomena. To control the temperature and pressure, several variants of the multicanonical method have been developed, such as multibaric−isothermal (MUBA), isobaric−multithermal (MUTH), and multibaric−multithermal (MUBATH) MC methods,[26,27] as well as the MD method.[28,29] These three generalized MC methods can sample at various pressures and/or temperatures. The ISOBATH method and the three generalized ISOBATH methods (MUBA, MUTH, and MUBATH) are important for simulations of phase transitions. For an abrupt change in volume with the phase transition, it is important to consider the volume change in the phase transition simulation. The advantage of the generalized ISOBATH method is that it generates configurations in a wide energy space and/or volume space. The disadvantage of the generalized ISOBATH method is that calculation of the non-Boltzmann weight factor is difficult and depends on the width of the energy or volume space that is treated as the generalized ISOBATH ensemble. Moreover, it is difficult to determine the width of the energy or volume space, especially in first-order phase transition simulations. If we can eliminate the difficulty related to calculating the non-Boltzmann weight factor, these methods would be more powerful and convenient. In addition, researchers require a range of temperatures and/or pressures to calculate various physical properties because they want to compare the physical properties under different conditions with the predictions from molecular simulations.

In the multicanonical method, we normally choose the range of energy or volume, but the range of temperature or pressure is chosen when the ensemble is treated as the multicanonical ensemble. The energy and volume are extensive variables. If the system size changes, the range of energy or volume should be changed. Thus, we would like to control the configurations or phenomena in simulations with the temperature or pressure for the replica-exchange or simulated-tempering method. It would be useful if we could set the range of intensive variables, such as temperature and pressure, in the multicanonical method, similar to what is done in the replica-exchange and simulated-tempering methods.

The multicanonical MC method, which is the temperature-controlling method in the multicanonical ensemble with constant volume, has been proposed.[30] In this article, we propose a temperature-controlling method for the MUTH ensemble and a pressure-controlling method for the MUBA ensemble. The new methods make the MUTH and MUBA methods more powerful and more convenient.

2. MONTE CARLO SAMPLING ALGORITHMS

In this section, we first review some familiar methods that use the ISOBATH, MUBA, and MUTH algorithms. We then present a new variant of the MUTH and MUBA methods.

2.1. ISOBATH Algorithm. In the ISOBATH ensemble, the probability $P_{NPT}(E, V; T_0, P_0)$ of a system with energy E and volume V at temperature T_0 and pressure P_0 is given by

$$P_{NPT}(E, V; T_0, P_0) \propto n(E, V) \times W_{NPT}(E, V; T_0, P_0) \quad (1)$$

where $n(E, V)$ is the density of states with energy E and volume V. $W_{NPT}(E, V)$ is the weight factor in the NPT ensemble:

$$W_{NPT}(E, V; T_0, P_0) = \exp[-\beta_0(E + P_0V)] \quad (2)$$

The inverse temperature β_0 is defined as

$$\beta_0 = \frac{1}{kT_0} \quad (3)$$

where k is the Boltzmann's constant.

ISOBATH MC simulations are performed by the Metropolis algorithm.[2] The probability distribution $P_{NPT}(E, V; T_0, P_0)$ can be determined by a histogram, $h(E, V)$, which is obtained from a simulation run as follows:

$$P_{NPT}(E, V; T_0, P_0) = \frac{h(E, V)}{\sum h(E, V)} \quad (4)$$

The energy space and volume space are divided into small bins. Then, $n(E, V)$ can be determined by

$$n(E, V) \propto \frac{P_{NPT}(E, V; T_0, P_0)}{W_{NPT}(E, V; T_0, P_0)} \quad (5)$$

