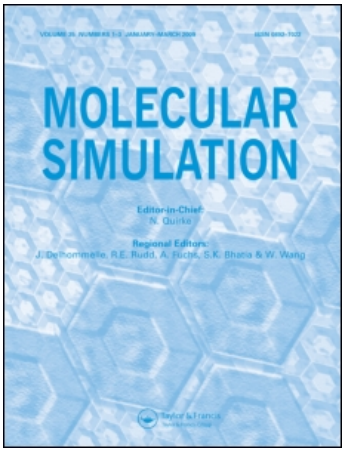

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Multibaric-Multithermal Ensemble Simulation for Simple Liquids

Hisashi Okumura[ab]; Yuko Okamoto[ab]
[a] Department of Theoretical Studies, Institute for Molecular Science, Aichi, Japan [b] The Graduate University for Advanced Studies, Aichi, Japan

To cite this Article Okumura, Hisashi and Okamoto, Yuko(2004) 'Multibaric-Multithermal Ensemble Simulation for Simple Liquids', Molecular Simulation, 30: 13, 847 — 852
To link to this Article: DOI: 10.1080/08927020412331298757
URL: http://dx.doi.org/10.1080/08927020412331298757

Molecular Simulation, Vol. 30 (13–15), 15 November–30 December 2004, pp. 847–852

Taylor & Francis
Taylor & Francis Group

Multibaric–Multithermal Ensemble Simulation for Simple Liquids

HISASHI OKUMURA[a,b,*] and YUKO OKAMOTO[a,b,†]

[a]*Department of Theoretical Studies, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan;* [b]*The Graduate University for Advanced Studies, Okazaki, Aichi 444-8585, Japan*

(Received January 2004; In final form August 2004)

We present a generalized isobaric–isothermal ensemble Monte Carlo (MC) algorithm, which we refer to as the multibaric–multithermal algorithm. This MC simulation performs a random walk widely in volume space and in potential energy space. From only one simulation run, one can calculate isobaric–isothermal ensemble averages in wide ranges of pressure and temperature. We demonstrate the effectiveness of this algorithm by applying it to a Lennard–Jones 12–6 potential system.

Keywords: Isobaric–isothermal; Lennard–Jones potential; Monte Carlo simulation

PACS Numbers: 64.70.Fx; 02.70.Ns; 47.55.Dz

INTRODUCTION

The Monte Carlo (MC) algorithm is one of the most widely used methods of computational physics. In order to realize desired statistical ensembles such as the canonical [1], isobaric–isothermal (ISOBATH) [2], and microcanonical [3] ensembles, corresponding MC techniques have been proposed [4,5]. Besides these physical ensembles, it is also common to simulate in artificial, generalized ensembles so that the multiple-minima problem in complex systems can be overcome (for recent reviews, see Refs. [6–8]). The multicanonical algorithm [9,10] is one of the most well known methods in generalized ensemble. In the multicanonical ensemble, a non-Boltzmann weight factor is used so that a free one-dimensional 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 in a wide range of temperature from one simulation run by the reweighting techniques [11,12].

We recently proposed a new MC algorithm in which one can obtain various ISOBATH ensembles from only one simulation run [13,14]. In this new algorithm, we introduced the idea of the multicanonical technique into the ISOBATH MC method. We refer to this method as the multibaric–multithermal (MUBATH) algorithm. This MC simulation performs a random walk in two-dimensional space; namely, volume space as well as potential energy space.

This method has the following advantages: (1) It allows the simulations to escape from any local-minimum-energy state and to sample the configurational space more widely than the conventional ISOBATH method. (2) One can obtain various ISOBATH ensembles from only one simulation run. (3) One can control pressures and temperatures similarly to real experimental conditions.

The outline of the present article is as follows. In the second section, we review briefly the recently proposed MUBATH algorithm [13]. In the third section, we present the computational details for the applications of these methods to a Lennard–Jones 12–6 potential system. In the fourth section, the results and discussions are presented. Concluding remarks follow in the fifth section.

METHODS

The probability distribution $P_{NVT}(E; T_0)$ for potential energy E in the canonical ensemble at absolute

*Corresponding author. E-mail: hokumura@ims.ac.jp
†E-mail: okamotoy@ims.ac.jp.

ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/08927020412331298757

temperature T_0 is given by the product of the density of states $n(E)$ and the Boltzmann weight factor $e^{-\beta_0 E}$:

$$\mathrm{P}_{\mathrm{NVT}}(E;T_0) = n(E)\,\mathrm{e}^{-\beta_0 E}, \tag{1}$$

where $\beta_0 = 1/k_{\mathrm{B}}T_0$ and k_{B} is the Boltzmann constant. Because $n(E)$ is a rapidly increasing function and the Boltzmann factor decreases exponentially, $\mathrm{P}_{\mathrm{NVT}}(E)$ is a bell-shaped distribution.

In the isobaric–isothermal (ISOBATH) ensemble, on the other hand, both potential energy E and volume V fluctuate. The distribution $\mathrm{P}_{\mathrm{NPT}}(E,V;T_0, P_0)$ for E and V at temperature T_0 and pressure P_0 is given by

$$\mathrm{P}_{\mathrm{NPT}}(E,V;T_0,P_0) = n(E,V)\,\mathrm{e}^{-\beta_0 H}, \tag{2}$$

where the density of states $n(E,V)$ is given as a function of E as well as V, and H is the "enthalpy" (without the kinetic energy contributions):

$$H = E + P_0 V. \tag{3}$$

This ensemble has bell-shaped distributions in both E and V, while the canonical ensemble has such a distribution only in E.

In the multicanonical ensemble, a non-Boltzmann weight factor $W_{\mathrm{mc}}(E)$ is used. This multicanonical weight factor is characterized by a flat probability distribution $P_{\mathrm{mc}}(E)$:

$$P_{\mathrm{mc}}(E) = n(E)W_{\mathrm{mc}}(E) = \text{constant}, \tag{4}$$

and thus a free random walk is realized in the potential energy space.

In the MUBATH ensemble, the simulation performs a random walk in both potential energy space and volume space. For the purpose of realizing such random walks, every state is sampled by the MUBATH weight factor $W_{\mathrm{mbt}}(E,V)$ so that a uniform distribution in both potential energy space and volume space may be obtained:

$$\begin{aligned} P_{\mathrm{mbt}}(E,V) &= n(E,V)W_{\mathrm{mbt}}(E,V) \\ &\equiv n(E,V)\exp\{-\beta_0 H_{\mathrm{mbt}}(E,V)\} \\ &= \text{constant}, \end{aligned} \tag{5}$$

where H_{mbt} is referred to as the MUBATH enthalpy. By replacing H_{mbt} by H, Eq. (5) will return to the ISOBATH distribution Eq. (2).

In order to perform the MUBATH MC simulation, 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 MUBATH enthalpy is consequently changed from $H_{\mathrm{mbt}}(E(\boldsymbol{s}^{(N)},V),V)$ to $H'_{\mathrm{mbt}} \equiv H_{\mathrm{mbt}}(E(\boldsymbol{s}'(N),V'),V')$ by these trial moves. The trial moves will now be accepted with the probability

$$\begin{aligned} \mathrm{acc}\,(o\to n) = \min(1, \exp[-\beta_0\{&H'_{\mathrm{mbt}} - H_{\mathrm{mbt}} \\ &- Nk_{\mathrm{B}}T_0 \ln(V'/V)\}]). \end{aligned} \tag{6}$$

The MUBATH weight factor is, however, not *a priori* known and has to be determined by the usual iterations of short simulations [15–18]. The first simulation is carried out at T_0 and P_0 in the ISOBATH ensemble. We use, namely

$$W^{(1)}_{\mathrm{mbt}}(E,V) = \exp\{-\beta_0 H^{(1)}_{\mathrm{mbt}}(E,V)\}, \tag{7}$$

where

$$H^{(1)}_{\mathrm{mbt}}(E,V) = E + P_0 V. \tag{8}$$

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

$$W^{(i+1)}_{\mathrm{mbt}}(E,V) = \exp\{-\beta_0 H^{(i+1)}_{\mathrm{mbt}}(E,V)\}, \tag{9}$$

