Quantum phase transition of water clusters: molecular dynamics simulations with a model potential

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Received 29 August 2003; revised 29 August 2003; accepted 3 December 2003

Abstract
We have performed molecular dynamics (MD) simulations on water octamer clusters with a model potential (SPC/F2). In addition to classical MD simulations, path integral MD simulations are performed to study quantum effects in the phase transitions of the system. Replica exchange method is used for efficient canonical samplings. Order parameters at various temperatures are calculated by classical and quantum simulations, respectively. It is found that the cluster exhibits quantum behavior in phase transitions around 100 K. The phase transition temperature is found to be lower by 25 K for quantum simulations, compared to the classical simulations.

Keywords: Quantum phase transition; Water cluster; Molecular dynamics; Path integral; Replica exchange method

1. Introduction
Understanding characteristic differences of condensed state of matter compared to gas phase is a subject of not only fundamental importance but also practical interest. Such interests are related with most areas of chemistry ranging from biological and environmental sciences to industrial applications. Molecular clusters are considered to serve as a link between these two extremes of microscopic and bulk properties of matter [1,2]. Despite its simple molecular structure, water clusters provide a challenging problem to study, since they involve rather complicated interplay of various interactions including vibration, bending and electrostatic interactions as well as Lennard–Jones (LJ) type interactions. There have been considerable amount of researches on water clusters both experimentally and theoretically [3,4]. Ab initio quantum calculations have been widely used to examine the energetic and structural properties of small water clusters in detail [5–9]. Searching the global energy minima is a very complicated problem especially as the size of a molecular system increases. It is one of the central problems not only for clusters but also for other complex systems such as polymers and bio-molecules [10–13].

Understanding thermodynamic properties of molecular clusters, especially, phase transition behavior of such systems, poses another challenge for theoretical and computational studies. Clusters exhibit properties related with phase changes, some of which are quite different from those of bulk matter. Unlike a bulk system with the well-defined melting/freezing point, clusters have distinct and separate freezing ($T_f$) and melting ($T_m$) points with nonzero temperature gap, $\Delta T = T_m - T_f$ [13]. Below $T_f$, the cluster exists in a relatively rigid ‘solid-like’ state, whereas it is relatively disordered and ‘liquid-like’ above $T_m$. The temperature range between $T_f$ and $T_m$ corresponds to a coexistence region where there is a dynamical equilibrium between the solid-like and liquid-like forms [14,15]. Several studies on the phase transition of water clusters are reported not only under the normal environment but also under the presence of other species and electric field [16–18].

In the present study, we studied the phase change of water clusters with a flexible water model (SPC/F2) [19]. Water clusters are expected to show non-negligible quantum effects. However, not many studies have been done on the quantum phase changes of water clusters with more realistic potentials while several reports are available on the clusters with LJ potentials [20–22]. The quantum characters of clusters interacting with LJ-type potentials can
be described qualitatively by a de Boer parameter defined as 
\[ \Lambda = \hbar / \sigma \sqrt{\epsilon / m} \]
where \( \sigma \) and \( \epsilon \) are the parameters for LJ potential. Such simplified picture may not be possible for water clusters with more complex potential forms. The ab initio electronic structure calculations reveal the wide spectrum of structures for water clusters depending on the cluster size [23–25], which may play important role in phase transitions.

In addition to a hybrid method combining quantum and classical dynamics for examining quantum effects, one needs a very efficient sampling method to explore the phase evolution of water clusters. Several methods such as path integral method [26], semiclassical Wigner–Kirkwood approach [27,28], and instantaneous normal mode scheme [29,30] can be used to study quantum effects on clusters. Calculations of the canonical properties with regular molecular dynamics (MD) or Monte Carlo (MC) simulations may give inaccurate results if the system tends to be trapped in local energy minima, resulting in incorrect Boltzmann sampling. Several strategies have been proposed to overcome such non-Ergodicity problem recently [31,32]. The replica exchange method (REM) [33,34], also known as replica MC, multiple Markov chain, or parallel tempering method, is considered to be one of the most promising sampling methods for complex systems. In this study, we applied REM to calculate the heat capacity of water octamer from low temperatures up to its melting region. Water octamer provides a useful model system for a couple of reasons. Recently, a significant effort has been focused on the studies of water clusters and related systems with typical length scales in the nanometer range [4,9,35–37]. Water octamer is known to be a small molecular cluster with a well-established melting behavior when described by several potential models [16,38].