2.2. MUTH Algorithm. A MUTH MC simulation is performed in a way that satisfies the following condition:[27]

$$\begin{aligned} \int dV P_{MUTH}(E, V; \beta_0 P_0) &\propto \int dV n(E, V) \exp\{-W_{MUTH}(E; \beta_0 P_0)E - \beta_0 P_0 V\} \\ &= \exp\{-W_{MUTH}(E; \beta_0 P_0)E\} \int dV n(E, V) \exp(-\beta_0 P_0 V) \\ &\equiv \text{constant} \end{aligned} \quad (6)$$

where $W_{MUTH}(E; \beta_0 P_0)$ is the weight factor in the MUTH ensemble. This weight factor, which we refer to as the MUTH weight factor, is a non-Boltzmann weight factor. In the MUTH ensemble, the probability distribution $P_{MUTH}(E, V; \beta_0 P_0)$ covers a wide range in the energy space. The sum of the probability distribution in the volume space $\int dV P_{MUTH}(E, V; \beta_0 P_0)$ becomes flat and covers a wide range in the energy space. According to eq 6, $W_{MUTH}(E; \beta_0 P_0)$ is determined by $n(E, V)$ as follows:

$$W_{MUTH}(E; \beta_0 P_0) = \frac{\ln\{\int dV n(E, V) \exp(-\beta_0 P_0 V)\}}{E} \quad (7)$$

However, $n(E, V)$ is not known a priori. Because the weight factor is given by the Boltzmann factor in the case of the ISOBATH MC simulation, we can perform an ISOBATH MC simulation and then estimate $n(E, V)$ by the multiple-histogram reweighting technique.[15,16] We calculate $W_{MUTH}(E; \beta_0 P_0)$ and then perform the MUTH MC simulation. Then, we perform the MUTH simulation, and $n(E, V)$ and $W_{MUTH}(E; \beta_0 P_0)$ are updated. This preliminary MUTH simulation is repeated until $\int dV P_{MUTH}(E, V; \beta_0 P_0)$ becomes flat and covers a sufficiently wide range in the energy space. Thereafter, the actual MUTH simulation is performed.

A MUTH MC simulation is performed with the Metropolis criterion, similar to the case of the ISOBATH MC simulation. The transition probability of state χ with potential energy E and volume V to state χ' with potential energy E' and volume V' in

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the system with MUTH weight factor $W_{MUTH}(E; \beta_0 P_0)$ is given by

$$w(x \to x') = \begin{cases} 1, & \text{if } \Delta \le 0, \\ \exp(-\Delta), & \text{if } \Delta > 0, \end{cases} \tag{8}$$

where

$$\Delta = W_{MUTH}(E'; \beta_0 P_0)E' - W_{MUTH}(E; \beta_0 P_0)E + \beta_0 P_0(V' - V) - N\ln(V'/V) \tag{9}$$

After the long MUTH production run, we update $n(E, V)$. We can calculate $P_{NPT}(E, V; T, P)$ at any temperature T and pressure P using eqs 1 and 2 if the temperature T and pressure P satisfy the following condition:

$$\frac{P}{kT} = \beta_0 P_0 \tag{10}$$

This condition is caused by the dependency of $W_{MUTH}(E; \beta_0 P_0)$ on the $\beta_0 P_0$ term.

2.3. MUBA Algorithm. A MUBA MC simulation is performed in a way that satisfies the following condition:[27]

$$\begin{aligned} &\int dE P_{MUBA}(E, V; \beta_0) \\ &\quad \propto \int dE n(E, V)\exp[-\beta_0\{E + W_{MUBA}(V; \beta_0)V\}] \\ &\quad = \exp\{-\beta_0 W_{MUBA}(V; \beta_0)V\} \int dE n(E, V)\exp(-\beta_0 E) \\ &\quad \equiv \text{constant} \end{aligned} \tag{11}$$

where $W_{MUBA}(V; \beta_0)$ is the weight factor in the MUBA ensemble. This weight factor, which we refer to as the MUBA weight factor, is a non-Boltzmann weight factor. In the MUBA ensemble, $P_{MUBA}(E, V; \beta_0)$ covers a wide range in the volume space instead of the energy space. The sum of the probability distribution in the energy space $\int dE P_{MUBA}(E, V; \beta_0)$ becomes flat and covers a wide range in the volume space. According to eq 11, $W_{MUBA}(V; \beta_0)$ is determined by $n(E, V)$ as follows:

$$W_{MUBA}(V; \beta_0) = \frac{\ln\{\int dE n(E, V)\exp(-\beta_0 E)\}}{\beta_0 V} \tag{12}$$