where

$$H^{(i+1)}_{\mathrm{mbt}}(E,V) = \begin{cases} H^{(i)}_{\mathrm{mbt}}(E,V) + k_{\mathrm{B}}T_0 \ln \mathrm{P}^{(i)}_{\mathrm{mbt}}(E,V), & \text{for } \mathrm{P}^{(i)}_{\mathrm{mbt}}(E,V) > 0, \\ H^{(i)}_{\mathrm{mbt}}(E,V), & \text{for } \mathrm{P}^{(i)}_{\mathrm{mbt}}(E,V) = 0. \end{cases} \tag{10}$$

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

After an optimal weight factor $W_{\mathrm{mbt}}(E,V)$ is determined, a long production simulation is performed for data collection. We can apply the reweighting techniques [11,12] to the results of this production run in order to calculate the ISOBATH ensemble averages at the designated temperature T and pressure P. The probability distribution, namely, $\mathrm{P}_{\mathrm{NPT}}(E,V;T,P)$ in the ISOBATH ensemble in wide ranges of T and P is given by

$$\mathrm{P}_{\mathrm{NPT}}(E,V;T,P) = \frac{\mathrm{P}_{\mathrm{mbt}}(E,V)W^{-1}_{\mathrm{mbt}}(E,V)\,e^{-\beta(E+PV)}}{\int \mathrm{d}V \int \mathrm{d}E\, \mathrm{P}_{\mathrm{mbt}}(E,V)W^{-1}_{\mathrm{mbt}}(E,V)\,e^{-\beta(E+PV)}}. \tag{11}$$

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

$$\langle A\rangle_{\mathrm{NPT}} = \int \mathrm{d}V \int \mathrm{d}E\, A(E,V)\mathrm{P}_{\mathrm{NPT}}(E,V;T,P). \quad (12)$$

COMPUTATIONAL DETAILS

We now give the details of our simulations. We consider a Lennard–Jones 12–6 potential system. The length and the energy are 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 such as the reduced length $r^* = r/\sigma$, and the reduced temperature $T^* = k_{\mathrm{B}}T/\epsilon$, and the reduced pressure $P^* = P\sigma^3/\epsilon$.

We used 500 particles ($N = 500$) in a cubic unit cell with periodic boundary conditions. We started the weight factor determination for the MUBATH simulation from a regular ISOBATH simulation at $T_0^* = 2.0$ and $P_0^* = 3.0$. These temperature and pressure values are respectively higher than the critical temperature T_{c}^* and the critical pressure P_{c}^* [19–24]. Recent reliable data are $T_{\mathrm{c}}^* = 1.3207(4)$ and $P_{\mathrm{c}}^* = 0.1288(5)$ [24]. The cutoff radius r_{c}^* was taken to be $L^*/2$. A cut-off correction was added for the pressure and the potential energy. In one MC sweep, we made the trial moves of all particle coordinates and the volume ($N+1$ trial moves altogether). For each trial move the Metropolis evaluation of Eq. (6) was made for MUBATH algorithm. In order to obtain flat probability distribution $P_{\mathrm{mbt}}(E, V)$, we carried out relatively short MC simulations of 100,000 MC sweeps and iterated the processes of Eqs. (9) and (10). In the present case, it was required to make 12 iterations to get an optimal MUBATH weight factor $W_{\mathrm{mbt}}(E, V)$. We then performed a long production run of 400,000 MC sweeps with each of the MUBATH algorithm. We chose the bin sizes of these distributions $\Delta E^*/N = 0.02$ and $\Delta V^*/N = 0.01$ for MUBATH simulation.

For the purpose of comparisons of the new method with the conventional one, we also performed the ISOBATH MC simulations of 400,000 MC sweeps with 500 Lennard–Jones 12–6 potential particles at several sets of temperature and pressure. They are carried out at $(T_0^*, P_0^*) = (2.0, 3.0)$, (1.6, 3.0), (2.4, 3.0), (2.0, 2.2) and (2.0, 3.8). The first set is the same as that of the MUBATH simulation.