2. Methods

2.1. Model potential energy for water

We have used SPC/F2 model for flexible water optimized for quantum simulations [19]. The inter-molecular interactions of the model include LJ interactions between oxygen atoms and Columbic interactions between oxygen and hydrogen atoms. The intra-molecular potential energy includes both O–H stretching and H–H bending motions. The total potential energy is given as

\[ V = V_{\text{inter}} + V_{\text{intra}}. \]

\[ V_{\text{intra}} = \sum_{i=1}^{N} \sum_{j=1}^{N} 4\epsilon \left[ \left( \frac{\sigma}{R_{ij}} \right)^{12} - \left( \frac{\sigma}{R_{ij}} \right)^{6} \right] + \sum_{m} \sum_{n} \frac{Q_{m}Q_{n}}{R_{mn}}. \]

\[ V_{\text{inter}} = \frac{2}{3} \sum_{i=1}^{N} \sum_{j=1}^{N} \rho_{n} D_{n} (b_{\text{OH}} - b_{\text{OH}}^{\text{eq}})^{2} + \frac{1}{2} b (b_{\text{HH}} - b_{\text{HH}}^{\text{eq}})^{2} + c (b_{\text{OH}} - b_{\text{OH}}^{\text{eq}} - 2b_{\text{OH}}^{\text{eq}}) (b_{\text{HH}} - b_{\text{HH}}^{\text{eq}}) + d (b_{\text{OH}} - b_{\text{OH}}^{\text{eq}}) (b_{\text{HH}} - b_{\text{HH}}^{\text{eq}}). \]

where \( R_{nm} \) is the distance between \( i \)th and \( j \)th oxygen atoms and \( R_{nm}^{\text{eq}} \) is the distance between the \( m \)th charge on the \( i \)th water molecule and \( n \)th charge on the \( j \)th molecule. The partial charges of oxygen and hydrogen atoms are \( q_{O} = -0.82 \) and \( q_{H} = 0.41 \), respectively, and the LJ parameters are \( \epsilon = 78.22 \text{ K} \) and \( \sigma = 3.165 \text{ Å} \). \( b_{12} \) is the bond distance between atoms 1 and 2 and \( b_{12}^{	ext{eq}} \) is equilibrium bond distance between them. The equilibrium values are \( b_{\text{OH}} = 1.0 \text{ Å} \) with \( \text{H–O–H} \) bond angle set to be \( 108.0^\circ \). Other parameters are \( \rho_{n} = 2.361 \text{ Å} \) and \( D_{n} = 0.708 \text{ mdyn Å} \).

2.2. Path integral molecular dynamics (PIMD)

We have used path integral MD (PIMD) for quantum mechanical simulations [26,39,40]. The quantum canonical partition function \( Z \) is given by

\[ Z = Tr[e^{-\beta H}] = \int dq \exp[-\beta V_{\text{eff}}(q)], \]

where \( \beta = 1/k_{B}T \) and \( H \) is the system Hamiltonian. Using indexed complete set of coordinates and \( e^{-\beta H} = (e^{-\beta L})^{P} \) with \( \beta = \beta/P \), it can be rewritten as

\[ Z = \prod_{t=1}^{P} \int dq_{t} \exp[-\beta V_{\text{eff}}(q_{t})]. \]

Feynman showed that for large number of discretizations \( P \), it can be described analytically in terms of quantum paths, i.e.

\[ Z = \left( \frac{m}{2\pi\hbar^{2}} \right)^{P/2} \prod_{t=1}^{P} dq_{t} \exp[-\beta V_{\text{eff}}(q_{t})]. \]

where the effective potential is given by

\[ V_{\text{eff}} = \sum_{t=1}^{P} \left[ \frac{mp}{2\hbar^{2}} (q_{t} - q_{t+1})^{2} + \frac{1}{P} V(q_{t}) \right]. \]

In the limit \( P \to \infty \) one obtains

\[ Z = \cdots \int dq(\tau) \exp\left\{-S[q(\tau)]/\hbar\right\}, \]

with

\[ S[q(\tau)] = \int_{0}^{\hbar} d\tau \left\{ \frac{m}{2} \dot{q}(\tau)^{2} + V[q(\tau)] \right\}. \]

