Simple Computer Experiments with Ordinary Ice

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Simple computer experiments in which various fractions of hydrogen bonds (H-bonds) in ice are allowed to break are presented in this paper. First, up to six million water molecules were used to build an artificial piece of ordinary hexagonal ice in the form of a cube, a monolayer, a bilayer, a trilayer, and thicker layers. Then, certain percentages of H-bonds were broken, and the obtained structures were examined. It was found that a large percentage of H-bonds must be broken in order to completely fragment the network of ice into clusters. For a cubic piece of ice, which can be considered bulk ordinary ice, this percentage is equal to 61% H-bonds, a figure also predicted as the threshold of the percolation theory for ice. If, as usually assumed, 13–20% of H-bonds are broken during melting (estimates based on the comparison between the heats of melting and sublimation of ice), the H-bond network of ice is not fragmented and the overwhelming majority of water molecules (>99%) belong to a new, distorted but unbroken network. The percentage of broken H-bonds required for full fragmentation of layers increases with the number of layers and reaches the bulk value of ice for 5–8 layers. This value is consistent with the literature observation that films of water thicker than 20–30 Å have properties close to those of the bulk structure.

1. Introduction

By considering that the main difference between liquid water and ice consists of the percentage of hydrogen bonds (H-bonds) of the latter being broken, we determined, by suitable computer experiments, the fractions of water molecules which are present as clusters and as a continuous network as a function of the percentage of broken H-bonds. The calculations have been carried out for both bulk and multilayer ice.

It is well-known [1,2] that water molecules in ordinary ice (Ih) have a tetrahedral structure. Every molecule is located in the center of a regular tetrahedron as a central molecule, has four nearest neighbors at the corners of this regular tetrahedron, and is linked through an H-bond with each of its nearest neighbors. This configuration leads to many (nonplanar) cycles that contain an even number of water molecules, the smallest cycle being hexagonal,[1–2] thus the reason this ice is called hexagonal (Ih).

Cold liquid water (liquid water at 0 °C) is a very structured liquid which possesses numerous features resembling the ordinary ice (Ih). Indeed,[1–6] (i) the number of nearest neighbors is 4.4 (4 in ice), (ii) the water molecules in cold water have only small deviations from the tetrahedral coordination of ice, (iii) the length of an H-bond ($r_{OO} = 2.82$ Å, r_{OO} being the distance between the centers of the oxygen atoms of two H-bonded water molecules) is only a little longer than in ice ($r_{OO} = 2.76$ Å), and (iv) the average number of H-bonds per molecule is 3.6 (in ice it is 4). This picture of liquid water was recently challenged by Wernet et al.[7] who investigated the first coordination sphere in liquid water by X-ray absorption spectroscopy and X-ray Raman scattering. According to them, most molecules in liquid water have only two H– bonds; in one of them the molecule acts as a strong acceptor and in the

other as a strong donor.[7] This means that at room temperature in liquid water there are more than 80% broken H-bonds than in ice (Ih).[7–8] This opinion has been critically discussed in the literature.[8–9]

By comparing the heats of melting and sublimation one finds that only 13% of H-bonds in ice are broken upon melting [2]. A similar result (19%) was recently suggested on the basis of a heuristic density-functional method.[10] Many other estimates of the percentage of broken H-bonds are available in the literature.[3,11] These estimates, based both on experimental results obtained by various techniques and on theoretical models, provided values ranging from 2 to 72%,[3,11] which are dependent on the definition used for an H-bond in liquid water.[12–13]

In this paper, computer experiments have been performed in which various percentages of H-bonds in ice (Ih) were considered broken and the structures of the "liquids" thus obtained are presented as a function of them. A relatively large number, 6×10^6 molecules of water, were used to form a "piece" of ice (Ih). First, this piece of ice was created in the form of a cube, which can be considered as a model for bulk ice. Then, the same number of water molecules was used to "construct" an artificial "monolayer", "bilayer", "trilayer", and so on. Second, certain percentages of H-bonds in ice were randomly broken, and the structures thus obtained were examined. Finally, the obtained results were compared with the available models of liquid water and experimental results.

