Transactions of the Materials Research Society of Japan 29 [8] 3783-3786 (2004)

Monte Carlo Simulations in New Generalized Isobaric-Isothermal Ensemble

Hisashi Okumura and Yuko Okamoto*
Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan, Fax: 81-564-53-4660
The Graduate University for Advanced Studies, Okazaki, Aichi 444-8585, Japan, Fax: 81-564-53-4660
e-mail: hokumura@ims.ac.jp
*e-mail: okamotoy@ims.ac.jp

We propose a new generalized-ensemble algorithm, which we refer to as the multibaric-multithermal Monte Carlo method. The multibaric-multithermal Monte Carlo simulations perform random walks widely both in volume space and in potential energy space. From only one simulation run, one can calculate isobaric-isothermal-ensemble averages at any pressure and any temperature.
Key words: multibaric-multithermal ensemble, Monte Carlo, Lennard-Jones

1. INTRODUCTION

Monte Carlo (MC) algorithm is one of the most widely used methods of computational physics. In order to realize desired statistical ensembles, corresponding MC techniques have been proposed [1, 2, 3]. The first MC simulation was performed in the canonical ensemble in 1953 [1]. The canonical probability distribution $\mathrm{P}_{NVT}(E)$ for potential energy E is given by the product of the density of states $n(E)$ and the Boltzmann weight factor $\mathrm{e}^{-\beta_0 E}$:

$$\mathrm{P}_{NVT}(E) = n(E)\mathrm{e}^{-\beta_0 E} , \qquad (1)$$

where β_0 is the inverse of the product of the Boltzmann constant k_B and temperature T_0 at which simulations are performed. Since $n(E)$ is a rapidly increasing function and the Boltzmann factor decreases exponentially, $\mathrm{P}_{NVT}(E)$ is a bell-shaped distribution.

The isobaric-isothermal (ISOBATH) MC simulation [2] is also extensively used. This is because most experiments are carried out under the constant pressure and constant temperature conditions. Both potential energy E and volume V fluctuate in this ensemble. The distribution $\mathrm{P}_{NPT}(E,V)$ for E and V is given by

$$\mathrm{P}_{NPT}(E,V) = n(E,V)\mathrm{e}^{-\beta_0 H} . \qquad (2)$$

Here, the density of states $n(E,V)$ is given as a function of both E and V, and H is the "enthalpy":

$$H = E + P_0 V , \qquad (3)$$

where P_0 is the pressure at which simulations are performed. This ensemble has bell-shaped distributions in both E and V.

Besides the above physical ensembles, it is now almost a default to simulate in artificial, generalized ensembles so that the multiple-minima problem. (for a recent review, see Ref. [4]). The multicanonical algorithm [5] is one of the most well known such methods. In multicanonical ensemble, a non-Boltzmann weight factor $W_\mathrm{mc}(E)$ is used. The multicanonical weight factor is characterized by a flat probability distribution $\mathrm{P}_\mathrm{mc}(E)$:

$$\mathrm{P}_\mathrm{mc}(E) = n(E)W_\mathrm{mc}(E) = \text{const.} , \qquad (4)$$

and thus a free random walk is realized in the potential energy space. This enables the simulation to escape from any local-minimum-energy state and to sample the configurational space more widely than the conventional canonical MC algorithm. Another advantage is that one can obtain various canonical ensemble averages at any temperature from a single simulation run by the reweighting techniques [7]. However, it is difficult to compare the simulation conditions with experimental environments of constant pressure, since the simulations are performed in a fixed volume.

Recently, we proposed a new MC algorithm in which one can obtain various ISOBATH ensembles from only one simulation [6]. In other words, we introduced the idea of the multicanonical technique into the ISOBATH ensemble MC method. We call this method the multibaric-multithermal (MUBATH) algorithm. This MC simulation performs random walks in volume space as well as in potential energy space. As a result, this method has the following advantages: (1) It allows the simulation to escape from any local-minimum-energy state (2) One can obtain various ISOBATH ensembles not only at any temperature, but also at any pressure from only one simulation run. (3) One can control pressures and temperatures similarly to real experimental conditions.