In PIMD, one obtains averaged properties of quantum canonical ensemble by sampling the system using MD simulations with the effective potential described above.
Practically, sampling the system under the effective potential with the Cartesian coordinates suffer from poor convergence due to the stiff harmonic force constant involved especially as the number of discretization \( P \) increases. In our PIMD simulations, we used normal mode coordinates instead of Cartesian coordinates to improve sampling efficiency [40]. The normal mode transformation diagonalizes a significant portion of the Feynman action functional. The normal mode transformation is obtained by using a Fourier expansion of the paths given as

\[
q_s = \sum_{n=1}^{P} \alpha_n \exp[2\pi i (s-1)(n-1)/P].
\]

Applying the transformation to harmonic spring terms in effective potential and using the orthonormality relation

\[
\sum_{n=1}^{P} \exp[2\pi i n(j+k)/P] = P \delta_{i,j-k},
\]

gives

\[
\frac{mp}{2\hbar^2 \beta^2} \sum_{i=1}^{P} (q_s - q_{s+1})^2 = \frac{mp}{2\hbar^2 \beta^2} \sum_{n=1}^{P} \alpha_n \alpha_{n+2} - 2P[1 - e^{-2\pi i(n-1)/P}].
\]

The normal modes \( \alpha_n \) are complex. Now redefining the normal mode \( \alpha_n \) as \( P \) even

\[
\begin{align*}
\alpha_1 &= \alpha_1, \\
\alpha_P &= \alpha_P, \\
\alpha_{2n-2} &= \sqrt{2} R[\alpha_n], \quad (n = 2, \ldots, P/2), \\
\alpha_{2n-1} &= \sqrt{2} I[\alpha_n], \quad (n = 2, \ldots, P/2),
\end{align*}
\]

where \( R[\alpha] \) and \( I[\alpha] \) are the real and imaginary part of \( \alpha \), respectively, and the harmonic term is given by

\[
\frac{mp}{2\hbar^2 \beta^2} \sum_{i=1}^{P} (q_s - q_{s+1})^2 = \frac{mp}{2\hbar^2 \beta^2} \sum_{n=1}^{P} \lambda_n \alpha_n^2,
\]

where \( \lambda_1 = 0 \), \( \lambda_P = 4P \), and

\[
\lambda_{2n-1} = \lambda_{2n-2} = 2P[1 - \cos[2\pi (n-1)/P]].
\]

The fact that the harmonic term is diagonalized allows more efficient sampling.

### 2.3. Replica exchange method and simulation details

In REM, several independent trajectories (or replicas) run at different temperatures simultaneously. Then, a trajectory exchange is attempted between two neighboring replicas with a pre-determined interval. There should be considerable overlap of the energy distributions between the replicas to have reasonable acceptance probability for trajectory exchange while keeping the detailed balance condition. The replica exchange introduces stochastic jumps of the system, preventing the trajectory from trapping to local energy minima. Therefore efficient sampling of the canonical properties can be achieved. Initial version of the method was proposed for MC scheme and Sugita and Okamoto [41] later developed a MD version. Once the energy distributions at different replicas are obtained, the canonical properties at any temperature between the minimum and the maximum temperatures used in REM can be calculated easily by multiple histogram re-weighting technique [42]. In general, the expectation value of physical property \( A \) at temperature \( T = 1/k_B \beta \) is given by

\[
\langle A \rangle_T = \frac{\sum_{E} A(E)P(E; \beta)}{\sum_{E} P(E; \beta)},
\]

where \( P(E, \beta) \) is the probability distribution at temperature \( T \). In REM, the energy distribution can be expressed in terms of the energy distributions of the replicas as [43]

\[
P(E; \beta) = \sum_{m=1}^{K} S_m^{-1} N_m(E) e^{-\beta E},
\]

where \( e^{-\beta E} = \sum_{E} P(E; \beta_m) \lambda \) and \( N_m(E) \) is the energy distribution of \( m \)th replica, \( \beta_m = 1/k_B T_m \) with \( m \)th replica temperature \( T_m \), \( n_m \) is the number of replica, and \( S_m = 1 + 2T_m \) with \( T_m \) as the integrated autocorrelation time at temperature \( T_m \).