The MUBA MC simulation is performed with the Metropolis criterion, similar to the case of the ISOBATH MC simulation. The transition probability of state χ with potential energy E and volume V to state χ' with potential energy E' and volume V' in the system with MUBA weight factor $W_{MUBA}(V; \beta_0)$ is given by

$$w(x \to x') = \begin{cases} 1, & \text{if } \Delta \le 0, \\ \exp(-\Delta), & \text{if } \Delta > 0, \end{cases} \tag{13}$$

where

$$\Delta = \beta_0\{E' - E + W_{MUBA}(V'; \beta_0)V' - W_{MUBA}(V; \beta_0)V\} - N\ln(V'/V) \tag{14}$$

After the long MUBA production run, we update $n(E, V)$. We can calculate $P_{NPT}(E, V; T, P)$ at any temperature T using eqs 1 and 2 if the temperature T satisfies the following condition:

$$\frac{1}{kT} = \beta_0 \tag{15}$$

This condition is caused by the dependency of $W_{MUBA}(V; \beta_0)$ on the β_0 term.

2.4. Selected MUTH Algorithm. In a MUTH ensemble, the temperature is not defined. The transition probability from state χ_i with potential energy E_i and volume V_i to state χ_j with potential energy E_j and volume V_j is described by eq 8. Here, we introduce our own variant of the MUTH algorithm in which we explicitly use the temperature range to control the simulation.

The temperature-like parameter $T^{MUTH}(E_i, E_j)$ and β-like parameter $\beta^{MUTH}(E_i, E_j)$ are defined as

$$\beta^{MUTH}(E_i, E_j)(E_j - E_i) = W_{MUTH}(E_j; \beta_0 P_0)E_j - W_{MUTH}(E_i; \beta_0 P_0)E_i \tag{16}$$

$$\beta^{MUTH}(E_i, E_j) = \frac{1}{kT^{MUTH}(E_i, E_j)} \tag{17}$$

Transformation of eq 16 gives

$$\beta^{MUTH}(E_i, E_j) = \frac{W_{MUTH}(E_j; \beta_0 P_0)E_j - W_{MUTH}(E_i; \beta_0 P_0)E_i}{E_j - E_i} \tag{18}$$

In the MUTH ensemble, $W_{MUTH}(E; \beta_0 P_0)$ only has variable energy E. Therefore, $T^{MUTH}(E_i, E_j)$ and $\beta^{MUTH}(E_i, E_j)$ do not depend on V.

In the MUTH simulation with temperature ranging from T_{min} (β_{min}) to T_{max} (β_{max}), we impose the following condition for any i and j ($E_i < E_j$):

$$\beta_{max} \le \beta^{MUTH}(E_i, E_j) \le \beta_{min} \tag{19}$$

This condition is equivalent to

$$\beta_{max} \le \frac{W_{MUTH}(E_{i+1}; \beta_0 P_0)E_{i+1} - W_{MUTH}(E_i; \beta_0 P_0)E_i}{E_{i+1} - E_i} \le \beta_{min} \tag{20}$$