2. Methodology and Program Code

Experiment [1,2] has shown that every molecule of water in ice is located in the center of a tetrahedron and has four hydrogen bonds with its neighbors, which are located at the vertexes of the tetrahedron. This gives rise to a structure which can be represented as multiple interconnected sheets parallel to the *xy*-plane (see Figure 1 for an illustration of a single sheet). Each sheet consists of a grid of nonplanar hexagons with

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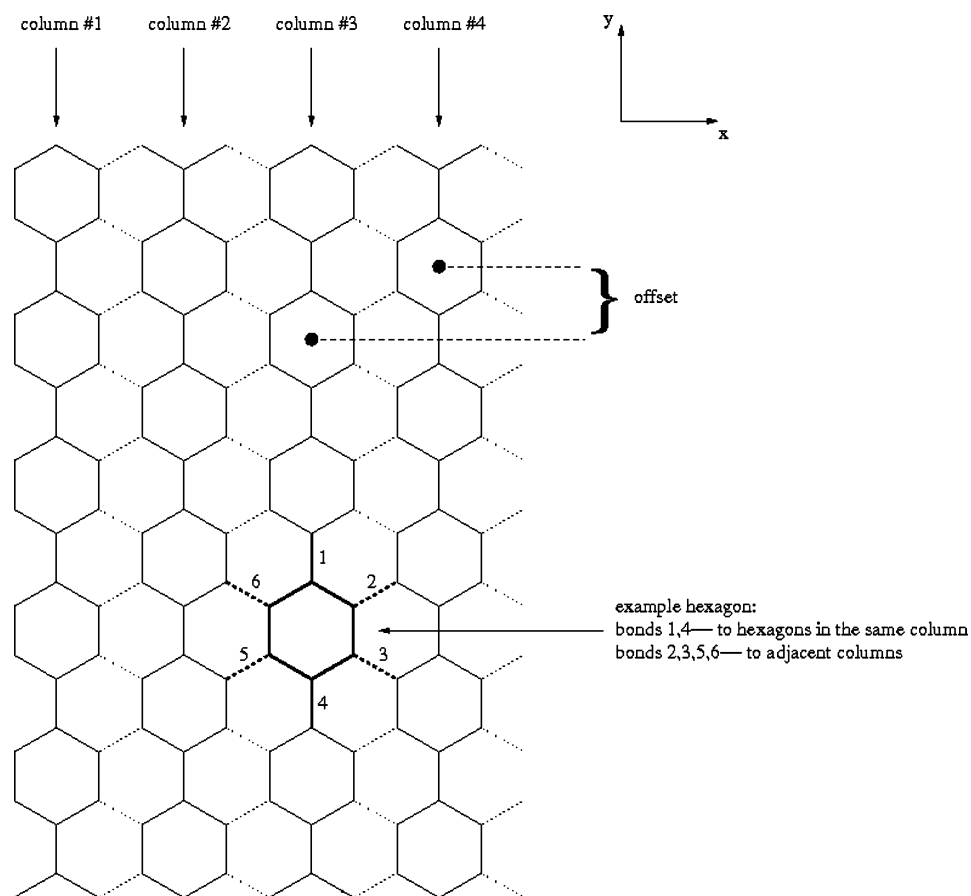† E-mail: ishulgin@eng.buffalo. edu.

Figure 1. Illustration of the ice structure discussed in the paper (only one layer is shown for clarity).

vertexes in the negative and positive *y* direction, each containing six water molecules. The sheets are made up of parallel columns of hexagons in the *y* direction, with adjacent columns offset in the *y* direction by half the distance between the centers of adjacent hexagons. Each hexagon is connected with six neighboring hexagons in the sheet—one above and one below in the same column, as well as two in the left neighboring column and two in the right. The sheets also possess connections between them, as described below. Although the program uses rows of regularly spaced hexagons, its topological structure is as that of real ice, the regularity being simply a coding tool. Each water molecule in ice has four bonds: Two bonds are with neighboring molecules in the hexagon.[1-2] Another bond connects its hexagon to a neighboring hexagon in the same sheet; since each hexagon contains six molecules, it is connected to six other hexagons in the same sheet. Finally, the fourth bond is between sheets. If the molecules in a given hexagon are numbered around the perimeter from one through six, the odd-numbered molecules would bond to the sheet above, while the even-numbered ones would have bonds with the sheet below.

The program has four inputs—three for the dimensions of the lattice and one for the percentage of broken bonds. The first three inputs are integers specifying the width, length, and height of the ice structure. The height provides the number of sheets of molecules created; the width and length give the number of columns of hexagons and the length of each column. Thus, the total number of molecules created is six times the product of the width, length, and height. When the program receives the command-line inputs, it creates the lattice. The sheets are created individually by a loop that runs a number of iterations that is equal to the number of sheets. Then, the proper number of hexagons is created which are connected as described above.

Finally, the sheets are connected as already explained. Obviously, the molecules located on the surface of the lattice end up with less than four bonds.

