

01 Apr 1983

Structural Studies of Low Temperature Ice I_h Using a Central Force Potential Model

Peter W. Deutsch

Barbara N. Hale

Missouri University of Science and Technology, bhale@mst.edu

Richard C. Ward

Donald A. Reago Jr.

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Physics Commons](#)

Recommended Citation

P. W. Deutsch et al., "Structural Studies of Low Temperature Ice I_h Using a Central Force Potential Model," *Journal of Chemical Physics*, vol. 78, no. 8, pp. 5103-5107, American Institute of Physics (AIP), Apr 1983. The definitive version is available at <https://doi.org/10.1063/1.445378>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Structural studies of low temperature ice I_h using a central force potential model^{a)}

Peter W. Deutsch

Physics Department, Pennsylvania State University, Monaca, Pennsylvania 15061

Barbara N. Hale, Richard C. Ward, and Donald A. Reago, Jr.

Department of Physics and Graduate Center for Cloud Physics Research, University of Missouri-Rolla, Rolla, Missouri 65401

(Received 15 September 1982; accepted 21 December 1982)

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 I_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 ($\leq 10^{-28}$ esu cm²). 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 Å, 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 ≈ 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 H₂O on model substrates,¹⁻³ in which the revised central force potentials of Stillinger and Rahman (RSL2)⁴ are used to represent the H₂O-H₂O interactions. These same potentials are being used to simulate ice formation on substrates with the intent of determining the effectiveness of the substrate in nucleating ice. Hence, a knowledge of the properties of an isolated bulk ice I_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 Rice⁵ have studied a proton ordered ice I_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 I_h structure at low temperatures. In this work the unit cell of 192 molecules has initially zero dipole moment and small ($\leq 10^{-28}$ esu cm²) 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 I_h structure.

In Sec. II we present the 192 molecule model ice I_h

unit cell, describe the initial static total potential energy minimization procedure, and detail the restrictions under which the Metropolis Monte Carlo simulations are carried out at 20 and 200 K. In Sec. III we present the results of the static minimization and the Monte Carlo simulations. Comments and conclusions are given in Sec. IV.

II. THE MODEL UNIT CELL AND DESCRIPTION OF THE CALCULATIONS

The 192 molecule unit cell for the model ice I_h structure consists of four crinkled layers of 48 molecules each. Each crinkled layer contains two planar layers with four molecules along \hat{x} and six molecules along the \hat{y} direction. The xy planes are parallel to the basal face of the wurtzite structure formed by the oxygen atoms. Hydrogens are placed relative to each oxygen so that the dipole moment of each H₂O molecule bisects (and is in the plane of) the O-O-O tetrahedral angles. A scheme of placing the positive charges along the O-O bonds is adapted from that developed by Mruzik⁶ and results in a 192 molecule array which has zero dipole moment and which can be periodically continued in all directions. The array also has small quadrupole and octupole moments: for the case in which the intramolecular H-O-H angles are tetrahedral Q_{zz} (Q_{yy}) $\approx + (-) 2 \times 10^{-28}$ esu cm² and $Q_{xx} \approx 7 \times 10^{-29}$ esu cm². The coding for placement of the hydrogens is given in Appendix A. The wurtzite structure is generated from an assumed O-O distance, which we define to be R_0 .

In the initial minimization procedure the intramolecular O-H distance r_0 , the intramolecular H-O-H angle θ_0 , and R_0 are varied to minimize the total potential energy of the 192 molecules using the revised central force potentials of Stillinger and Rahman.⁴ After determining

^{a)}This material is based upon work supported in part by the National Science Foundation under Grant No. ATM80-15790.

