We study the water octamer in a uniform electric field using the all-exchanges parallel tempering Monte Carlo method in the canonical ensemble. The heat capacity, quenched energy configurations, and the order parameter $Q_4$ are employed to understand the phase changes observed as a function of temperature and the strength of the applied electric field. At a low field strength of 0.1 V Å$^{-1}$ a solidlike to liquidlike “melting” transition is detected. The corresponding heat capacity peak appears around 206 K, where $Q_4$ shows a significant change of slope. For $E \geq 0.5$ V Å$^{-1}$ such features are absent. However, at $E=0.5$ V Å$^{-1}$ we find a solidlike to solidlike transition between cubic and extended structures around $T \sim 25$ K. © 2006 American Institute of Physics.

I. INTRODUCTION

Water clusters exhibit interesting thermodynamic and structural properties. For example, a peak in the heat capacity as a function of temperature is interpreted as the finite system analog of a phase change. A number of simulations have been carried out to investigate the behavior of the water octamer, where an order parameter based on bond orientations can be used to monitor the two phaselike forms. Below the melting region the solidlike phase is dominated by two low-energy cubic structures with $S_4$ and $D_{2d}$ symmetries, while in the liquidlike phase a large number of noncubic structures are sampled. These two phases are separated by a high potential energy barrier, which leads to quasigeneric behavior. Numerous techniques have been developed to tackle this problem, including jump-walk Monte Carlo and parallel tempering (PT) (or replica exchange).

The effect of an external electric field on aqueous media is important in many areas of science and technology. Calculations for water clusters under the influence of electric fields have also been carried out. Nanotubes based on square faces have been characterized for ($H_2O$)$_{32}$ at low electric field strength ($<0.28$ V Å$^{-1}$), and a quasicrystalline phase, similar to cubic ice, was detected at higher fields ($\geq 0.6$ V Å$^{-1}$). In ($H_2O$)$_{40}$ an increase of the polarization with temperature was found. 1 The behavior of water trimer as a function of the external electric field strength has also been studied in detail. For high fields a linear configuration is favored, where the monomer dipoles are aligned with the external field. Recent ab initio calculations showed how the molecules in small water clusters (trimer, tetramer, and pentamer) tend to align their dipole moments along the direction of the field for high electric field strength.

In a complementary paper we describe how the potential energy surface (PES) changes for small water clusters in a uniform electric field. We demonstrate that compact structures are preferred at low electric field and more extended structures at high field. Similar results were obtained for different rigid-body empirical potentials. We also found that increasing the electric field strength decreases the average number of hydrogen bonds, because the field restricts the orientational degrees of freedom of the molecules.

In this paper we consider the classical thermodynamics of water octamer in the presence of a uniform electric field, focusing on the phase changes. We use the TIP4P rigid-body model to describe the interaction between water molecules. Simulations are performed using the PT Monte Carlo method in the canonical ensemble, with all-exchange moves.

II. METHODS

We separate the total potential energy as

$$U_{\text{total}} = U_{\text{water-water}} + U_{\text{e field}},$$

where the first term corresponds to the rigid-body nonpolarizable TIP4P model for the interaction between water molecules, which includes pairwise Lennard-Jones and Coulomb terms. This model has been employed before to study homogeneous water clusters, water clusters containing metallic cations, and water clusters interacting with a C$_{60}$ molecule. 2

