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An Application of the Multicanonical Monte Carlo Method to the Bulk Water System

Chizuru Muguruma,¹ Yuko Okamoto,^{2,3} and Masuhiro Mikami⁴

¹ Faculty of Liberal Arts, Chukyo University, Toyota, Aichi 470–0393, Japan

² Department of Theoretical Studies, Institute for Molecular Science, Okazaki, Aichi 444–8585,
Japan

³ Department Functional Molecular Science, The Graduate University for Advanced Studies,
Okazaki, Aichi 444–8585, Japan

⁴ Research Institute for Computational Sciences, National Institute of Advanced Industrial Science
and Technology, Tsukuba, Ibaraki 305–8568, Japan

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An Application of the Multicanonical Monte Carlo Method to the Bulk Water System[#]

Chizuru Muguruma,^{1,*} Yuko Okamoto,^{2,3} and Masuhiro Mikami⁴

¹ Faculty of Liberal Arts, Chukyo University, Toyota, Aichi 470–0393, Japan

² Department of Theoretical Studies, Institute for Molecular Science, Okazaki, Aichi 444–8585, Japan

³ Department Functional Molecular Science, The Graduate University for Advanced Studies, Okazaki, Aichi 444–8585, Japan

⁴ Research Institute for Computational Sciences, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305–8568, Japan

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Abstract

Motivation. Powerful Monte Carlo algorithm may solve the multiple–minima problem for the bulk water system.

Method. The multicanonical algorithm is based on a non–Boltzman weight factor and produces flat probability distribution of potential energy artificially. The method allows the system to rove through the complex potential energy surface without getting trapped in a local minimum state, and has been proven to be efficient for studying first–order phase transitions of complex systems such as spin glasses and proteins. One of the features of the method is that the expectation values of thermodynamic properties can be calculated as a function of temperature by applying the histogram–reweighting techniques to the results of one long production run.

Results. In the present study, we determined the multicanonical weight factor that can produce flat probability distribution of potential energy corresponding to the temperature range from 170 to 630 K. From the peak of the heat capacity, we found a phase transition at 190 K. The lower energy structures and oxygen–oxygen radial distribution functions imply that the structure at lower temperatures is irregular. However, the average number of hydrogen bonds per water molecule is nearly equal to four at low temperatures, which suggests the formation of amorphous ice.

Conclusions. We conclude that the phase transition we found in the present study is the one between liquid water and amorphous ice. In order to study first–order phase transition between water and crystalline ice with the multicanonical algorithm, we have to obtain more precise multicanonical weight factor in the low energy region.

Keywords. Multicanonical Monte Carlo method; TIP4P water; bulk water; phase transition; amorphous ice.

Abbreviations and notations

MUCA, multicanonical algorithm

g_{OO} , oxygen–oxygen radial distribution function

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* Correspondence author; phone: +81–565–45–0971; fax: +81–565–46–1298; E–mail: muguruma@lets.chukyo-u.ac.jp.

1 INTRODUCTION

The great advancement of computer technology and simulation technique has made computer simulation an effective tool in many fields of chemistry and physics. However, simulations of complex systems with many degrees of freedom such as spin glasses and biopolymers are still greatly hampered by the multiple–minima problem. This is because conventional canonical simulations at low temperatures tend to get trapped in one of huge number of local–minimum states on the potential energy surface.

The multicanonical algorithm (MUCA) [1,2] has been introduced as one of efficient methods to overcome the multiple–minima problem in simulations of complex systems [1–7] (for recent reviews, see Refs. [8] and [9]). The algorithm is based on an artificial, non–Boltzman weight factor and performs a free one–dimensional random walk in potential energy space, which allows the simulation to avoid getting trapped in states of energy local minima. Moreover, one can calculate the expectation values of thermodynamic quantities as a function of temperature by applying the histogram–reweighting techniques [10] to the results of one long production run.

Bulk water system is another complex system that suffers from the multiple–minima problem. In particular, phase transition of ice formation has been very difficult for molecular simulations and only a few successful results have been reported [11–16]. In the present study, we apply the multicanonical Monte Carlo (MUCAMC) method to the bulk water system.

This article is organized as follows. In Section 2, the MUCAMC method is briefly described. We report the results of the MUCAMC simulation of a bulk water system in Section 3. Concluding remarks follow in Section 4.