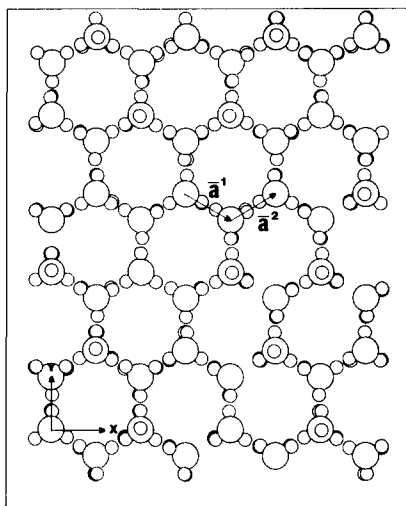


FIG. 1. View of the static potential energy minimized model ice I_h unit cell of 192 H_2O molecules with zero dipole moment, looking along the c axis. All of the molecules in the unit cell are projected onto the xy plane. The \bar{a}^1 and \bar{a}^2 are lattice vectors used to determine the \bar{k}^1 and \bar{k}^2 for the structure factors.

the parameters R_0 , r_0 , and θ_0 for the static minimal energy configuration, Metropolis⁷ Monte Carlo simulations at 20 and 200 K are run for 1.6×10^6 and 0.9×10^6 steps, respectively, with each H_2O 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, $S(\bar{k}^1)$ and $S(\bar{k}^2)$ 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 $S(\bar{k}_i)$ are given by

$$S(\bar{k}_i) = N^{-1} \left| \sum_{j=1}^N \exp(i\bar{k}_i \cdot \bar{r}_j) \right|^2, \quad (1)$$

TABLE I. Results for the average intermolecular potential energy per molecule $\langle V/N \rangle$, the average magnitude of the dipole moment for the unit cell of 192 molecules $\langle p \rangle$, the average structure factors for the two-dimensional projections of the six membered rings in crinkled layers $\langle S(\bar{k}^1) \rangle$, and the root-mean-square displacement of the oxygen atoms $\langle \Delta r^2 \rangle^{1/2}$; N_{mc} is the number of Monte Carlo steps in the run. The average for V/N is taken over 600 000 steps; the other averages are over 200 000 steps. The first row in the table refers to the static total potential energy minimized structure—where all oxygens are on lattice points of the wurtzite structure and all H_2O dipole moments bisect the O—O—O tetrahedral angles.

N_{mc} (10^6)	T (K)	$\langle V/N \rangle$ (kcal/mol)	$\langle p \rangle$ (D)	$\langle S(\bar{k}^1) \rangle$	$\langle S(\bar{k}^2) \rangle$	$\langle \Delta r^2 \rangle^{1/2}$ (Å)
...	...	-14.5	0	192	192	...
1.7	20	-15.2	2.8	154	148	0.1
0.9	200	-14.3	3.3	109	113	0.3

where N and \bar{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

$$\langle \Delta r^2 \rangle = N^{-1} \sum_{j=1}^N \langle |\bar{r}_j^0 - \bar{r}_j|^2 \rangle, \quad (2)$$

where \bar{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° for R_0 , r_0 , and θ_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 cm². 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 θ_0) to be varied and restricts the H_2O dipole moments to bisect

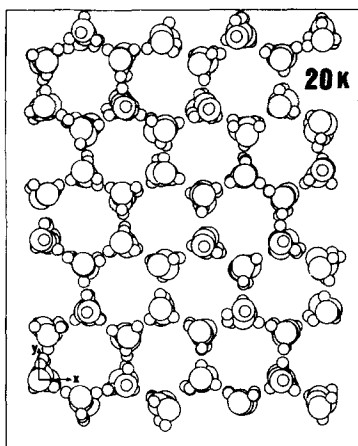


FIG. 2. Snapshot of the 20 K equilibrated 192 molecule unit cell of the model ice I_h structure looking along the c axis. All the molecules are projected onto the xy plane. The snapshot is after 1.6×10^6 Monte Carlo steps.

the O-O-O tetrahedral angles. The 20 K calculation, however, allows all the (rigid) H_2O 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 $r^{-2.4}$. Figure 3 shows the projection of the four crinkled layers in the unit cell at 200 K.