In order to assess the statistical accuracies, we performed these MC simulations from four different initial conditions in all the algorithms. The error bars were estimated by the standard deviations from these different simulations.

RESULTS AND DISCUSSION

We now present the results of the MUBATH simulation of the Lennard–Jones system. Figure 1 shows the probability distributions of E^*/N and V^*/N from the MUBATH simulations. Figure 1(a) shows $\mathrm{P}_{\mathrm{NPT}}(E^*/N, V^*/N)$ from the ISOBATH simulation first carried out in the process of Eqs. (7) and (8) (i.e., $T_0^* = 2.0$ and $P_0^* = 3.0$). It is a bell-shaped distribution. As performing the iteration procedure of Eqs. (9) and (10), $\mathrm{P}_{\mathrm{mbt}}(E^*/N, V^*/N)$ will become flat and broad gradually as shown in Fig. 1(b). This fact implies that the MUBATH MC simulation indeed sampled the configurational space in wider ranges of energy and volume than the conventional ISOBATH MC simulation.

Given the optimal weight factors, we now examine how widely the energy range and volume range are covered by the random walks by these simulations. Figure 2 shows the time series of E^*/N. Figure 2(a) gives the results from the conventional ISOBATH MC simulations at $(T^*, P^*) = (1.6, 3.0)$ and (2.4, 3.0), while Fig. 2(b) presents that of the MUBATH simulation. The potential energy fluctuates in narrow ranges in the conventional ISOBATH simulations. They fluctuate only in the ranges of $E^*/N = -4.0 \sim -3.6$ and $E^*/N = -5.1 \sim -4.7$ at the higher temperature of $T^* = 2.4$ and at the lower temperature of $T^* = 1.6$, respectively. On the other hand, the MUBATH MC simulation performs a random walk that covers both energy ranges.

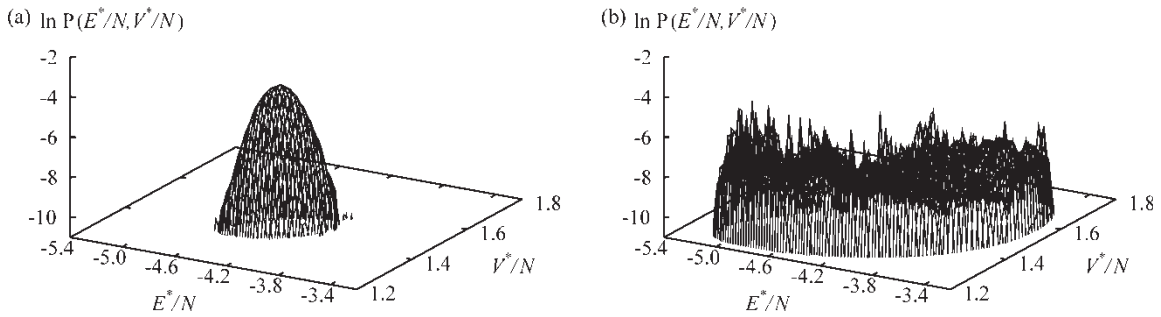

FIGURE 1 The probability distribution from the (a) initial isobaric–isothermal simulation and (b) production run of the multibaric–multithermal simulation after 12 iterations.