2 METHODS

2.1 Multicanonical Algorithm

Although the multicanonical algorithm is explained in detail elsewhere [8,9], we give a short overview in this subsection for completeness. In the canonical ensemble, the probability distribution of the potential energy E , $P_B(E;T)$, is given by the product of the density of states $n(E)$ and the Boltzmann weight factor $W_B(E;T)$:

$$P_B(E;T) \propto n(E)W_B(E;T) = n(E)e^{-\beta E}, \quad (1)$$

where β is the inverse temperature $1/k_B T$ with the Boltzmann constant k_B and temperature T . Because $n(E)$ is a rapidly increasing function and $W_B(E;T)$ decreases exponentially, $P_B(E;T)$ generally has a bell–like shape.

In multicanonical ensemble, each state is weighted by a non–Boltzmann weight factor $W_{mu}(E)$,

which we refer to as the multicanonical weight factor, so that a uniform potential energy distribution is obtained:

$$P_{mu}(E) \propto n(E)W_{mu}(E) \equiv \text{constant} . \quad (2)$$

In this artificial ensemble, one-dimensional free random walk in the potential energy space can be carried out. The random walk allows the system to escape from any local-minimum-energy states and to sample the configurational space much more widely with a smaller number of simulation steps than the conventional canonical Monte Carlo or molecular dynamics methods.

From the definition of Eq. (2), the multicanonical weight factor is inversely proportional to the density of the states, and is written as follows:

$$W_{mu}(E) \equiv e^{-S(E)/k_B} = \frac{1}{n(E)} , \quad (3)$$

where $S(E)$ is the entropy in the microcanonical ensemble:

$$S(E) = k_B \ln n(E) . \quad (4)$$

Since the density of states of the system is usually unknown, the multicanonical weight has to be determined numerically by iterations of short preliminary runs. In the present study, we employ the iterative procedure from Ref. [5].

A multicanonical Monte Carlo simulation is performed, for instance, with the usual Metropolis criterion [17]: the transition probability of state x with potential energy E to state x' with potential energy E' is given by

$$w(x \rightarrow x') = \begin{cases} 1, & \text{for } \Delta S \leq 0, \\ \exp(-\Delta S/k_B) & \text{for } \Delta S > 0, \end{cases} \quad (5)$$

where

$$\Delta S \equiv S(E') - S(E) . \quad (6)$$

Once the multicanonical weight factor (equivalently the entropy $S(E)$) is given, one performs a long multicanonical production run. By monitoring the potential energy throughout the simulation, one can find the global-minimum-energy state. Moreover, adopting the reweighting techniques, the expectation value of a physical quantity A at any temperature $T (= 1/k_B\beta)$ is given by

$$\langle A \rangle_T = \frac{\sum_E A(E)n(E)e^{-\beta E}}{\sum_E n(E)e^{-\beta E}} , \quad (7)$$

where the optimal density of states $n(E)$ is given by the single-histogram reweighting techniques [10]:

$$n(E) = \frac{H_{mu}(E)}{W_{mu}(E)}, \quad (8)$$

and $H_{mu}(E)$ is the recorded histogram of the probability distribution of potential energy $P_{mu}(E)$ that was obtained from the production run. For instance, the heat capacity is calculated by the following equation:

$$C_V = \frac{\langle E^2 \rangle_T - \langle E \rangle_T^2}{k_B T^2}. \quad (9)$$

2.2 Computational Details

We chose the periodic cubic cell, with an edge size of 12.78 Å containing 64 water molecules, as a basic cell (the density is 0.917 g/cm³). The TIP4P potential [18] was employed for the water–water intermolecular interaction. The electrostatic potential was calculated by the Ewald summation techniques [19]. We remark that we do not observe evaporations of water molecules in the present study because we fix the volume (we are only interested in liquid–solid phase transitions). As we described in Subsection 2.1, the MUCAMC simulation consists of two steps. First, we determined the multicanonical weight factor by iterations in Ref. [5]. In each iteration the MUCAMC simulation with 10⁵ Monte Carlo sweeps was performed. Our Monte Carlo simulation is performed by choosing a water molecule randomly and updating its coordinates with Metropolis criterion [17]. One Monte Carlo sweep consists of 64 such updates. After the multicanonical weight factor was determined, we then made one long production run of 5×10⁶ Monte Carlo sweeps. The step size of coordinate updates was determined so that the acceptance ratio is 0.5 in the canonical Monte Carlo simulation at 500 K, and was fixed for all MUCAMC simulations.

