Structural studies of low temperature ice \(l_h\) using a central force potential model\(^a\)

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The revised central force potentials of Stillinger and Rahman [J. Chem. Phys. 68, 666 (1978)] are used to study the binding energy, structure, and multipole moments of a periodic ice \(l_h\) sample with a unit cell of 192 water molecules. The initial configuration for the unit cell has each oxygen in a wurtzite structure and intramolecular H-O-H angles symmetrically positioned in the tetrahedral O-O-O angles. Hydrogens are placed such that the total dipole moment for the unit cell is zero and the diagonal quadrupole moments are small (\(\leq 10^{-18}\) esu cm\(^3\)). Subject to these restrictions, a static energy minimization on the periodic ice crystal yields an optimal O-O separation, intramolecular O-H distance, and intramolecular H-O-H angle of 2.78, 0.972 A, and 101.0°, respectively. Starting from this idealized wurtzite configuration, Metropolis Monte Carlo runs on the periodic system are made at 20 and 200 K. At 20 K, the equilibrated system has an average intermolecular potential energy per molecule of -15.2 kcal/mol and structure factors which have decreased to about 80% of the initial values. The dipole moment for the unit cell is \(\approx 3 \) D. The equilibrated system at 200 K appears to be modified only by temperature dependent vibrational effects.

I. INTRODUCTION

This work has been motivated by our previous studies of \(H_2O\) on model substrates, \(^1\)\(^-\)\(^3\) in which the revised central force potentials of Stillinger and Rahman (RSL2)\(^4\) are used to represent the \(H_2O-H_2O\) interactions. These same potentials are being used to simulate ice formation on substrates with the intent of determining the effect of the substrate in nucleating ice. Hence, knowledge of the properties of an isolated bulk ice \(l_h\) sample (as generated by RSL2) is crucial to interpreting the results of the ice-substrate simulations. In this study we examine the low temperature structure and electric dipole moment of a periodic ice sample with a unit cell of 192 molecules. Monte Carlo studies are made at 20 and 200 K and compared with a static total potential energy minimization on a periodic wurtzite structure at 0 K. Morse and Rice\(^5\) have studied a proton ordered ice \(l_h\) model with a four molecule unit cell, and made a more extensive examination of the ice structures generated by several effective pair potentials (including RSL2) for water. The present study differs from the latter using RSL2 primarily in the size and proton arrangement of the unit cell, and in the use of Monte Carlo methods to simulate the ice \(l_h\) structure at low temperatures. In this work the unit cell of 192 molecules has initially zero dipole moment and small (\(\leq 10^{-20}\) esu cm\(^3\)) quadrupole moments. The Monte Carlo studies at 20 and 200 K examine the relaxation of the structure (as molecules within the unit cell are shifted and rotated independently) and display the temperature dependent effects on the overall ice \(l_h\) structure.

In Sec. II we present the 192 molecule model ice \(l_h\)

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the parameters $R_0$, $r_0$, and $\theta_0$ for the static minimal energy configuration. Metropolis\textsuperscript{7} Monte Carlo simulations at 20 and 200 K are run for $1.6 \times 10^8$ and $0.9 \times 10^8$ steps, respectively, with each H$_2$O internally rigid. At 20 K the dimensions of the unit cell are varied after equilibration of the system and the initial values are found to give the minimal intermolecular potential energy. To make the calculations feasible, each molecule is assumed to interact only with molecules within a radius of 5 Å, or with approximately 17 other molecules. The average dipole moment, the average intermolecular potential energy, the mean square displacement of the O atoms, and the structure factors for a two-dimensional projection of the six-membered rings in the crinkled layers are calculated in the Monte Carlo simulations. The lattice vectors used in the structure factors, $S(k^2)$ and $S(k^3)$ are shown in Fig. 1—which also shows a projection of the four crinkled layers of the initial configuration onto the $xy$ plane. The (two-dimensional) structure factors $S(k^1)$ are given by

$$S(k^1) = N^{-1} \sum_{j=1}^{N} \exp(i k^1 \cdot \vec{r}_j)$$

where $N$ and $\vec{r}_j$ are the number of molecules in the unit cell and the position vector of the $j$th oxygen, respectively. The mean square displacement of the oxygen atoms $\langle \Delta r^2 \rangle$, is calculated from

$$\langle \Delta r^2 \rangle = N^{-1} \sum_{j=1}^{N} \langle | \vec{r}_j^2 - \vec{r}_j |^2 \rangle,$$

where $\vec{r}_j^0$ is a fixed initial position vector for the $j$th oxygen atom. The $\langle \rangle$ denote Monte Carlo averages.