Once the lattice is created, the bonds are randomly destroyed in a proportion specified at the command line. There is a linked list of sheets in the structure, and each sheet involves a linked list of bonds; thus, all bonds are processed using a double nested loop. For each bond, a random number between 0 and 1 is generated and compared to the specified probability (which is also between 0 and 1); if the random number is smaller, the bond is deleted. When a bond is deleted, it acquires the property "deleted", which is used later in the program.

Finally, the number and size of the resulting fragments must be found. If the probability used is very small, it is possible that no molecule or group of molecules becomes separated from the original structure and the original lattice is preserved. For calculating the size of a given piece, each molecule has the method "pull", which removes the molecule and any molecules attached to it from the lattice. Using the "pull" method, a depth-first search is run to find the number of molecules in each separate piece.[14]

3. Calculations

The hardware limitations of the program mainly rest with the creation of the lattice in the memory and the calculation of the cluster sizes. The program was designed on a personal machine with 512 MB RAM which could handle lattices of up to one million molecules in its memory, albeit very slowly. The lattices used for the final results, containing up to 6×10^6 molecules, had to be created on a supercomputer with up to 5 GB RAM. Thus, this aspect of the program is dependent directly

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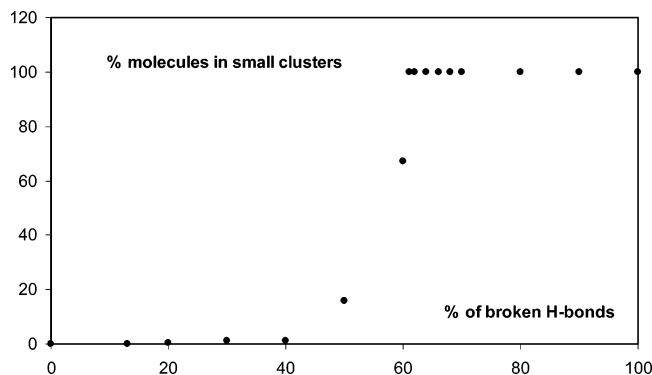

Figure 2. Percentage of molecules in small clusters (compared to the total of 6×10^6 molecules of water) as a function of percentage of broken H-bonds.
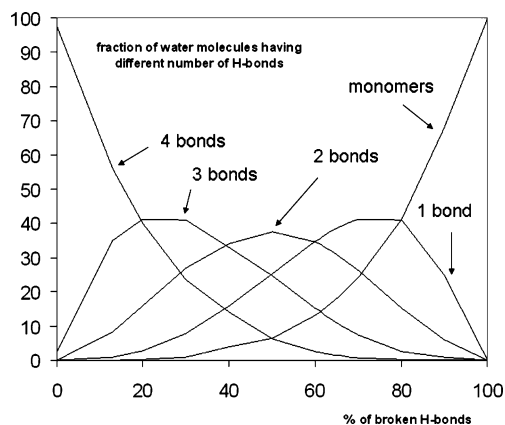

Figure 3. Percentages of water molecules having 4, 3, 2, 1, and 0 H-bonds as functions of the percentage of broken H-bonds.

TABLE 1: Average Size of Clusters as a Function of Percentage of Broken H-bonds

percentage of broken H-bonds (%)	average size of clusters expressed as number of water molecules in the cluster
61	3.9
64	3.4
66	3.0
68	2.7
70	2.5
80	1.7
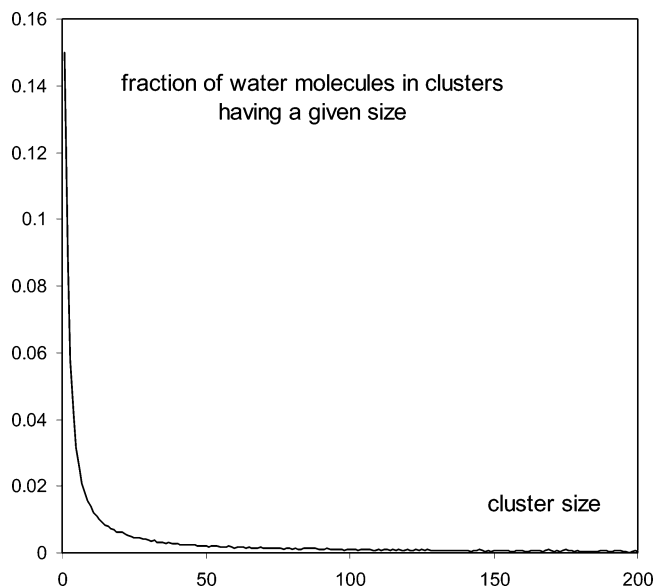
Figure 4. Distribution of the fraction of clusters when 61% of the H-bonds in ice are broken.

on the amount of RAM available and is indefinitely expandable. The second shortcoming, regarding the cluster sizes, does not have a simple solution. The depth-first search algorithm used for finding the sizes of the clusters ran into limitations in terms of the stack size on the machines used. Thus, only clusters smaller than 3000 molecules could be extracted. The solution to the problem would be a more efficient data structure for storing the molecules and their bonds, which allows for a more efficient breadth-first search.