The second term of Eq. (1) corresponds to the interaction between water molecules and a uniform electric field applied in the $z$ direction,

$$U_{\text{e field}} = -E \sum_j q_j z_j,$$

where $E$ is the electric field strength, $q_j$ is the partial charge on site $j$ of a water molecule, and $z_j$ is the $z$ Cartesian coordinate of partial charge $j$. Angle-axis coordinates are used to represent the rigid-body degrees of freedom. More details of the potential energy function are available elsewhere.
In atomic and molecular clusters with complex energy landscapes, standard Monte Carlo or molecular dynamics simulations may suffer from quasigrodicity. In particular, large potential energy barriers between thermodynamically relevant regions of configuration space are rarely crossed, preventing effective equilibration. However, the PT Monte Carlo or replica exchange method has been employed successfully to treat such systems, including LJ$_{38}$, LJ$_{309}$, Ar$_{f}$, and water clusters. The PT algorithm is closely related to the jump-walk Monte Carlo method and employs parallel canonical Metropolis Monte Carlo trajectories at different temperatures. Exchange moves between replicas at adjacent temperatures are attempted at regular intervals and are accepted with probability

$$P_{nm} = \min\left[1, \exp(\beta_n - \beta_m(U(R_n) - U(R_m)))\right],$$

where $\beta_n = (k_B T_n)^{-1}$, $\beta_m = (k_B T_m)^{-1}$, and $k_B$ is the Boltzmann constant. $U(R_n)$ and $U(R_m)$ are the potential energies of the configurations at temperatures $T_n$ and $T_m$, respectively.

Calvo, inspired by the kinetic Monte Carlo method, recently proposed an alternative way of performing exchange moves in PT Monte Carlo simulations. In this approach, the exchange probabilities $P_{nm}$ between all pairs $(n,m)$ are calculated. The acceptance rate for exchanges between replicas decreases exponentially with the temperature difference, i.e., the overlap of the energy histograms between two nonadjacent replicas could be zero. However, if these moves are successful, the convergence of the simulation can be accelerated. Calvo demonstrated the efficiency of the method in LJ$_{13}$ and LJ$_{31}$ clusters and two simple spin systems.

To satisfy detailed balance, the possibility of performing no exchange is included with a relative (unnormalized) probability $P_i = 1$. By denoting each pair $(n,m)$ using a single number $k$ ($k=0$ means that the move is not executed), the normalized probability can be defined as

$$\bar{P}_k = \frac{P_k}{\sum_j P_j}.$$  

We randomly select one specific move $k$ according to the probability defined in Eq. (4).

In order to benchmark this all-exchanges parallel tempering (AEPT) method, we have compared it with the standard PT approach for the water octamer in the absence of an electric field. In this study a constraining sphere is used, whose radius must be small enough to prevent evaporation and large enough to have a negligible effect on the thermodynamic properties. We employed a radius of 4.25 Å, the same value as that of Tharrington and Jordan, and 50 replicas at different temperatures between 5 and 280 K. In each run the global potential energy minimum was employed as the initial configuration. To compare the PT and AEPT methods $10^8$ and $5 \times 10^7$ Monte Carlo steps were run to equilibrate the system at each temperature, respectively; statistics were then collected for the same number of steps. Translational and rotational moves were attempted with target acceptance ratios of 0.2 each. In the PT calculations exchange moves between adjacent replicas were attempted with probability $\nu = 0.1$. The heat capacity was evaluated from fluctuations of the potential energy in both simulations (Fig. 1).

**III. RESULTS**

In this section we present our results for water octamer at different electric field strengths as a function of temperature and varying uniform electric field strengths using the AEPT approach. The field strengths considered are $E=0.1$, $0.2$, $0.3$, $0.4$, $0.5$, and $1$ V Å$^{-1}$, and our results are compared with those obtained for the free water octamer with $E=0$ V Å. Trajectories were run for $10^8$ equilibration steps followed by $10^8$ production steps for each replica. The other parameters are summarized in Table I.