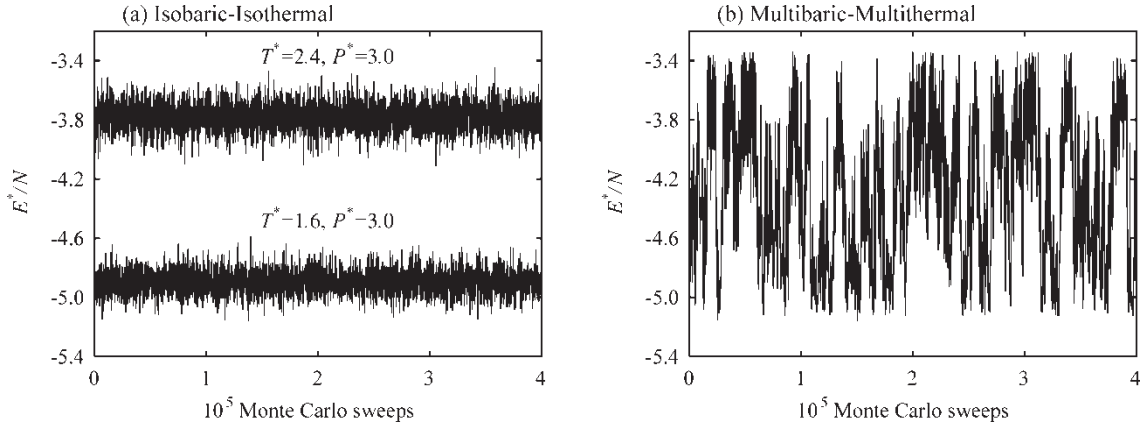

FIGURE 2 The time series of E^*/N from (a) the isobaric–isothermal MC simulations at (T^*, P^*) = (2.4, 3.0) and at (T^*, P^*) = (1.6, 3.0) and (b) the multibaric–multithermal MC simulation.

Figure 3 shows the time series of V^*/N. Figure 3(a) gives the results from the conventional ISOBATH simulations at (T^*, P^*) = (2.0, 3.8) and (2.0, 2.2), while Fig. 3(b) presents that of the MUBATH simulation. The volume fluctuates in narrow ranges in the conventional ISOBATH MC simulations. They fluctuate only in the ranges of $V^*/N = 1.3 \sim 1.4$ and $V^*/N = 1.5 \sim 1.6$ at the higher pressure of $P^* = 3.8$ and at the lower pressure of $P^* = 2.2$, respectively. In contrast, the MUBATH simulation (Fig. 3(b)) performs a random walk that covers both volume ranges.

In order to investigate the T^* and P^*/T^* ranges in which the ISOBATH and the MUBATH method can determine average physical quantities correctly by the reweighting techniques, we show $\langle E^*/N\rangle_{\mathrm{NPT}}$ and $\langle V^*/N\rangle_{\mathrm{NPT}}$ as functions of P^*/T^* at several T^* in Figs. 4(a) and 5(a) and in Figs. 4(b) and 5(b), respectively. Figure 4 is for the ISOBATH simulation and Fig. 5 is for the MUBATH simulation. Figures 4 and 5 also show two equations of states of the Lennard–Jones 12–6 potential fluid which are estimated by Johnson *et al.* [25] and by Sun and Teja [26]. The areas in which the average quantities of our simulations agree well with these equations of states are indicated by dotted lines in Figs. 4 and 5.

One cannot calculate physical quantities correctly by combining the ISOBATH algorithm with the reweighting techniques except at T^* and P^*/T^* close to T_0^* and P_0^*/T_0^*, respectively as shown in Fig. 4. As T^* or P^*/T^* is going far from T_0^* or P_0^*/T_0^*, the error bars of any physical quantities and the deviations from its correct value will get large. The ranges in which $\langle E^*/N\rangle_{\mathrm{NPT}}$ and $\langle V^*/N\rangle_{\mathrm{NPT}}$ are correct and are $1.6 \le T^* \le 2.5$ and $1.0 \le P^*/T^* \le 1.9$.

On the other hand, the MUBATH simulation enables us to calculate physical quantities in wide ranges of both P^*/T^* and T^*. Figure 5 shows that the MUBATH data agree with the equations of states well in $1.0 \le T^* \le 3.4$ and $0.1 \le P^*/T^* \le 2.8$. That is, the MUBATH simulation provides correct average quantities in the ranges of T^* and P^*/T^* about three times wider than the ISOBATH simulation. It is necessary to use the MUBATH method to determine