III. RESULTS

The static energy minimization procedure results in the optimal values $2.78$, $0.972$ Å, and $101.0^\circ$ for $R_0$, $r_0$, and $\theta_0$, respectively. For this undistorted ice $I_h$ (wurtzite) structure the average intermolecular potential energy per molecule is $-14.5$ kcal/mol. The calculation of the latter number uses the same cutoff for the potential as the Monte Carlo calculations. The total dipole moment for the unit cell is zero and the diagonal quadrupole moments are $\leq 10^{-28}$ esu cm$^3$. The optimal $R_0$ gives a density of $0.9$ g cm$^{-3}$.

At 20 K the Monte Carlo equilibration is started using the idealized wurtzite structure for the unit cell described above and occurs in about $10^6$ Monte Carlo steps. Averages are taken over succeeding steps. The 200 K system is started from the 20 K system (after 245 000 steps) and equilibrates after about 300 000 steps. Averages for the 200 K system are taken after equilibration. The results for the two temperatures are shown in Table I. The decrease in average intermolecular potential energy per molecule from $-14.5$ (for the initial configuration) to $-15.2$ kcal/mol at the end of the 20 K Monte Carlo run indicates a relaxation of the molecules into a more tightly bound structure in which the hydrogens are rotated slightly from the symmetric positions in the O–O–O tetrahedral bond angles (see Fig. 2). This is also reflected in the increase in the total dipole moment of the unit cell (from 0 to 2.8 D). Shifts in the oxygen positions produce a decrease in the structure factors from 192 to about 150 and are primarily due to temperature effects. A direct test of the temperature effect is not possible by comparing the static and the 20 K results since the static energy minimization procedure allows only three parameters ($R_0$, $r_0$, and $\theta_0$) to be varied and restricts the H$_2$O dipole moments to bisect

<table>
<thead>
<tr>
<th>$N_{mc}$ (10$^4$)</th>
<th>$T$ (K)</th>
<th>$\langle V/N \rangle$ (kcal/mol)</th>
<th>$\langle \rho \rangle$ (D)</th>
<th>$\langle S(k^1) \rangle$</th>
<th>$\langle S(k^2) \rangle$</th>
<th>$\langle \Delta r^2 \rangle^{1/2}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,7</td>
<td>20</td>
<td>-15.2</td>
<td>2.8</td>
<td>154</td>
<td>148</td>
<td>0.1</td>
</tr>
<tr>
<td>0,9</td>
<td>200</td>
<td>-14.3</td>
<td>3.3</td>
<td>109</td>
<td>113</td>
<td>0.3</td>
</tr>
</tbody>
</table>

the O–O–O tetrahedral angles. The 20 K calculation, however, allows all the (rigid) H$_2$O molecules to translate and rotate independently—subject to the interaction potential. At the end of the 200 K Monte Carlo run the average intermolecular potential energy per molecule rises (from that at 20 K) to $-14.3$ kcal/mol. Using this and some preliminary results at 300 and 100 K the virial theorem (assuming zero external pressure) predicts that the average effective potential between molecules is proportional to $r^{-6.4}$. Figure 3 shows the projection of the four crinkled layers in the unit cell at 200 K.