The number of replicas used is 16 and the replica exchange interval was set to every 250 MD steps with simulation time step of 20 a.u. (about 0.48 fs). Nose–Hoover thermostat with chain length of two was used as a thermostat [44]. Each atom is coupled with independent thermostat for maximum efficiency [45,46]. Verlet algorithm is used as the MD integrator [47]. Initially, water octamer cluster with random geometry was prepared and usual MD simulation was performed for each replica. The corresponding temperatures for the 16 replicas are 24.3, 27.3, 31.5, 36.3, 42, 49, 57, 66, 80, 90, 102, 130, 160, 200, 230, and 250 K. After preparation of the initial structure, each replica was subject to regular MD simulation without replica exchange for 240 ps. Then the replica exchange was turned on and the simulation lasted for about 1.1 ns. We have discarded initial 0.25 ns simulation after starting the replica exchange from our sampling to ensure equilibrium. The number of ‘pseudo particle’ \( P \) in our quantum PIMD simulation is 24 [19]. In both classical and quantum cases, we have performed 10 independent simulations to collect the data.
3. Results and discussions

The average replica exchange acceptance probability was about 37% in both classical and quantum REM simulations and the resulting energy distributions are shown on Figs. 1 and 2, respectively. The heat capacity based on the energy fluctuations for classical simulations is shown in Fig. 3. It can be seen that the phase transition occurs around 125 K and the $\Delta T$ is rather wide with the value of about 75 K. Calculation of the quantum heat capacity is rather tricky since the quantum energy fluctuations from PIMD simulations depends on the use of the energy estimator [48, 49]. Even though the heat capacity can be calculated from the derivative of the energy with respect to the temperature, it involves rather high statistical noise. Instead of calculating the heat capacities as a function of temperature for PIMD simulations, we examined the Lindemann’s order parameter [50] to characterize the phase transition. The Lindemann’s parameter is defined as

$$\delta = \frac{2}{n(n-1)} \sum_{i<j} \frac{(\delta r_{ij})^2}{r_{ij}}^{1/2},$$

where $n$ is the number of molecules in a cluster and $r_{ij}$ is the distance between $i$th and $j$th oxygen atoms. The calculated Lindemann’s parameters are plotted for both quantum and classical simulations in Fig. 4. It is known that the phase transition point is $\delta = 0.1$, [16] which is about 125 K for classical results, consistent with the heat capacity calculations (Fig. 3). The phase transition point for quantum simulations is found to be 100 K, lower by 25 K compared to the classical case. It is interesting to note that the temperature range, $\Delta T = T_m - T_i$, is similar for both classical and quantum clusters.

The main focus of the present paper is on the quantum phase transition of water clusters as a function of temperature. There have been some previous studies on the canonical properties of water clusters. Tsai and Jordan used jump walking method to overcome slow barrier-crossing problem in MC simulations of $(H_2O)_8$ cluster [51]. Ishikawa et al. and Liu and Jordan used REM to calculate cluster canonical properties from classical simulations [52,53]. To our knowledge, the present study provides a first example of combining quantum mechanical simulations with REM to investigate quantum canonical properties of clusters.

The validity of the results obtained from the present study largely depends on the model potential used for water clusters. It is known that the phase transition behavior shows some differences depending the water potentials used [54]. The parameters of the current water model may not be suitable for describing cluster systems since they are fitted based on the bulk water properties. One may need a scheme where accurate potentials are evaluated on the fly as in ab initio MD simulations [55]. Combining such Car–Parrinello approach with REM and PIMD can provide an ideal methodology for studying quantum behavior of clusters, but it is beyond current computational capabilities. Alternatively, one can introduce more realistic water potentials such as polarizable water model based on cluster ab initio calculations or dissociable water model [56–58].

In the present study, only thermodynamic behavior related with phase transitions was examined. One may
investigate some structural aspects of water clusters as well as other properties such as dipole moment using similar methods. It will be also interesting to employ recently proposed scheme of understanding the phase transition of small systems [59–61]. By studying the size evolution of clusters systematically, one can examine the boundary between bulk and microscopic (molecular) behavior. In the case of phase transition behavior, such boundary corresponds to $\Delta T = 0$. Using the methods we have presented, it would be possible to investigate the evolution of behavior of waters, including the quantum effects, from clusters to bulk water by changing the cluster size, which will be the subject for future study.

Acknowledgements

This research was supported by the Korea Research Foundation Grant (2001-003-D00058). SJ acknowledges the Research Professorship of the BK21 Division of the Chemistry and the Molecular Engineering. We appreciate Y. Pak and F. Li for helpful discussions.

References