3 RESULTS AND DISCUSSION

With the multicanonical Monte Carlo method, we expect to obtain a free random walk in potential energy space and thus a flat energy distribution. Time series of the total potential energy from the production run is shown in Figure 1(a). We indeed see a random walk between around –20 and –45 kJ/mol. Time series of the total potential energy obtained by the conventional canonical Monte Carlo simulations with 10⁶ MC sweeps at temperatures 200 and 500 K are also shown in Figure 1(b) for comparison. Average values from these simulations at 200 and 500 K are –41.8 and –24.6 kJ/mol, respectively. Hence, the multicanonical simulation of Figure 1(a) covers the energy range which corresponds to that at least between 200 and 500 K. Covering a wide temperature range in a single simulation run is one of the advantages for using the multicanonical algorithm.

Figure 2 shows the histogram of the potential energy distribution that was obtained by the MUCAMC production run. In the figure, we regard the histogram that exceeds 10⁵ as flat. This

implies that the multicanonical ensemble is realized in the potential energy range between -46 and -20 kJ/mol.

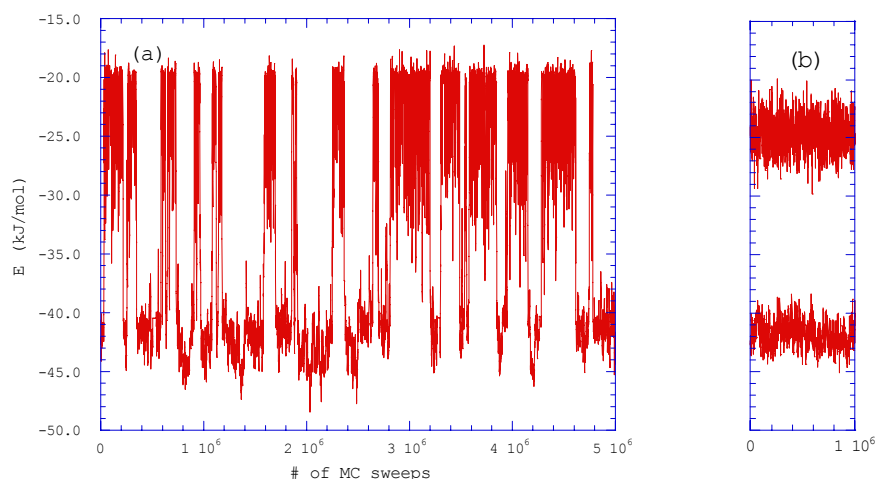


Figure 1. Time series of total potential energy obtained by (a) a long production run of the MUCAMC simulation and (b) the conventional canonical Monte Carlo simulations at temperatures 200 and 500 K.

Another advantage for using the multicanonical algorithm is that entropy can be calculated directly as a function of total potential energy (see Eqs. (4) and (8)). The entropy calculated by the MUCAMC simulation is shown in Figure 3. Since we can only calculate the relative values of the entropy, we set the absolute value of the entropy to 0 at the lowest energy of the production run.

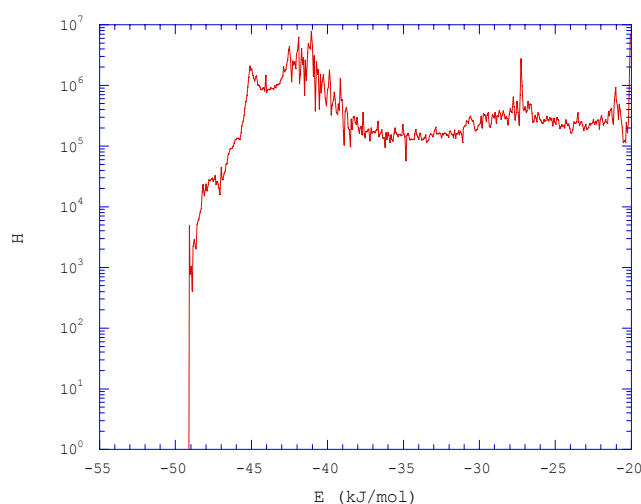


Figure 2. Histogram of the total potential energy distribution that was obtained by the MUCAMC production run.