2. THEORY

In the MUBATH ensemble, every state is sampled by a weight factor $W_{\rm mbt}(E,V) \equiv \exp\{-\beta_0 H_{\rm mbt}(E,V)\}$ ($H_{\rm mbt}$ is referred to as the MUBATH enthalpy) so that a uniform distribution in both potential energy space and volume space is obtained:

$$\mathrm{P}_{\rm mbt}(E,V) = n(E,V) W_{\rm mbt}(E,V) = \text{const.} \quad (5)$$

We call $W_{\rm mbt}(E,V)$ the MUBATH weight factor.

In order to perform the MUBATH MC simulation, we follow the conventional ISOBATH MC techniques [2]. In this method, we perform Metropolis sampling on the scaled coordinates $\boldsymbol{s}_i = L^{-1}\boldsymbol{r}_i$ ($\boldsymbol{r}_i$ are the real coordinates) and the volume V (here, the particles are placed in a cubic box of a side of size $L \equiv \sqrt[3]{V}$). The trial moves of the scaled coordinates from $\boldsymbol{s}_i$ to $\boldsymbol{s}'_i$ and of the volume from V to V' are generated by uniform random numbers. The enthalpy is accordingly changed from $H(E(\boldsymbol{s}^{(N)},V),V)$ to $H'(E(\boldsymbol{s}'^{(N)},V'),V')$ by these trial moves. The trial moves will be accepted with the probability

$$\mathrm{acc}(\mathrm{o}\to\mathrm{n}) = \min\Big(1, \exp\Big[-\beta_0\Big\{H'-H-Nk_BT_0\ln\Big(\frac{V'}{V}\Big)\Big\}\Big]\Big) , \quad (6)$$

where N is the total number of particles.

Replacing H by $H_{\rm mbt}$, we can perform the MUBATH MC simulation. The MUBATH enthalpy is changed from $H_{\rm mbt}(E(\boldsymbol{s}^{(N)},V),V)$ to $H'_{\rm mbt}(E(\boldsymbol{s}'^{(N)},V'),V')$ by the trial moves. The trial moves will be accepted with the probability

$$\mathrm{acc}(\mathrm{o}\to\mathrm{n}) = \min\Big(1, \exp\Big[-\beta_0\Big\{H'_{\rm mbt}-H_{\rm mbt}-Nk_BT_0\ln\Big(\frac{V'}{V}\Big)\Big\}\Big]\Big) . \quad (7)$$

The MUBATH probability distribution $\mathrm{P}_{\rm mbt}(E,V)$ is obtained by this scheme.

In order to calculate the ISOBATH ensemble average, we employ the reweighting techniques [7]. The probability distribution $\mathrm{P}_{NPT}(E,V;T,P)$ at any temperature T and any pressure P in the ISOBATH ensemble is given by

$$\mathrm{P}_{NPT}(E,V;T,P) = \frac{\mathrm{P}_{\rm mbt}(E,V)\, W^{-1}_{\rm mbt}(E,V)\, \mathrm{e}^{-\beta(E+PV)}}{\int dV \int dE\, \mathrm{P}_{\rm mbt}(E,V)\, W^{-1}_{\rm mbt}(E,V)\, \mathrm{e}^{-\beta(E+PV)}} . \quad (8)$$

The expectation value of a physical quantity A at T and P is estimated from

$$< A >_{NPT} = \frac{< A(E,V) W^{-1}_{\rm mbt}(E,V) \mathrm{e}^{-\beta(E+PV)} >_{\rm mbt}}{< W^{-1}_{\rm mbt}(E,V) \mathrm{e}^{-\beta(E+PV)} >_{\rm mbt}} , \quad (9)$$

where $< \cdots >_{\rm mbt}$ is the MUBATH ensemble average.