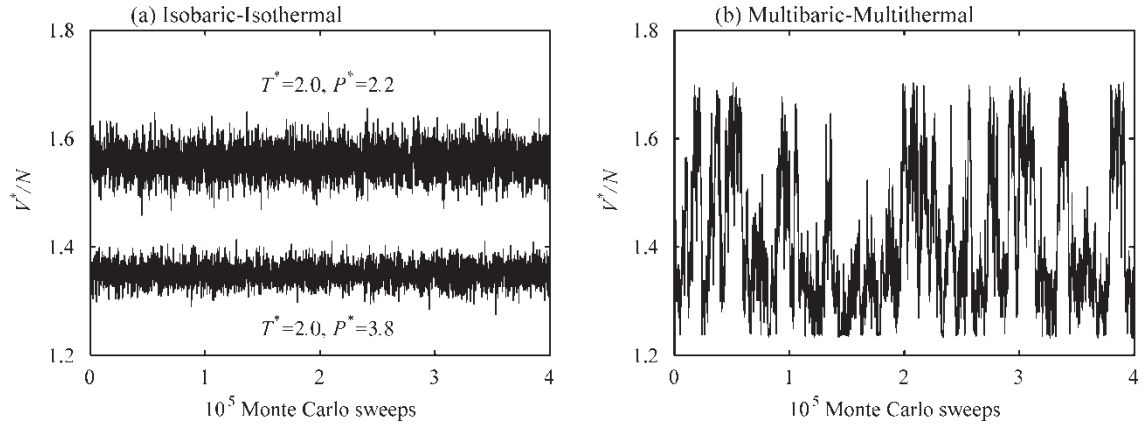

FIGURE 3 The time series of V^*/N from (a) the isobaric–isothermal MC simulations at (T^*, P^*) = (2.0, 3.8) and at (T^*, P^*) = (2.0, 2.2) and (b) the multibaric–multithermal MC simulation.

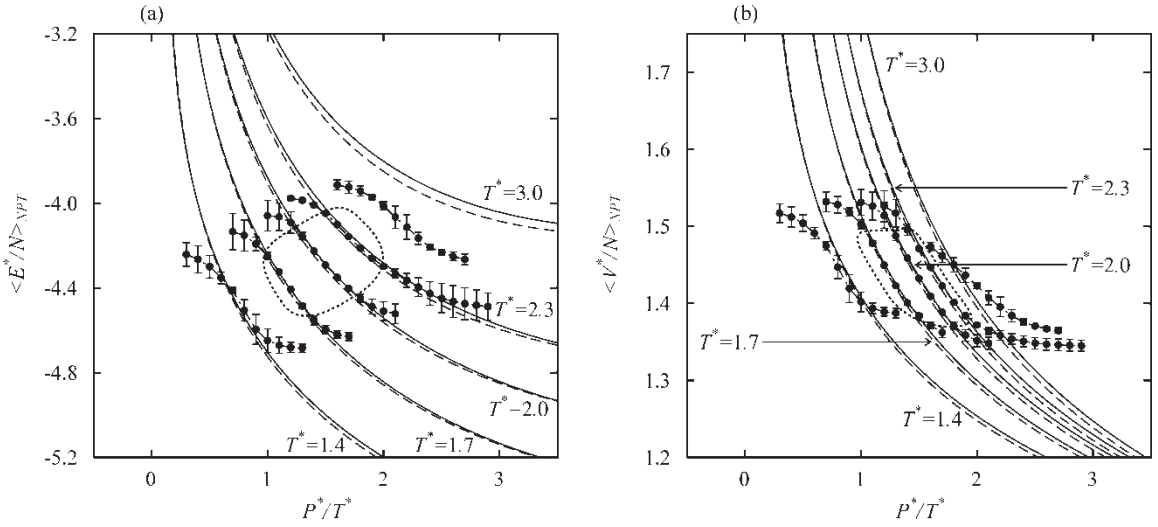

FIGURE 4 Average quantity calculation by the isobaric–isothermal MC simulation. (a) Average potential energies per particle $\langle E^*/N\rangle_{NPT}$ and (b) average volumes per particle $\langle V^*/N\rangle_{NPT}$. Filled circles: Combination of the isobaric–isothermal MC simulation and the reweighting technique. Solid lines: Equation of states calculated by Johnson *et al.* [25]. Broken lines: Equation of states calculated by Sun and Teja [26]. Doted lines indicate the area in which the results by reweighting techniques agree well with the equations of states.

physical quantities at T^* and P^*/T^* far from T_0^* and P_0^*/T_0^*. The important point is that one can obtain a desired ISOBATH distribution at numerous temperatures and pressures by these generalized ISOBATH algorithms from a single simulation run. This is the outstanding advantage when compared to the conventional ISOBATH MC algorithm, in which simulations have to be carried out separately at each temperature and pressure.