Structure factors for rotated and length scaled \vec{a}^i vectors show no enhancement at 20 and 200 K. Since ice I_c is so close in structure to ice I_h , structure factors for ice I_c are also examined. Views of the zx and yz plane

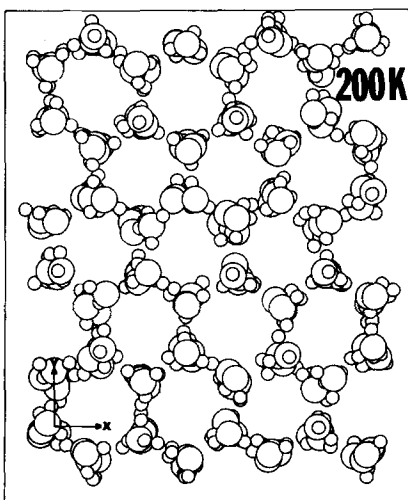


FIG. 3. Snapshot of the 200 K equilibrated 192 molecule unit cell of the model ice I_h structure looking along the c axis. All the molecules are projected onto the xy plane. The snapshot is after 9.0×10^5 Monte Carlo steps.

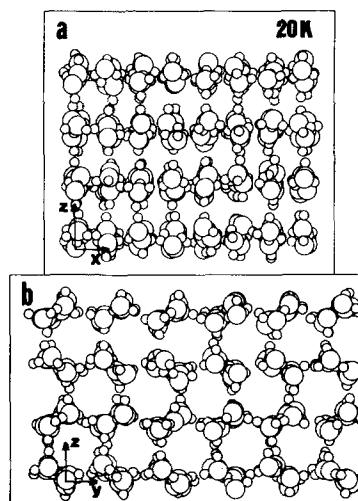


FIG. 4. Snapshot of the equilibrated 20 K ice unit cell (after 1.6×10^6 Monte Carlo steps) with projection of the molecules onto the (a) zx and (b) yz planes. The xy plane is parallel to the (0001) plane of the ice I_h structure.

projections of the unit cell (see Fig. 4) indicate that the z direction would be along the $[101]$ direction of ice I_c —should this structure be emerging with the introduction of temperature effects. However, structure factors for \vec{k}_c^i and $4\vec{k}_c^i$ (where the \vec{k}_c^i are reciprocal lattice vectors for the ice I_c (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

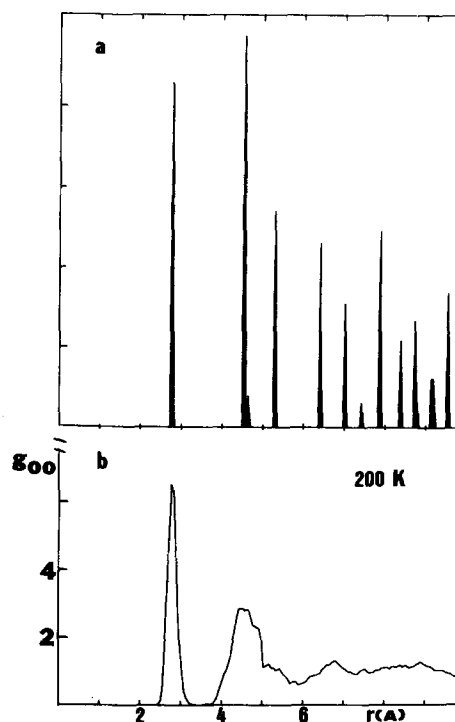


FIG. 5. (a) The position and relative size of the oxygen-oxygen pair correlation peaks in the initial configuration. (b) the oxygen-oxygen pair correlation function g_{00} for the 200 K equilibrated ice I_h model; averages are over 3×10^5 Monte Carlo steps.

\vec{k}_c^i vectors produce no orientation for which all three structure factors are large. Hence, we see no evidence for the emergence of ice I_c 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 Rahman⁴ to study a periodic ice I_h 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 oxygens 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_h . Structure factors for ice I_c 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 ≈ 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).⁵ 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.⁹⁻¹² However, such discussions seem inappropriate for the present simple model for ice I_h . It would be interesting to repeat the present study using the polarization model of Stillinger and David.¹³ In progress are equilibrations of the 192 molecule unit cell ice I_h 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 AgI substrate using this unit cell and periodic boundary conditions parallel to the substrate surface plane.