The weight factor $W_{\rm mbt}(E,V)$ is obtained by the usual iteration of short simulations [8]. The first simulation is carried out at T_0 and P_0 in the ISOBATH ensemble. Namely, we use

$$W^{(1)}_{\rm mbt}(E,V) = \exp\{-\beta_0 H^{(1)}_{\rm mbt}(E,V)\} , \quad (10)$$

where

$$H^{(1)}_{\rm mbt}(E,V) = E + P_0 V . \quad (11)$$

The i-th simulation is performed with the weight factor $W^{(i)}_{\rm mbt}(E,V)$ and let $\mathrm{P}^{(i)}_{\rm mbt}(E,V)$ be the obtained distribution. The $(i+1)$-th weight factor $W^{(i+1)}_{\rm mbt}(E,V)$ is then given by

$$W^{(i+1)}_{\rm mbt}(E,V) = \exp\{-\beta_0 H^{(i+1)}_{\rm mbt}(E,V)\} , \quad (12)$$

where

$$H^{(i+1)}_{\rm mbt}(E,V) = H^{(i)}_{\rm mbt}(E,V) + k_BT_0 \ln \mathrm{P}^{(i)}_{\rm mbt}(E,V) . \quad (13)$$

For convenience, we make E and V discrete into bins and use histograms to calculate $\mathrm{P}^{(i)}_{\rm mbt}(E,V)$. We iterate this process until a reasonably flat distribution $\mathrm{P}^{(i)}_{\rm mbt}(E,V)$ is obtained.

3. MONTE CARLO SIMULATIONS

We considered a Lennard-Jones 12-6 potential system. We used 500 particles ($N = 500$) in a cubic

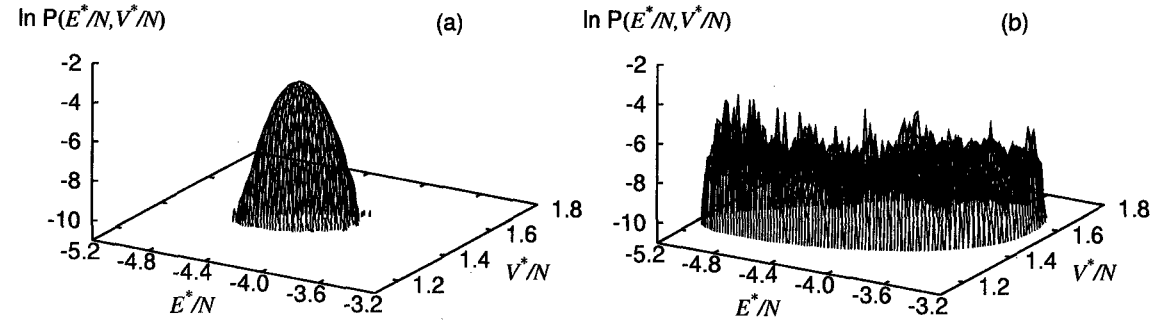

Fig. 1: (a) The probability distribution $\mathrm{P}_{NPT}(E^*/N, V^*/N)$ in the ISOBATH simulation at $(T_0^*, P_0^*) = (2.0, 3.0)$ and (b) the probability distribution $\mathrm{P}_{\rm mbt}(E^*/N, V^*/N)$ in the MUBATH simulation.

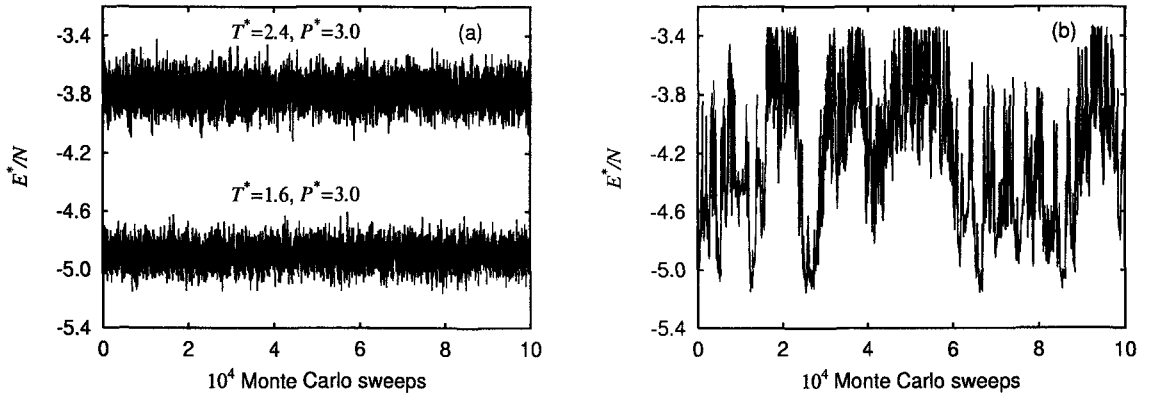

Fig. 2: The time series of E^*/N from (a) the conventional ISOBATH MC simulations at $(T^*, P^*) = (2.4, 3.0)$ and at $(T^*, P^*) = (1.6, 3.0)$ and (b) the MUBATH MC simulation.