Applying the reweighting techniques to the results of the MUCAMC production run, we can calculate physical quantities as a function of temperature (see Eq. (7)). For instance, the average potential energy that was calculated at every 10 K from 150 to 630 K is shown in Figure 4. In Figure 2 above, we found that the energy histogram is flat in the range between -46 and -20 kJ/mol, within which we have sufficient sampling. From Figure 4, this energy range corresponds to the temperature range between 170 and 630 K (the average values are thus reliable in this range). The average energy in Figure 4 monotonically increases as the temperature is raised. The slope seems to suddenly change around 200 K, suggesting the existence of some kind of phase transition.

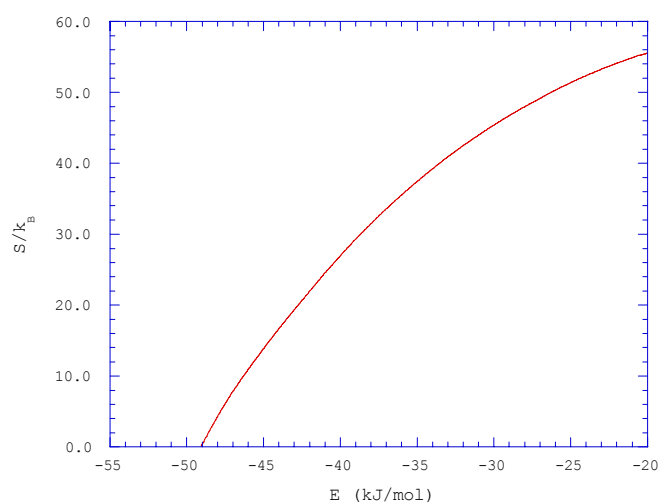


Figure 3. The entropy as a function of potential energy that was obtained by the MUCAMC production run.

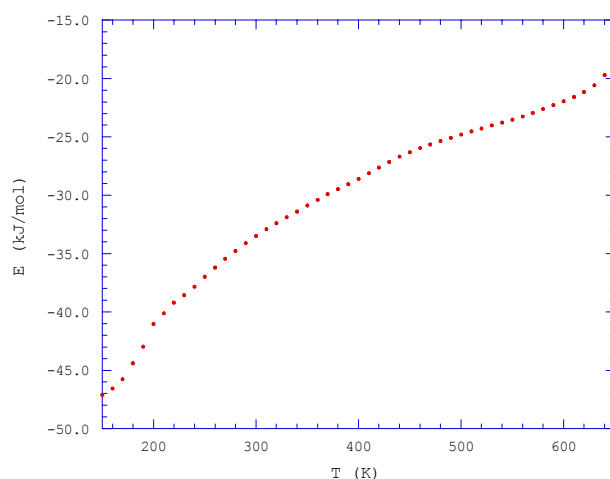


Figure 4. The change in average potential energy obtained by the MUCAMC calculation. Averaged energies were calculated every 10 K.

If there is a phase transition around 200 K, one should observe a peak in the heat capacity. This quantity is calculated by the reweighting techniques (see Eq. (9)) and shown in Figure 5. A remarkable peak at 190 K is indeed observed.

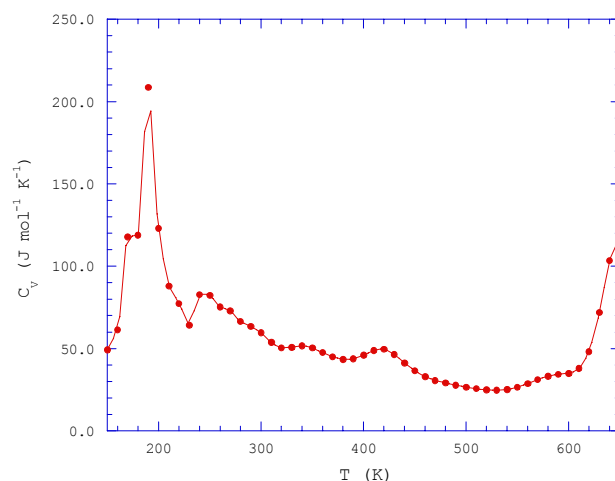


Figure 5. Heat capacity C_V as a function of temperature. The values at each temperature are interpolated.