The region encircled by the dotted curves in Fig. 5 is the super critical region, that is, this system is not in the liquid–gas coexistence. The MUBATH algorithm is also applicable to the phase transition region. We will present the results of these applications in the future communications.

CONCLUSIONS

In this article, we presented a new generalized-ensemble MC algorithm, namely the multibaric–multithermal algorithm. We successfully applied this method to the Lennard–Jones 12–6 potential system. The advantage of our method is that the simulations sample the configurational space more widely than the conventional ISOBATH MC method. Therefore, one can obtain various ISOBATH ensemble averages from only one simulation run in wide ranges of T and P/T by the MUBATH simulation. Because of this advantage, we think that these new algorithms will be of use for investigating a large variety of more complex systems such as proteins, polymers,

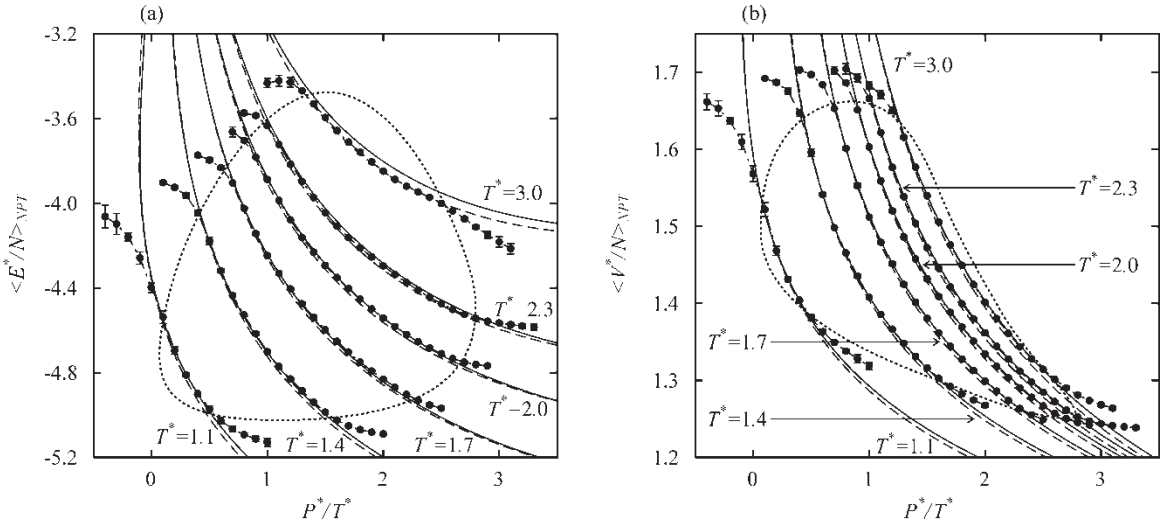

FIGURE 5 Average quantity calculation by the multibaric–multithermal MC simulation. Filled circles: Combination of the multibaric–multithermal MC simulation and the reweighting technique. Filled circles: Combination of the isobaric–isothermal MC simulation and the reweighting technique. Solid lines: Equation of states calculated by Johnson *et al.* [25]. Broken lines: Equation of states calculated by Sun and Teja [26]. Doted lines indicate the area in which the results by reweighting techniques agree well with the equations of states.

supercooled liquids and glasses. It will be also useful to study the problem in which the pressure is important, for example, pressure induced phase transitions.