The energy E_{i+1} is the energy of a neighboring bin of higher energy. We define the selected MUTH (SMUTH) weight factor $W_{SMUTH}(E_i; \beta_0 P_0)$ as follows:

$$\beta'(E_i) = \frac{W_{MUTH}(E_{i+1}; \beta_0 P_0)E_{i+1} - W_{MUTH}(E_i; \beta_0 P_0)E_i}{E_{i+1} - E_i} \tag{21}$$

$$\beta'(E_i) = \begin{cases} \beta_{max} & \text{if } \beta'(E_i) < \beta_{max} \\ \beta_{min} & \text{if } \beta'(E_i) > \beta_{min} \\ \beta'(E_i) & \text{otherwise} \end{cases}$$

$$W_{SMUTH}(E_{i+1}; \beta_0 P_0) = \frac{\beta'(E_i)(E_{i+1} - E_i) + W_{SMUTH}(E_i; \beta_0 P_0)E_i}{E_{i+1}} \tag{22}$$

In a SMUTH simulation, the subsequent MC simulation is performed with $W_{SMUTH}(E_i; \beta_0 P_0)$ rather than $W_{MUTH}(E_i; \beta_0 P_0)$. The other processes in the simulation are the same as those in a MUTH simulation. The $n(E, V)$ from the MUTH simulation is

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converted to $P_{NPT}(E, V; T, P)$ using eq 2 at any temperature from T_{min} to T_{max} and pressure P that satisfy eq 10 and

$$T_{min} \le T \le T_{max} \tag{23}$$

$W_{SMUTH}(E_i; \beta_0 P_0)$ can be used in the MUTH MD simulation.

2.5. Selected MUBA Algorithm. In a MUBA ensemble, the pressure is not defined. The transition probability from state χ_i with potential energy E_i and volume V_i to state χ_j with potential energy E_j and volume V_j is described by eq 13. Here, we introduce our own variant of the MUBA algorithm in which we explicitly use the pressure range to control the simulation.

The pressure-like parameter $P^{MUBA}(V_i, V_j)$ is defined as

$$P^{MUBA}(V_i, V_j)(V_j - V_i) = W_{MUBA}(V_j; \beta_0)V_j - W_{MUBA}(V_i; \beta_0)V_i \tag{24}$$

Transformation of eq 24 gives

$$P^{MUBA}(V_i, V_j) = \frac{W_{MUBA}(V_j; \beta_0)V_j - W_{MUBA}(V_i; \beta_0)V_i}{V_j - V_i} \tag{25}$$

In the MUBA ensemble, $W_{MUBA}(V; \beta_0)$ has only variable V. Therefore, the pressure-like parameter $P^{MUBA}(V_i, V_j)$ does not depend on E.

In the MUBA simulation with pressure ranging from P_{min} to P_{max}, we impose the following condition for any i and j ($V_i < V_j$):

$$P_{min} \le P^{MUBA}(V_i, V_j) \le P_{max} \tag{26}$$

This condition is equivalent to

$$P_{min} \le \frac{W_{MUBA}(V_{i+1}; \beta_0)V_{i+1} - W_{MUBA}(V_i; \beta_0)V_i}{V_{i+1} - V_i} \le P_{max} \tag{27}$$

The volume V_{i+1} is the volume of a neighboring bin of higher volume. We define the selected MUBA (SMUBA) weight factor $W_{SMUBA}(V; \beta_0)$ as follows:

$$P'(V_i) = \frac{W_{MUBA}(V_{i+1}; \beta_0)V_{i+1} - W_{MUBA}(V_i; \beta_0)V_i}{V_{i+1} - V_i} \tag{28}$$

$$P'(V_i) = \begin{cases} P_{max} & \text{if } P'(V_i) > P_{max} \\ P_{min} & \text{if } P'(V_i) < P_{min} \\ P'(V_i) & \text{otherwise} \end{cases}$$

$$W_{SMUBA}(V_{i+1}; \beta_0) = P'(V_i)(V_{i+1} - V_i) + W_{SMUBA}(V_i; \beta_0)V_i \tag{29}$$

In a SMUBA simulation, the subsequent MC simulation is performed with $W_{SMUBA}(V; \beta_0)$ rather than $W_{MUBA}(V; \beta_0)$. The other processes in the simulation are the same as those in the MUBA simulation. $n(E, V)$ from the MUBA simulation is converted to $P_{NPT}(E, V; T, P)$ using eq 2 at temperature T_0 and any pressure from P_{min} to P_{max}. $W_{SMUBA}(V; \beta_0)$ can be used in the MUBA MD simulation.