We now want to decide what kind of phase transition we have identified. The phase in higher temperature belongs to liquid water phase, while we have less information about the phase in lower temperature. In order to know the structure of the phase, the oxygen–oxygen radial distribution function, g_{OO} , was calculated by the reweighting techniques. In Figure 6 the results for $T = 150$, 250, and 500 K are shown. Those that were obtained by the conventional canonical Monte Carlo simulations are also shown in Figure 6 and they are essentially in agreement with those from the MUCAMC simulation.

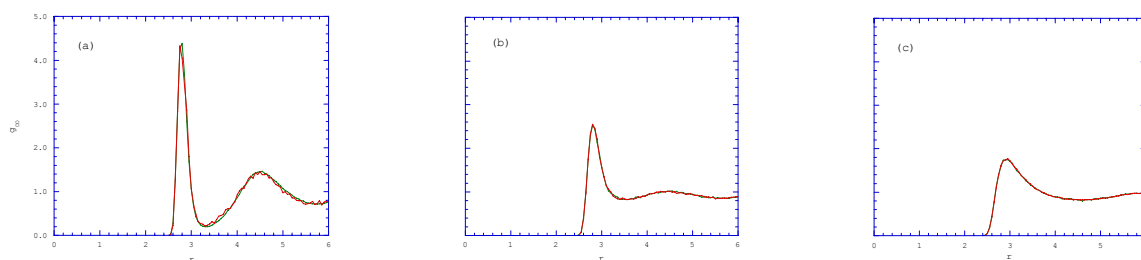


Figure 6 The oxygen–oxygen radial distribution function g_{OO} at (a) 150 K (b) 250 K, and (c) 500 K. The results that were obtained from the MUCAMC production run by the reweighting techniques are shown in red curve and those from the conventional canonical Monte Carlo simulation are in green curve. Distances are in Å.

We emphasize that only one MUCAMC simulation was necessary to obtain the g_{OO} 's for a wide temperature range, while we need many simulation runs to cover this temperature range by conventional canonical simulations. The result at 250 K is typical for bulk water and has peaks at

around 2.9 and 4.5 Å. The first peak is observed at all three temperatures. The peak is sharper at 150 K, whereas that is broader at 250 K and even more broader at 500 K. The second peak that is observed at both 150 K and 250 K is shifted to around 5.8 Å and less pronounced at 500 K. The shape of g_{OO} at 150 K implies that hydrogen bonding is much stronger than in bulk water but that the orientational flexibility remains. This suggests that we have an amorphous ice at 150 K.

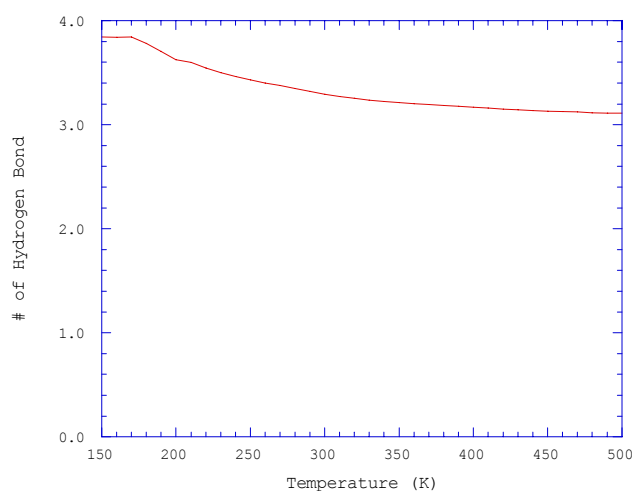


Figure 7. The average number of hydrogen bonds per water molecule.