**TABLE I. Parameters employed in the AEPT Monte Carlo simulations.**

<table>
<thead>
<tr>
<th>Electric field (V Å$^{-1}$)</th>
<th>Range of temperatures (K)</th>
<th>Sphere radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5–280</td>
<td>4.25</td>
</tr>
<tr>
<td>0.1</td>
<td>5–280</td>
<td>4.25</td>
</tr>
<tr>
<td>0.2</td>
<td>5–280</td>
<td>4.25</td>
</tr>
<tr>
<td>0.3</td>
<td>5–280</td>
<td>6.00</td>
</tr>
<tr>
<td>0.4</td>
<td>5–200</td>
<td>6.00</td>
</tr>
<tr>
<td>0.5</td>
<td>5–200</td>
<td>6.00</td>
</tr>
<tr>
<td>1.0</td>
<td>5–200</td>
<td>6.00</td>
</tr>
</tbody>
</table>

**FIG. 1.** Heat capacity for the free water octamer calculated from the PT (full line) and AEPT (dotted line) methods as a function of temperature.

$C_v(T) = 3k_B + \frac{\langle U^2 \rangle - \langle U \rangle^2}{k_BT^2}$,

where $N$ is the number of water molecules. Both methods produce a heat capacity peak at $T \sim 212$ K, in good agreement with previous results. In fact, the two curves in Fig. 1 are practically coincident, indicating that the convergence of the AEPT approach is faster than that for standard PT. Hence we consider only the AEPT approach for all the subsequent simulations in finite electric fields.
observed: the interaction with the field dominates the PES and favors extended structures with aligned dipoles,\(^{25}\) so that orientationally disordered structures are unfavorable. Preliminary results in which the heat capacity curve was analyzed up to 280 K revealed no additional features, and we therefore omit the range above 200 K.

At intermediate electric field strength, namely, \(E=0.5\ \text{V} \cdot \text{Å}^{-1}\), a well-defined peak in \(C_v\) occurs at \(T\sim 25\ \text{K}\). This peak is also seen if we calculate the derivative of the heat capacity from Eq. 5.

\[
\left(\frac{\partial C_v(T)}{\partial T}\right)_v = \frac{1}{k_B T} \left[ \langle U^3 \rangle + 2\langle U \rangle^3 - 3\langle U^2 \rangle \langle U \rangle \right] - 2k_BT \langle (U^2) - \langle U \rangle^2 \rangle.
\]

(6)

To interpret these results in more detail we consider order parameters introduced by Steinhardt \textit{et al.} for the bulk Lennard-Jones system.\(^{36}\) In particular, we consider the parameter \(Q_4\), which is constructed from a rotationally invariant combination of spherical harmonics up to order \(l\). In previous work \(Q_4\) has been applied successfully to treat Lennard-Jones clusters,\(^{37}\) where

\[
Q_4 = \frac{1}{N_b} \left( \frac{4\pi}{9} \sum_{m=-4}^{4} \sum_{r_{ij}} Y_{4,m}(\theta_{ij}, \phi_{ij}) \right)^2. \quad (7)
\]

Here \(N_b\) is the number of “bonds” (defined as nearest neighbors within a given cutoff distance), \(r_{ij}\) is the distance between \(i\) and \(j\) atoms of different molecules, and \(Y_{4,m}(\theta_{ij}, \phi_{ij})\) is a spherical harmonic. \(\theta_{ij}\) and \(\phi_{ij}\) are the polar and azimuthal angles, respectively, of the vector that points from the center of mass of the cluster to the midpoint of each bond. In the present work we based the calculation of \(Q_4\) on the O–H covalent bonds and employed the algorithm described by Nigra \textit{et al.}\(^{14}\) Figure 3 shows \(\langle Q_4 \rangle\) as a function of temperature for four different electric field strengths.