3. COMPUTATIONAL DETAILS

3.1. Details of the System. We placed 108 Lennard–Jones argon atoms in a cubic cell with periodic boundary conditions. The length and energy were scaled in units of the Lennard–Jones diameter σ and the depth of the potential ε, respectively. We use an asterisk (*) for the reduced quantities. The transformation of reduced units to real units for Lennard–Jones argon is given in Table 1.[31]

Table 1. Transformation of Reduced Units to Real Units for Lennard–Jones Argon

quantity	reduced units		real units
energy	$E^* = 1$	↔	$E = 0.9961$ kJ mol^{-1}
distance	$r^* = 1$	↔	$r = 3.405$ Å
temperature	$T^* = 1$	↔	$T = 119.8$ K
volume	$V^* = 1$	↔	$V = 39.48$ Å^3
pressure	$P^* = 1$	↔	$P = 41.9$ MPa

A pair of particles separated by distance r_{ij} interact with energy $v(r_{ij})$ through the Lennard–Jones pair potential:

$$v(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{30}$$

These interactions are truncated at r_c, which is half the length of the edge size L ($r_c = L/2$):

$$v(r) = \begin{cases} v(r) & \text{if } r \le r_c \\ 0 & \text{if } r > r_c \end{cases} \tag{31}$$

The total potential energy of the system is defined as

$$E = \sum_{i=1}^{N-1}\sum_{j>i}^{N} v(r) + E_N^c \tag{32}$$

The E_N^c term is the correction for the energy truncation, which is defined as

$$E_N^c = 2\pi N\rho \int_{r_c}^{\infty} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] r^2 dr = \frac{8}{9}\pi N\sigma^3\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{9} - 3\left(\frac{\sigma}{r_c}\right)^{3}\right] \tag{33}$$

where ρ is the number density.

3.2. Simulation Conditions. In the ISOBATH simulations, the temperature was set to 1.0 or 2.0. The pressure was set to 1.0, 2.0, or 3.0. We confirmed that these temperatures and pressures were higher than the critical temperature and pressure.[32]

To ensure that the probability distributions in the SMUTH and SMUBA simulations can properly cover the probability distributions in the ISOBATH simulations, the temperature and pressure ranges in the SMUTH and SMUBA simulations were set to be similar to the ISOBATH simulations. In the SMUTH simulation, the temperature range was set to 1.0–2.0. The parameter $\beta_0 P_0$ was set to 1.0. In the SMUBA simulation, the pressure range was set to 1.0–3.0, and the temperature was set to 2.0.

For each system, an ISOBATH simulation was performed with 1.0×10^5 MC sweeps for equilibrium and 1.0×10^6 MC sweeps for analysis. The MUTH and MUBA simulations were performed for 1.0×10^5 MC sweeps to calculate the weight factor. We performed these simulations five times. In the fifth simulation, we confirmed that the probability distribution became flat and covered a wide range in the energy space

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(MUTH simulation) or volume space (MUBA simulation). Afterward, a simulation of 1.0×10^6 MC sweeps was performed and used for analysis.

4. RESULTS AND DISCUSSION

We now show the results of the ISOBATH, SMUTH, and SMUBA simulations to confirm the methods. Figure 1 shows