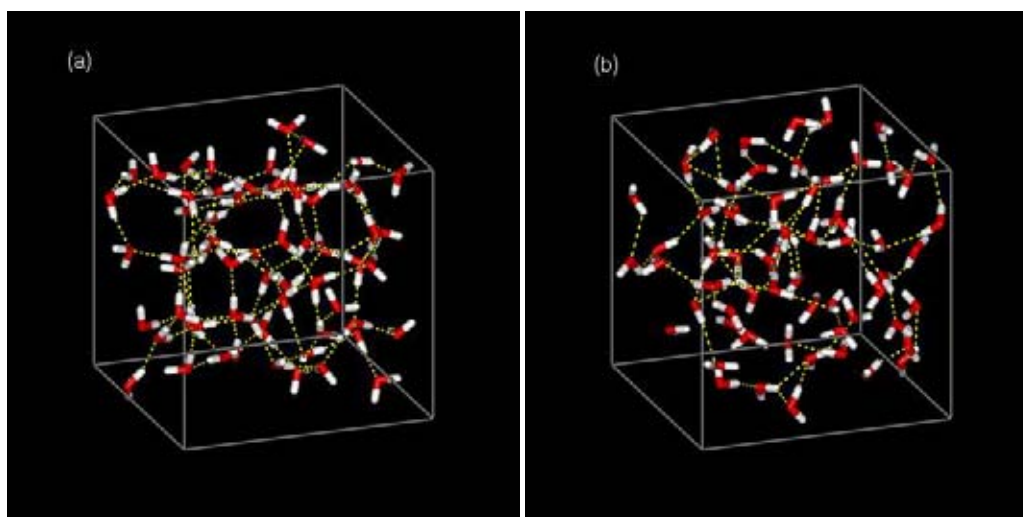


Figure 8 Snapshots obtained by the conventional canonical Monte Carlo simulations at temperatures (a) 150 K and (b) 500 K. The total potential energy is, respectively, (a) -47.85 kJ/mol and (b) -25.12 kJ/mol. Hydrogen bonds are drawn in yellow dashed lines.

Moreover, the average number of hydrogen bonds per water molecule was calculated as a function of temperature from the results of the MUCAMC production run by the reweighting techniques. Here, we consider that the hydrogen bond is formed when the distance between the

acceptor oxygen and hydrogen atom is less than or equal to 2.5 Å. The results are shown in Figure 7. The number is 3.84 below 180 K. This should be compared with the ideal value, four, of the crystalline ice, which indicates that only 4 % of possible hydrogen bonds are broken. This is another evidence for the formation of amorphous ice at low temperatures.

Finally, the snapshots that were obtained by the conventional canonical Monte Carlo simulations at temperatures 150 and 500 K are shown in Figure 8. Water molecules are arranged irregularly at both temperatures. However, at 150 K, we observe some regularity in the hydrogen bond patterns that is characteristic for the amorphous ice formation.

4 CONCLUSIONS

We applied the multicanonical Monte Carlo method to the bulk water system. The method is suitable for systems that have complex potential energy surfaces. In the present study, the multicanonical weight factor that we determined turned out to be reliable for the energy range between –46 and –20 kJ/mol, which corresponds to the temperature range between 170 and 630 K. We found a phase transition at 190 K. By studying the oxygen–oxygen radial distribution function and the average number of hydrogen bonds per water molecule, we concluded that the phase transition that we found is between amorphous ice and liquid water. Although we did not obtain crystalline ice in the present study, we believe that this can be achieved by determining a more accurate multicanonical weight factor in lower energy regions.

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Biographies

Chizuru Muguruma is associate professor of general chemistry at Chukyo University. After obtaining a Master of Science degree from Ochanomizu University under the guidance of Professor H. Hosoya, she pursued a doctor's degree under the supervision of Professor K. Morokuma and obtained Ph.D. degree in theoretical chemistry from the Graduate University for Advanced Studies. She then undertook postdoctoral research with Professor K. Nakanishi at Kurashiki University for Science and the Arts. More recently, she has collaborated on projects with Drs. M. Mikami and Y. Okamoto.

Yuko Okamoto is associate professor of theoretical molecular science at the Institute for Molecular Science, Okazaki National Research Institutes and the Graduate University for Advanced Studies. After obtaining a Ph.D. degree in elementary particle physics from Cornell University under the supervision of Professor T. Kinoshita, he worked as a postdoctoral research associate of Professor R. E. Marshak at Virginia Polytechnic Institute and State University. He then became assistant professor and later associate professor at Nara Women's University. Since 1995 he holds the present positions. His current research interests include generalized–ensemble algorithms for simulations of complex systems and protein folding.

Masuhiko Mikami is deputy director of Research Institute for Computational Sciences (RICS) at National Institute of Advanced Industrial Science and Technology (AIST). After obtaining doctor degree of science in computational chemistry from Tokyo Institute of Technology, he joined Fujitsu Limited and studied molecular simulation method at Research Center of Computational Sciences. Then he moved to National Institute of Material and Chemical Research. More recently, he is a project sub–leader of the nano–technology program at New Energy and Industrial Technology Development Organization (NEDO).