Structure factors for rotated and length scaled $\bar{a}^2$ vectors show no enhancement at 20 and 200 K. Since ice $I_h$ is so close in structure to ice $I_h$, structure factors for ice $I_h$ are also examined. Views of the $zx$ and $zy$ plane projections of the unit cell (see Fig. 4) indicate that the $z$ direction would be along the [101] direction of ice $I_h$—should this structure be emerging with the introduction of temperature effects. However, structure factors for $\bar{a}^2$ and $4\bar{a}^2$ (where the $\bar{a}^2$ are reciprocal lattice vectors for the ice $I_h$ (fcc) structure with lattice constant equal to 6.42 Å and [101] parallel to $\hat{z}$) are all small for the 20 and 200 K systems. Rotation of the

![Image of molecular structure](image1.png)

**FIG. 2.** Snapshot of the 20 K equilibrated 192 molecule unit cell of the model ice $I_h$ structure looking along the $c$ axis. All the molecules are projected onto the $xy$ plane. The snapshot is after $1.6 \times 10^5$ Monte Carlo steps.

![Image of molecular structure](image2.png)

**FIG. 4.** Snapshot of the equilibrated 20 K ice unit cell (after $1.6 \times 10^5$ Monte Carlo steps) with projection of the molecules onto the (a) $zx$ and (b) $zy$ planes. The $xy$ plane is parallel to the (0001) plane of the ice $I_h$ structure.

![Image of molecular structure](image3.png)

**FIG. 3.** Snapshot of the 200 K equilibrated 192 molecule unit cell of the model ice $I_h$ structure looking along the $c$ axis. All the molecules are projected onto the $xy$ plane. The snapshot is after $9.0 \times 10^5$ Monte Carlo steps.

![Image of molecular structure](image4.png)

**FIG. 5.** (a) The position and relative size of the oxygen–oxygen pair correlation peaks in the initial configuration. (b) the oxygen–oxygen pair correlation function $g_{oo}$ for the 200 K equilibrated ice $I_h$ model; averages are over $3 \times 10^5$ Monte Carlo steps.
$\mathbf{R}_i$ vectors produce no orientation for which all three structure factors are large. Hence, we see no evidence for the emergence of ice $I_6$ after about $10^6$ Monte Carlo steps. A larger periodic unit cell or longer runs might produce different results. The latter extensions of the study have not been made. Figure 5 shows O–O pair correlation functions for the idealized static and the 200 K systems.

IV. COMMENTS AND CONCLUSIONS

We have used the revised central force potentials of Stillinger and Rahman to study a periodic ice $I_6$ system with a unit cell of 192 molecules and small dipole moment. A static minimization of the total potential energy of the idealized system with oxygen in a wurtzite structure yields an optimal O–O separation, (intramolecular) O–H distance, and (intramolecular) H–O–H angle equal to 2.78, 0.972 Å, and 101.0°, respectively. Metropolis Monte Carlo runs starting with this initial configuration at 20 and 200 K show some relaxation from the static minimal energy wurtzite structure, and indicate that the rigid water molecules have rotated slightly from their original orientations in which the dipole moments are symmetrically placed in the O–O–O bond angles. There is an increase in the binding energy per molecule as the system relaxes from the idealized wurtzite configuration to the equilibrated configuration at 20 K. This is not unexpected since the two systems have different constraints. From the 20 and 200 K results (and from preliminary data at 100 and 300 K) the binding energy per molecule appears to decrease linearly with increasing $kT$—suggesting that thermal effects are responsible for the reduced structure factors for ice $I_6$. Structure factors for ice $I_6$ are also examined and we find no evidence of the latter structure. The total average dipole moment for the 192 molecule unit cell at 20 K is $\approx 3$ D and the quadrupole and octupole moments remain small. Binding energies per molecule for the initial static configuration (14.3 kcal/mol) and for the equilibrated systems at 20 (15.2 kcal/mol) and 200 K (14.3 kcal/mol) are larger than that reported by Morse and Rice (12.4 kcal/mol). The differing proton arrangement and the smaller (intramolecular) H–O–H angle are no doubt responsible for the larger binding energies per molecule in the present work.