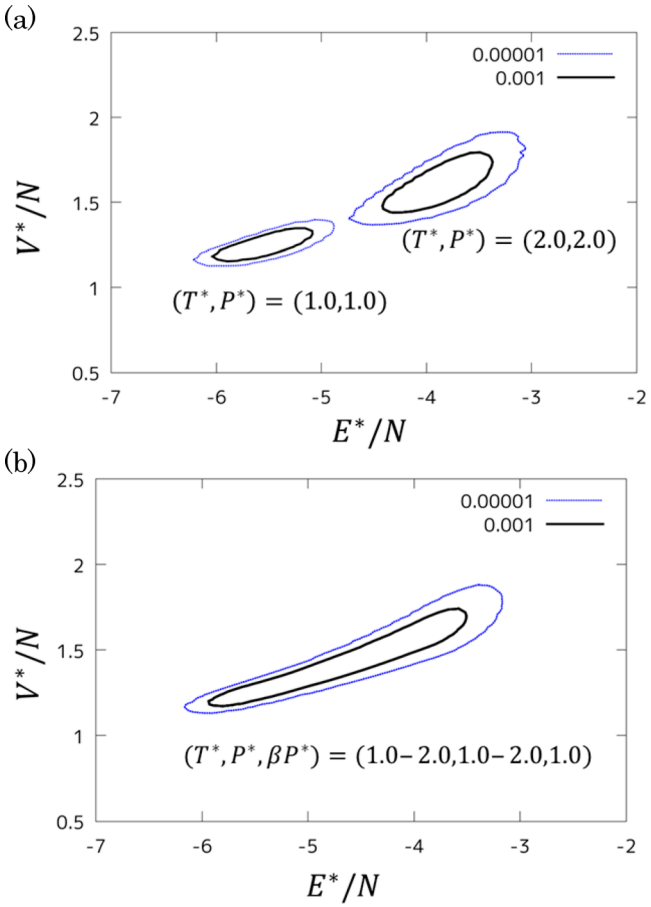

Figure 1. Contour plots of the probability distributions $P(E^*/N, V^*/N; T^*, P^*)$. (a) From the ISOBATH simulations at $(T^*, P^*) = (1.0, 1.0), (2.0, 2.0)$. (b) From the SMUTH simulation at $(T^*, P^*, \beta P^*) = (1.0–2.0, 1.0–2.0, 1.0)$.

log-scale contour plots of the probability distributions of E^*/N and V^*/N from the ISOBATH and SMUTH simulations. The probability distribution in Figure 1b generated with the SMUTH simulation covers the energy range and the volume range corresponding to the probability distribution generated with the ISOBATH simulation in Figure 1a. The SMUTH method can generate the probability distribution according to the temperature and pressure ranges. Figure 2a shows the sum of the probability distribution $P(E^*/N)$ in the same energy range. Each probability distribution generated with the SMUTH simulation for a certain temperature range is flat and covers the energy range corresponding to the ISOBATH ensemble for the temperature range. We define the parameter $\beta^{SMUTH}(E)$ in the SMUTH simulation as follows:

$$\beta^{SMUTH}(E_i) = \frac{W_{SMUTH}(E_{i+1}; \beta_0 P_0)E_{i+1} - W_{SMUTH}(E_i; \beta_0 P_0)E_i}{E_{i+1} - E_i} \quad (34)$$