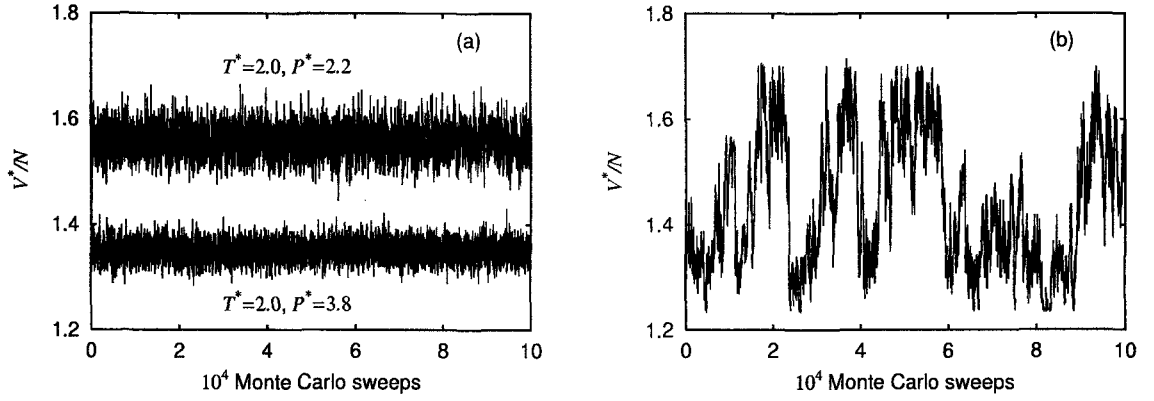

Fig. 3: The time series of V^*/N from (a) the conventional ISOBATH MC simulations at $(T^*, P^*) = (2.0, 2.2)$ and at $(T^*, P^*) = (2.0, 3.8)$ and (b) the MUBATH MC simulation.

unit cell with periodic boundary conditions. The length and the energy are scaled in units of the Lennard-Jones diameter and the minimum value of the potential, respectively. We use an asterisk $(*)$ for the reduced quantities.

We started the MUBATH weight factor determination from a regular ISOBATH simulation at $T_0^* = 2.0$ and $P_0^* = 3.0$. These temperature and pressure are respectively higher than the critical temperature T_c^* and the critical pressure P_c^* [9, 10]. Recent reliable data are $T_c^* = 1.3207(4)$ and $P_c^* = 0.1288(5)$ [10]. The cutoff radius r_c^* was taken to be $L^*/2$. A cut-off correction was added for the pressure and potential energy. In one MC sweep we made the trial moves of all particle coordinates and the volume ($N + 1$ trial moves altogether). In order to obtain a flat probability distribution $\mathrm{P_{mbt}}(E, V)$, we carried out the MC simulations of 100,000 MC sweeps and made 12 iterations of the process of Eqs. (12) and (13). We then performed a long MUBATH MC simulation of 400,000 MC sweeps with this $W_{\mathrm{mbt}}(E, V)$.

For the purpose of comparisons of the new method with the conventional one, we also performed the conventional ISOBATH MC simulations of 100,000 MC sweeps at several sets of T^* and P^*. The temperature ranged from $T^* = 1.6$ to 2.6 and the pressure from $P^* = 2.2$ to 3.8.

Figure 1(a) is the probability distribution $\mathrm{P}_{NPT}(E^*/N, V^*/N)$ from the ISOBATH simulation. It is a bell-shaped distribution. On the other hand, Fig. 1(b) is the probability distribution $\mathrm{P_{mbt}}(E^*/N, V^*/N)$ from the MUBATH simulation finally performed. It shows a flat distribution, and the MUBATH MC simulation indeed sampled the configurational space in wider ranges of energy and volume than the conventional ISOBATH MC simulation.