We note that the optimal (intramolecular) O–H distance and H–O–H angle result in a dipole moment per molecule of 1.96 D. This is slightly larger than the monomer vapor value of 1.86 D. Dipole moments per molecule in ice which are larger than those in the vapor have been discussed. However, such discussions seem inappropriate for the present simple model for ice $I_6$. It would be interesting to repeat the present study using the polarization model of Stillinger and David. In progress are equilibrations of the 192 molecule unit cell ice $I_6$ system at 300, 350, and 400 K, using the revised central force potentials. We are also examining the structure of water/ice layers on a model Ag1 substrate using this unit cell and periodic boundary conditions parallel to the substrate surface plane.

ACKNOWLEDGMENTS

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APPENDIX

The coding for the four crinkled ice $I_6$ layers is as follows:

(a) $3, -1, 1, -2, -1, 3, -3, 2, -1, 1, -2, -2, 1, 3,
   -2, 3, -3, -3, -3, 2, -1, -1, 2,$
(b) $1, 2, -2, -2, 3, -3, 2, -1, -2, -1, 1,
   -1, 2, -2, -1, -3, 3, -3, -1, -1,$
(c) $1, -3, 1, -2, -3, 1, 1, -2, 3, 1, 3,
   -2, 1, -1, -2, 2, -2, 1, -1, 3, -3, 2,$
(d) $-1, 1, -3, 3, -2, 2, -1, 1, -2, 3, 3, -2,
   -1, -1, 3, -3, -2, 2, -2, 1, 1,$

(a) $3, -3, 3, -2, -2, -3, -3, -3, -3, -1, 1, -2,
   -2, 3, 2, -1, -1, 1, 3, 3, -3, 2, -1, -1,$
(b) $-3, -1, 3, -3, -3, 1, 1, -2, 2, -2, -1, 1,
   -1, 3, 1, -2, 2, -2, -1, 3, -3, 3, 3,$
(c) $2, -2, -1, 2, -2, -2, -2, 3, 3, -3, 3,
   -1, 3, -3, 3, -1, 1, -2, -2, 1, 1,$
(d) $-3, 2, -3, 2, 3, -1, 1, -2, 2, -1, 3, 1, 1,
   -3, -2, -3, 3, 1, 3, -1, 1, -2, -2, 3,$

The numbers above refer to the projections of the (tetrahedral) bond directions onto the xy plane. The numbering is counterclockwise—with the projection of the number 1 bond (number 3 bond) along $\hat{z}$ ($-\hat{z}$) in the layers marked a and d (b and c). See Fig. 1 for the orientation of the unit cell with respect to the $(x, y, z)$ coordinate system. As mentioned in the text, the unit cell consists of 192 molecules arranged in eight (planar) layers of 24 molecules. The easiest way to use the above coding is to number the molecules in the planes, starting with number 1 at $(0, 0, 0)$ and moving left to right with increasing numbers. The 25th molecule has its center of mass at $(R_0 \sqrt{2}/3, -R_0 \sqrt{2}/3, -R_0/3).$ Note that in Fig. 1, there are four molecules in each line of constant $y$ and $z$, and six rows of four molecules in one planar layer. The above eight rows of 24 numbers refer to the proton "coding" for molecules 1 through 192—in order. The coding is as follows. A positive integer (say, 3) indicates that the hydrogens are along the other two bond directions (1 and 2). Negative integers indicate that one hydrogen is along $\hat{z}$ ($-\hat{z}$) in layers marked a and c (layers marked b and d) and the other hydrogen is along the numbered bond given. Different proton arrangements can be generated by noting that in each of the eight rows of 24 numbers there are four each of the numbers $\pm 1, \pm 2$, and $\pm 3$. This generates the zero dipole moment and minimal quadrupole and octupole moments for the unit cell. Each layer must, of course, satisfy the hydrogen bonding rules for ice $I_6$ and be
properly bonded to the layers above and below. For nonperiodicity the layer Ia must fit beneath layer IVd and the bonds in the perimeters of the eight planes must satisfy the "ice rules" when the cell is translated along the x and y directions. The above coding is taken from that devised by Mrzlik and is similar to that reported by Cota and Hoover for smaller unit cells.

6M. Mrzlik (private communication).