The supercomputer used for calculations was the Young machine at the Center for Computational Research at the University of Buffalo. For the program to be executed using several processors, a computer-specific script was adopted.

4. Results of Computations

4.1. Bulk Ice. The results of the calculations have shown that a cubic piece of ice containing about 6×10^6 molecules of water cannot be broken up completely into small clusters when less than 61% of H-bonds are broken. This means that when 13−20% of H-bonds (usual estimates from the comparison between the heats of sublimation and melting of ice) are broken, the above piece of ice is still an unbroken entity and all the contained water molecules are connected in a network of H-bonds. The fraction of water molecules in clusters as a function of the percentage of broken H-bonds is presented in Figure 2. The fractions of water molecules having 4, 3, 2, 1, and 0 H-bonds calculated by the present simulations are presented in Figure 3. Figure 3 shows that there is a maximum for the fraction of water molecules having two H-bonds at $p = 0.5$, (where $p = 10^{-2} \times$ percentage of broken H-bonds), a

maximum for the fraction of water molecules having one H-bond at $p = 0.75$, and a maximum for the fraction of water molecules having three H-bonds at $p = 0.25$. Let us note that the fractions of water molecules having 4, 3, 2, 1, and 0 H-bonds can be also calculated using probability theory (see refs 15−16) and that the results obtained via the latter theory can serve as a test for the correctness of our simulations. If H-bonds are broken randomly with a probability p, then the fraction of water molecules with four H-bonds is given by $(1 - p),^4$ with three H-bonds by $C_4^1 \cdot p \cdot (1 - p)^3$, with two H-bonds by $C_4^2 \cdot p^2 \cdot (1 - p)^2$, with one H-bond by $C_4^1 \cdot p^3 \cdot (1 - p)$, and with zero bonds (water monomers) by $p,^4$ where C_i^j is the number of combinations of i objects taken j at a time. The results based on probability theory coincide with those provided by simulations and presented in Figure 3.

According to the results obtained by computer experiments, if more than 61% H-bonds are broken, the piece of ice will be completely fragmented into clusters. The average size of such clusters is provided in Table 1. The frequency of the clusters having various sizes is presented in Figure 4.

4.2. Several Layers of Ice. The same calculations were carried out for several (1−13) layers of ice. Each layer consisted of a sheet of hexagons as described in section 2 "Methodology and Program Code". As expected, in this case smaller percentages of H-bonds have to be broken for clusters to be generated. The results are presented in Figure 5 which shows that whereas for bulk ice (a cubic piece) 61% percent of broken H-bonds are required to generate separate clusters, this figure becomes 38% for a monolayer, 48% for a bilayer, and 61% for 5−8 layers of ice.
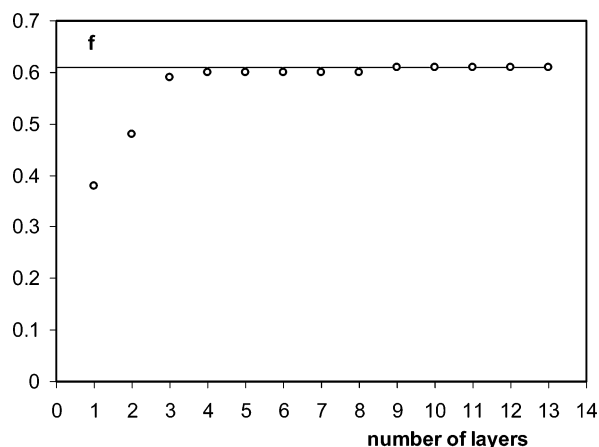
Figure 5. Fraction of broken H-bonds (f) required for full fragmentation in clusters of several layers of ice. The solid line represents the fraction of broken H-bond (0.61) required for full fragmentation of the bulk ice (a cubic piece).