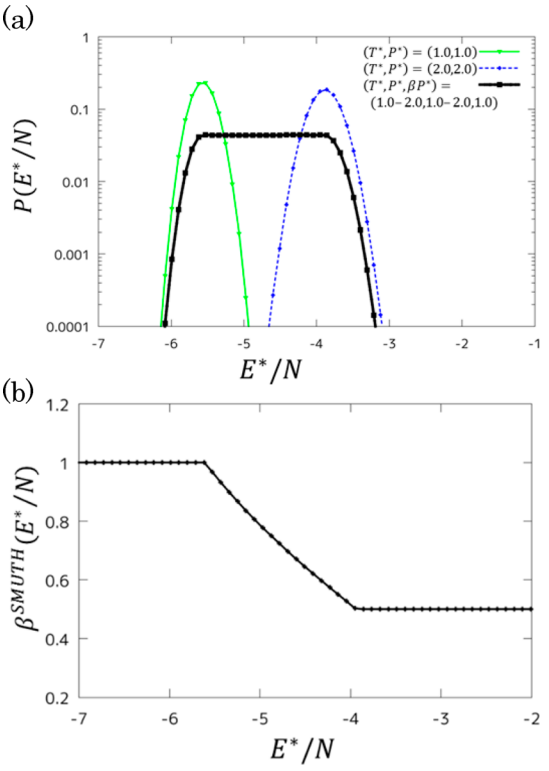

Figure 2. (a) Plots of the potential energy distributions of the ISOBATH simulation at $(T^*, P^*) = (1.0, 1.0), (2.0, 2.0)$ and SMUTH simulation at $(T^*, P^*, \beta P^*) = (1.0–2.0, 1.0–2.0, 1.0)$. (b) Parameter $\beta^{SMUTH}(E^*/N)$ in the SMUTH simulation at $(T^*, P^*, \beta P^*) = (1.0–2.0, 1.0–2.0, 1.0)$.

Figure 2b shows plots of $\beta^{SMUTH}(E)$ against E^*/N for the SMUTH simulation. According to eq 20, the following condition should be satisfied:

$$\text{SMUTH simulation from } T = 1.0 \text{ to } T = 2.0 : 0.5 \le \beta^{SMUTH}(E) \le 1.0$$

As shown in Figure 2b, the parameter $\beta^{SMUTH}(E)$ is actually in the specified range in the SMUTH simulation. The parameter $\beta^{SMUTH}(E)$ cannot go outside the set range. The SMUTH method generates only the probability distribution in the temperature range $T = 1.0–2.0$.

Figure 3b shows that the probability distribution generated with the SMUBA simulation covers the energy and the volume ranges corresponding to the probability distribution generated with the ISOBATH ensemble in Figure 3a. The SMUBA method can generate the probability distribution according to the pressure range.

Figure 4a shows the sum of the probability distribution $P(V^*/N)$ in the same volume. Each probability distribution generated with a SMUBA simulation for a certain pressure range is flat and covers the volume range corresponding to the ISOBATH ensemble for the pressure range. We define the parameter $P^{SMUBA}(V)$ as follows:

$$P^{SMUBA}(V_i) = \frac{W_{MUBA}(V_{i+1}; \beta_0)V_{i+1} - W_{MUBA}(V_i; \beta_0)V_i}{V_{i+1} - V_i} \quad (35)$$

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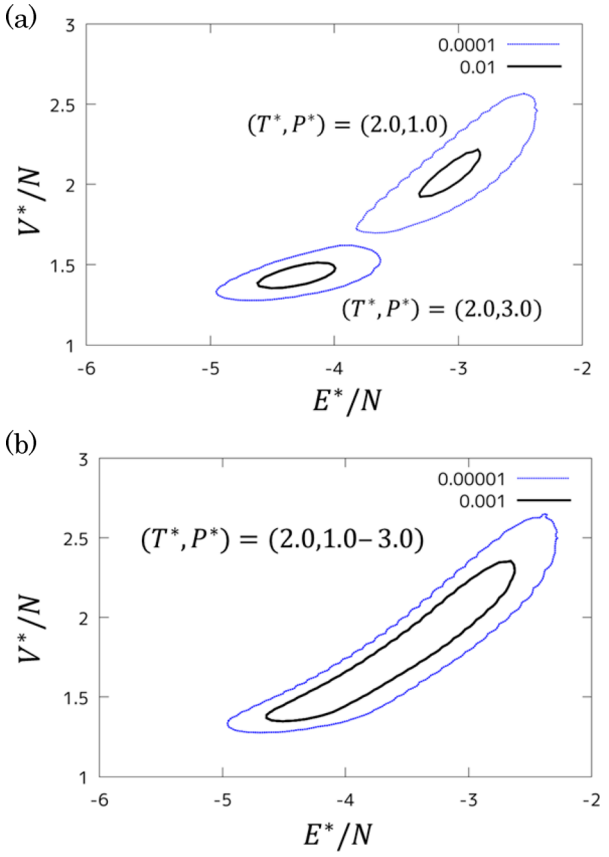

Figure 3. Contour plots of the probability distributions $P(E^*/N, V^*/N; T^*, P^*)$. (a) From the ISOBATH simulations at $(T^*, P^*) = (2.0,1.0)$, (2.0, 3.0). (b) From the SMUBA simulation at $(T^*, P^*) = (2.0,1.0-3.0)$.