At \(E\leq 0.1\ \text{V} \cdot \text{Å}^{-1}\) \(Q_4\) remains constant below the melting region where the system is confined to configurations based on cubic structures. At higher temperatures \(Q_4\) decreases due to contributions from noncubic structures.\(^{15}\) At \(E=1\ \text{V} \cdot \text{Å}^{-1}\) \(Q_4\) is larger because the electric field dominates the interaction, and it tends to align the dipole moments, so the order parameter increases. However, \(Q_4\) decreases monotonically with temperature. For \(E=0.5\ \text{V} \cdot \text{Å}^{-1}\) \(Q_4\) shows a significant change around 25 K. Below that temperature the system mostly samples the global potential energy minimum with \(C_4\) symmetry, and the order parameter is close to the values obtained for \(E<0.1\ \text{V} \cdot \text{Å}^{-1}\). However, at higher temperature \(Q_4\) first increases abruptly and then decreases monotonically. To understand these trends in more detail we carried out 10 000 quenches to local minima at regular intervals for each temperature with the three different field strengths. Figure 4 shows the percentage of quenches that result in minima belonging to three different morphologies as a function of temperature for \(E=0.1\ \text{V} \cdot \text{Å}^{-1}\). At temperatures below 160 K the two cubic structures dominate the distribution of quench minima (Fig. 4). However, above 160 K this population decreases, and noncubic structures are increasingly sampled. Around 200 K the probability of quenching to a higher-energy minimum based on a
cubic morphology reaches a maximum of roughly 20%. These results at low electric field strength (≤0.1 V Å\(^{-1}\)) are consistent with the conclusions of Nigra et al.\(^{14}\) and Tharrington and Jordan\(^{15}\) for free water octamer.

The quench distributions at \(E=0.5\) V Å\(^{-1}\) (Fig. 5) are consistent with the heat capacity and \(Q_4\) curves in Figs. 2 and 3, respectively. At low temperature the global potential energy minimum has the maximum quench probability. However, as the temperature increases, this probability rapidly decreases and the population of the second-lowest potential energy minimum starts to increase, reaching a maximum of 30% at \(T\sim20\) K. Around \(T\sim25\) K, at the position of the peak in the heat capacity, a crossover occurs between the occupation probability of the global minimum and an extended structure with two approximately perpendicular rings. The latter geometry attains a maximum quench probability of about 95% at around 60 K. Above 100 K, a second structure with two perpendicular rings attains a roughly constant quench probability of about 15%.

Figure 6 shows the quench probabilities at \(E=1\) V Å\(^{-1}\). The global potential energy minimum, corresponding to a structure with two approximately perpendicular rings, dominates the distribution for most of the temperature range. The free hydrogens lie slightly out of the plane of the two rings in this structure. As the temperature increases, the corresponding occupation probability decreases almost monotonically, and above 30 K the population of the third-lowest potential energy minimum starts to increase, reaching a maximum value of 30% at \(T\sim140\) K. This structure also has two perpendicular rings.

IV. CONCLUSIONS

We have studied the thermodynamics of the water octamer as a function of temperature and a uniform electric field strength using the TIP4P potential and all-exchanges parallel tempering simulations. At \(E\leq0.1\) V Å\(^{-1}\) the heat capacity curves display pronounced peaks corresponding to the finite system analog of a melting transition. At \(E=0.0\) and 0.1 V Å\(^{-1}\) the transition temperatures, corresponding to maxima in the heat capacity, are \(T\sim212\) K and \(T\sim206\) K, respectively. The order parameter \(Q_4\) shows a change in slope at these temperatures, and quenching confirms that the transition can be described in terms of the two lowest-energy cubic minima and noncubic structures.

At \(E=1\) V Å\(^{-1}\) the heat capacity curve does not show any pronounced peak and the melting transition is not well defined. In this regime the electric field dominates the potential energy, and orientationally disordered structures are unfavorable. Hence \(Q_4\) decreases smoothly as a function of temperature. The population of the global potential energy minimum dominates over most of the temperature range considered.

At \(E=0.5\) V Å\(^{-1}\), a solidlike to solidlike transition is marked by a peak in the heat capacity around \(T\sim25\) K. This peak is due to a transition between the two lowest-lying minima and an extended structure with two approximately perpendicular rings. \(Q_4\) also increases significantly at this temperature, reflecting the change in structure.

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