Acknowledgements

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

References

[1] Metropolis, N., Rosenbluth, A.W., Rosenbluth, M.N., Teller, A.H. and Teller, E. (1953) "Equation of state calculations by fast computing machines", *J. Chem. Phys.* **21**, 1087.
[2] McDonald, I.R. (1972) "*NpT*-ensemble Monte Carlo calculations for binary liquid mixtures", *Mol. Phys.* **23**, 41.
[3] Creutz, M. (1983) "Microcanonical Monte Carlo simulation", *Phys. Rev. Lett.* **50**, 1411.
[4] Allen, M.P. and Tildesley, D.J. (1987) *Computer Simulation of Liquids* (Clarendon Press, Oxford), p 110.
[5] Frenkel, D. and Smit, B. (2002) *Understanding Molecular Simulation From Algorithms to Applications* (Academic Press, San Diego), p 111.
[6] Hansmann, U.H.E. and Okamoto, Y. (1999) "The generalized-ensemble approach for protein folding simulations", *Ann. Rev. Comput. Phys. VI*, 129, D. Stauffer (Ed.) (World Scientific, Singapore).
[7] Mitsutake, A., Sugita, Y. and Okamoto, Y. (2001) "Generalized-ensemble algorithms for molecular simulations of biopolymers", *Biopolymers (Pept. Sci.)* **60**, 96.
[8] Berg, B.A. (2002) "Generalized ensemble simulations for complex systems", *Comp. Phys. Commun.* **147**, 52.
[9] Berg, B.A. and Neuhaus, T. (2002) "Multicanonical algorithms for first order phase transitions", *Phys. Lett.* **B267**, 249.
[10] Berg, B.A. and Neuhaus, T. (1992) "Multicanonical ensemble: a new approach to simulate first-order phase transitions", *Phys. Rev. Lett.* **68**, 9.
[11] Ferrenberg, A.M. and Swendsen, R.H. (1988) "New Monte Carlo technique for studying phase transitions", *Phys. Rev. Lett.* **61**, 2635.
[12] Ferrenberg, A.M. and Swendsen, R.H. (1989) "New Monte Carlo technique for studying phase transitions", *Phys. Rev. Lett.* **63**, 1658(E).
[13] Okumura, H. and Okamoto, Y. (2004) "Monte Carlo simulations in multibaric–multithermal ensemble", *Chem. Phys. Lett.* **383**, 391.
[14] Okumura, H. and Okamoto Y. (2004) "Monte Carlo Simulations in Generalized Isobaric-Isothermal Ensembles", *Phys. Rev. E*. **70**, 26702.
[15] Berg, B.A. and Celik, T. (1992) "New approach to spin-glass simulations", *Phys. Rev. Lett.* **69**, 2292.
[16] Lee, J. (1993) "New Monte Carlo algorithm: entropic sampling", *Phys. Rev. Lett.* **71**, 211.
[17] Lee, J. (1993) "New Monte Carlo algorithm: entropic sampling", *Phys. Rev. Lett.* **71**, 2353(E).
[18] Okamoto, Y. and Hansmann, U.H.E. (1995) "Thermodynamics of Helix-Coil transitions studied by multicanonical algorithms", *J. Phys. Chem.* **99**, 11276.
[19] Okumura, H. and Yonezawa, F. (2000) "Liquid-vapor coexistence curves of several interatomic model potentials", *J. Chem. Phys.* **113**, 9162.
[20] Okumura, H. and Yonezawa, F. (2001) "Expansion type of model fluids", *J. Phys. Soc. Jpn* **70**, 1006.
[21] Panagiotopoulos, A.Z. (2000) "Monte Carlo methods for phase equilibria of fluids", *J. Phys. Condens. Matter* **12**, R25.
[22] Caillol, J.M. (1998) "Critical-point of the Lennard–Jones fluid: a finite-size scaling study", *J. Chem. Phys.* **109**, 4885.
[23] Potoff, J.J. and Panagiotopoulos, A.Z. (1998) "Critical point and phase behavior of the pure fluid and a Lennard–Jones mixture", *J. Chem. Phys.* **109**, 10914.
[24] Okumura, H. and Yonezawa, F. (2001) "Reliable determination of liquid-vapor critical point by NVT plus test particle method", *J. Phys. Soc. Jpn* **70**, 1990.
[25] Johnson, J.K., Zollweg, J.A. and Gubbins, K.E. (1993) "The Lennard–Jones equation of state revisited", *Mol. Phys.* **78**, 591.
[26] Sun, T. and Teja, A.S. (1996) "An equation of state for real fluids based on the Lennard–Jones potential", *J. Phys. Chem.* **100**, 17365.