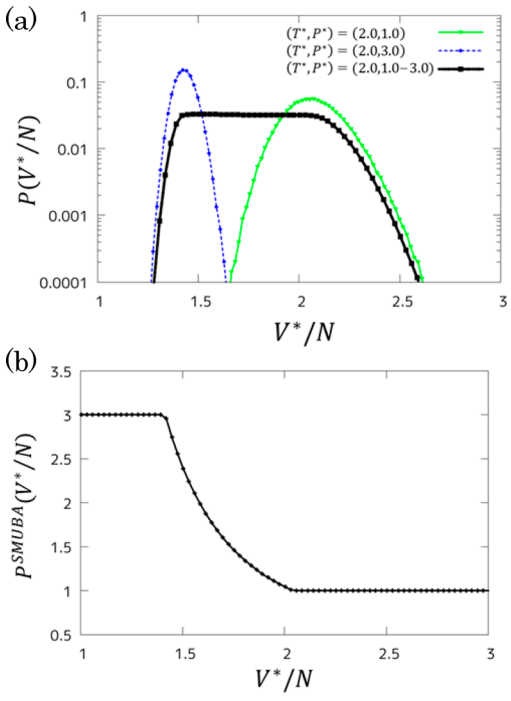

Figure 4. (a) Plots of the potential energy distributions of the ISOBATH simulations at $(T^*, P^*) = (2.0, 1.0)$, (2.0, 3.0) and SMUBA simulation at $(T^*, P^*) = (2.0, 1.0-3.0)$. (b) Parameter $P^{SMUBA}(V^*/N)$ in the SMUBA simulation at $(T^*, P^*) = (2.0, 1.0-3.0)$.

Figure 3b shows $P^{SMUBA}(V)$ against V^*/N for the SMUBA simulation. According to eq 27, the following condition should be satisfied:

$$\text{SMUBA simulation from } P = 1.0 \text{ to } P = 3.0$$
$$: 1.0 \le P^{SMUBA}(V) \le 3.0$$

As shown in Figure 4b, the parameter $P^{SMUBA}(V)$ is actually in the specified range in the SMUBA simulation. The parameter $P^{SMUBA}(V)$ cannot go outside the set range. The SMUBA method generates only the probability distribution in the pressure range $P = 1.0-3.0$.

Thus, the SMUTH and SMUBA methods work correctly. They complied with the specified range of simulation temperature or pressure and generated only the desired ensemble.

5. CONCLUSIONS

We have developed new variants of the MUTH and MUBA methods. The selected MUTH (SMUTH) method can set the temperature range when the weight factor is obtained without choosing the energy range. The selected MUBA (SMUBA) method can set the pressure range when the weight factor is obtained without choosing the volume range. The ranges of the probability distributions from the SMUTH and SMUBA methods cover a certain range of the probability distribution from the ISOBATH method in energy and volume space. Unfortunately, in the case of the MUBATH ensemble, these methods are not suitable. In our approach, we convert the difference of the multicanonical weight factor to the temperature or pressure. However, in the MUBATH ensemble, we cannot choose the temperature and pressure at the same time. In future work, we will consider these methods in the MUBATH ensemble.

The SMUTH and SMUBA methods are powerful and can be combined with other multicanonical methods, such as the multicanonical replica-exchange method[33] or the partial multicanonical method.[34,35] With a combination of the SMUTH or SMUBA method and the partial multicanonical method, a specific part of the potential energy of rotational angles or bond lengths is able to be treated as a different temperature or pressure range.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00195.

Derivation of eqs 20 and 27 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hideo-doi@keio.jp.

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Notes

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