5. Discussion of Results and Comparison with Available Models and Experimental Information

5.1. First, the results of computer experiments with a cubic piece of ice (Figures 2−4 and Table 1) will be examined.

A large number of water molecules (up to 6×10^6 water molecules) was considered in order to minimize the effect of water molecules located on the surface. Indeed, the number of molecules on the surface is small (approximately equal to $6((6 \times 10^6)^{1/3})^2 \approx 0.2 \times 10^6$, hence approximately 3.3% of the total number of water molecules). In addition, the numbers of water molecules having different numbers of H-bonds (Figure 3) coincide with those calculated using the probability theory.

Of course, the present simple computer experiment cannot be considered as an exact counterpart of the ice melting because[2] liquid water cannot be topologically related to ice by the simple breaking of the H-bonds of the latter. Indeed, our computer experiments deal only with energetic characteristics of the ice melting and do not account for changes in entropy and volume. However, the obtained results can be helpful in analyzing various liquid water models.

The number of models that describe the structure and properties of liquid water is enormous. They can be subdivided into two groups:[12] the uniform continuum models and the cluster or mixture models. The main difference between these two classes of models is their treatment of the H-bond network in liquid water; whereas the former assumes that a full network of H-bonds exists in liquid water, in the latter the network is considered broken at melting and that the liquid water is a mixture of various aggregates or clusters. The uniform continuum models stemmed from the classical publications of Bernal and Fowler,[17] Pople,[18] and Bernal.[19] Among the cluster or mixture models, reviewed in refs 2−6 and 12, one should mention the models of Samoilov,[20] Pauling,[21] Frank and Quist,[22] and Nemethy and Scheraga.[23]

If (as usually considered) 13% of H-bonds are broken during melting, the H-bond network of ice cannot be fragmented during melting and the overwhelming majority of water molecules (>99%) form a new distorted but unbroken network. This conclusion is not consistent with the cluster or mixture models, but it is compatible with the uniform continuum models. Arguments against the cluster or mixture models were presented by a number of authors.[2,15−16,24]

Our calculations lead to the conclusion that the H-bond network in ice is so dense that 13−20% of the H-bonds broken

cannot generate a mixture of disconnected clusters. They also show that the network of H-bonds in ice can be completely fragmented when ∼61 % of the H-bonds are broken. Let us note that this value (∼61 %) corresponds exactly to the threshold in the percolation theory for ice (Ih).[15−16]

Consequently in the "liquid" obtained after breaking 13−20% of the H-bonds (i) all water molecules belong to one network and are connected to each other by a weakened network of H-bonds, (ii) there are some large cavities formed as a result of the rupture of H-bonds, and (iii) these cavities cannot be stable and are prone to entropy-driven structural transformations. These transformations contribute to the entropic and volumetric changes associated with ice melting.

5.2. The several layers of ice considered in this paper represent artificial constructions of ice in a vacuum in which water molecules on the surface have interactions (H-bonds) with other molecules in the layer and in neighboring layers. These layers represent slices of ice and are very different from bulk ice. For example, 99.9% of water molecules in the monolayer have three H-bonds, about 50% in the bilayer have three H-bonds, and about 50% have four H-bonds in the bilayer.

The calculations regarding several layers of ice have shown that the percentage of broken H-bonds needed for full fragmentation of layers increases with an increasing number of layers and reaches the value for bulk ice at 5−8 layers.

Thin films of ice and water are of interest in the nanosciences.[25−30] Usually these films are considered to be confined between two solid surfaces (walls). It was found that films thicker than 20−30 Å have properties close to those of the bulk.[25−30] These observations are consistent with our results that the percentage of broken H-bonds required for full fragmentation of layers reaches the bulk value for 5−8 layers.

6. Conclusion

Simple computer experiments were performed to examine the ordinary ice (Ih) in which a fraction of hydrogen bonds have been broken. A large number (6×10^6) of water molecules were considered. The sample of ice was first constructed in a cubic form, and then the same amount of water molecules was used to build up mono-, bi-, tri-, etc. layers of ice.

The results of our calculations indicated that in all cases (the cubic sample, mono-, bi-, tri-, and more layers) the small amount of 13−20% of broken H-bonds, usually considered enough for melting, is not sufficient to break up the network of H-bonds into separate clusters. The so-called cluster or mixture models are not consistent with the results of the present simulations. From our results one can conclude that liquid water can be considered to consist of a deformed network with some H-bonds ruptured. In the case of bulk ice more than 61% of the H-bonds has to be broken for its complete fragmentation into clusters to occur. The same result was obtained via percolation theory.[15−16]

The calculations, carried out for several layers of ice, indicated that the percentage of ruptured H-bonds required for full fragmentation of the layers increases with increasing number of layers and reaches the bulk value for 5−8 layers.

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