Figure 2 shows the time series of E^*/N. Figure 2(a) gives the results of the conventional ISOBATH simulations at $(T^*, P^*) = (1.6, 3.0)$ and (2.4,3.0), while Fig. 2(b) presents those of the MUBATH simulation. The potential energy fluctuates in narrow ranges in the ISOBATH MC simulations. On the other hand, the MUBATH MC simulation performs a random walk in a wide energy range.

A similar situation is observed in V^*/N. In Fig. 3(a) we show the time series of V^*/N in ISOBATH simulations at $(T^*, P^*) = (2.0, 2.2)$ and (2.0,3.8), while in Fig. 3(b) we give those in the MUBATH

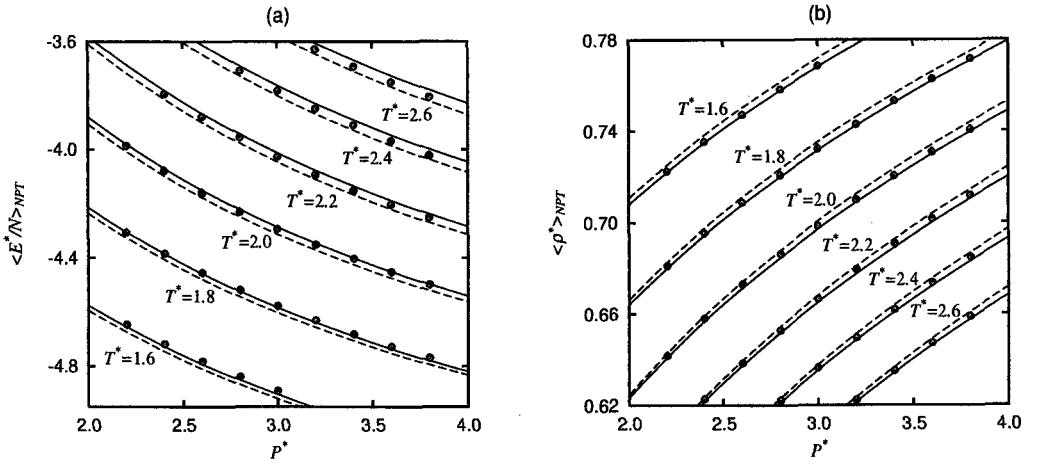

Fig. 4: (a) Average potential energy per particle $< E^*/N >_{NPT}$ and (b) average density $< \rho^* >_{NPT}$ at various temperature and pressure values. Open circles: MUBATH MC simulations. Open diamonds: Conventional ISOBATH MC simulations. Solid line: Equation of states calculated by Johnson et al. [11]. Broken line: Equation of states calculated by Sun and Teja [12].

simulation. The volume fluctuations in the conventional ISOBATH MC simulations are only in narrow ranges. On the other hand, the MUBATH MC simulation performs a random walk that covers even a wider volume range.

We calculated the ensemble averages of potential energy per particle, $< E^*/N >_{NPT}$, and density, $< \rho^* >_{NPT}$, at various temperature and pressure values by the reweighting techniques. They are shown in Figs. 4(a) and (b), respectively. The agreement between the MUBATH data and the ISOBATH data are excellent. Figures 4(a) and (b) also show two equations of states of the Lennard-Jones 12-6 potential fluid. One is determined by Johnson et al. [11] and the other by Sun and Teja [12]. Our MUBATH simulation results agree very well with those of these equations.

4. CONCLUSIONS

We proposed a new MC algorithm that is based on MUBATH ensemble. The advantage of this method is that the simulation performs random walks in both potential energy space and volume space and sample the configurational space much more widely than the ISOBATH MC method. Therefore, one can obtain various ISOBATH ensemble averages at any desired T and P from only one simulation run. This is an outstanding advantage over the conventional ISOBATH MC algorithm, in which simulations have to be carried out separately at each T and P. This method also allows one to specify a pressure and to compare simulation conditions directly with those of real experiments. The MUBATH algorithm will thus be of great use for investigating a large variety of complex systems such as proteins, polymers, supercooled liquids, and glasses. It will be particularly useful for the study of, for example, pressure induced phase transitions.

ACKNOWLEDGMENTS

This work was supported by NAREGI Nanoscience Project, Ministry of Education, Culture, Sports, Science and Technology, Japan.

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(Received October 13, 2003; Accepted April 24, 2004)