ACKNOWLEDGMENTS

The authors thank M. Mruzik for the method of arranging the hydrogens in the zero dipole periodic array. We also thank the computer support staff at the University of Missouri-Rolla and at Pennsylvania State University for assistance. One of the authors (PWD) wishes to thank Evelyn Deutsch for help with the computer calculations.

APPENDIX

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

- I(a) 3, -1, 1, -2, -1, 3, -3, 2, -1, 1, -2, -2, 1, 3, 2, -3, 2, -3, -3, 3, -2, 1, -1, 2,
- (b) 1, 2, -2, -2, 3, 3, -3, 2, -1, -2, 1, -2, -1, 1, -3, 2, 2, -1, 3, -3, 3, -3, 1, -1.
- II(c) -1, -3, 3, 1, -2, -3, 2, -1, 1, 3, -2, 1, 3, -2, 1, -1, -2, 2, -1, 2, -3, 3, -3, 2,
- (d) -1, 1, -3, 3, -2, 2, 2, 1, 3, -1, -2, 3, 3, -2, -1, -3, 1, -1, -3, -3, 2, -2, 2, 1.
- III(a) 3, -3, 2, -2, 2, -3, -3, -3, -1, 1, 1, -2, -2, 3, 2, 1, -1, 1, 3, 3, -2, 2, -1, -1,
- (b) -3, -1, 3, -2, -1, 2, -1, 2, -1, -3, 1, 1, -2, 1, -3, 2, 2, -2, -2, 1, 3, -3, 3, 3.
- IV(c) 2, 2, -1, 2, 1, -2, 2, -2, 3, 3, -3, -3, 3, -1, 3, -3, -1, 1, 1, -1, -3, 1, -2, -2,
- (d) -3, 2, -3, 2, 3, -1, 1, -2, 2, -1, 3, 1, -1, -3, -2, 2, -3, 1, 3, -1, 1, -2, 3, -2.

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{y} ($-\hat{y}$) 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 ± 1 , ± 2 , and ± 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_h and be

properly bonded to the layers above and below. For periodicity the layer Ia must fit beneath layer IV d 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 Mruzik⁶ and is similar to that reported by Cota and Hoover¹⁴ for smaller unit cells.

¹B. N. Hale and J. Kiefer, *J. Chem. Phys.* **73**, 923 (1980); B. N. Hale, J. Kiefer, S. Terrazas, and R. C. Ward, *J. Phys. Chem.* **84**, 1473 (1980).

²J. Kiefer and B. N. Hale, *J. Chem. Phys.* **67**, 3206 (1977); B. N. Hale, J. Kiefer, and C. A. Ward, *ibid.* **75**, 1991 (1981).

³R. C. Ward, J. M. Holdman, and B. N. Hale, *J. Chem. Phys.* **77**, 3198 (1982); R. C. Ward, B. N. Hale, and S. Terrazas,

J. Chem. Phys. **78**, 420 (1983).

⁴F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **68**, 666 (1978).

⁵M. D. Morse and S. A. Rice, *J. Chem. Phys.* **76**, 650 (1982); **74**, 6514 (1981).

⁶M. Mruzik (private communication).

⁷M. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

⁸C. W. Kern and M. Karplus, in *Water, A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972).

⁹C. A. Coulson and D. Eisenberger, *Proc. R. Soc. London Ser. A* **291**, 445 (1966).

¹⁰A. Rahman and R. H. Stillinger, *J. Chem. Phys.* **57**, 4009 (1972).

¹¹J. F. Nagle, *Chem. Phys.* **43**, 317 (1979).

¹²D. J. Adams, *Nature (London)* **293**, 447 (1981).

¹³F. H. Stillinger and C. W. David, *J. Chem. Phys.* **69**, 1473 (1978).

¹⁴E. Cota and W. G. Hoover, *J. Chem. Phys.* **67**, 3839 (1977).