Modeling the Ice VI to VII Phase Transition

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Abstract

Ice (solid water) is found in a number of different structures as a function of temperature and pressure. This project focuses on two forms: Ice VI (space group $P4_2/nmc$) and Ice VII (space group P$n3m$). An interesting feature of the structural phase transition from VI to VII is that both structures are "self clathrate," which means that each structure has two sublattices which interpenetrate each other but do not directly bond with each other. The goal is to understand the mechanism behind the phase transition; that is, is there a way these structures distort to become the other, or does the transition occur through the breaking of bonds followed by a migration of the water molecules to the new positions? In this project we model the transition first utilizing three dimensional visualization of each structure, then we mathematically develop a common coordinate system for the two structures. The last step will be to create a phenomenological Ising-like spin model of the system to capture the energetics of the transition. It is hoped the spin model can eventually be studied using either molecular dynamics or Monte Carlo simulations.

1 Overview of Ice

The known existence of many solid states of water provides insight into the complexity of condensed matter in the universe. The familiarity of ice and the existence of many structures deem ice to be interesting in the development of techniques to understand phase transitions. More specifically, how does the reorganization of water molecules
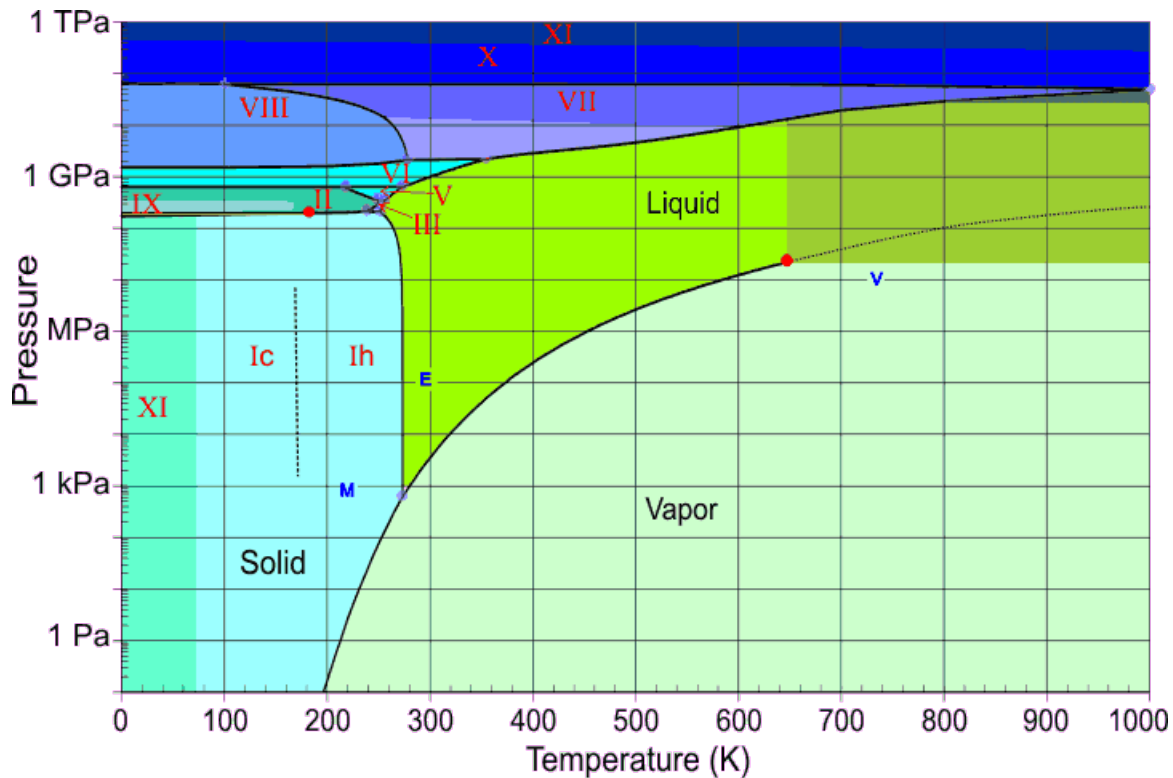

Figure 1: A Phase Diagram of water. Nine of the solid states are shown but more are known to exist. "E," "M," and "V" represent standard tempurature and pressure on Earth, Mars, and Venus, respectively [1].

occur from one phase to another; more generally, can these techniques be utilized to model phase transitions in other materials in different states? For crystallographers, ice has resemblances to phases found in SiO_2 and GeO_2. Also, similarities exist with the tetrahedral bond networks found in semiconductors and nine of the ice phases [2].

This project focuses on building a model for simulating the structural phase transition between ice VI and VII, which are two of nine structures that come from the same parent structure. The "parent" is being defined as: "disordered body centered cubic structure possessing different fractional concentrations of water molecules [3]."

The only ice structure found naturally on earth is hexagonal ice (I_h). The phase diagram shown in Fig. 1 represents the water molecule as a function of temperature and pressure, with the "E," "V," and "M" being standard atmosphere and pressure found on Earth, Venus, and Mars respectively. Nine of the solid phases are represented here, but more phases are known to exist.
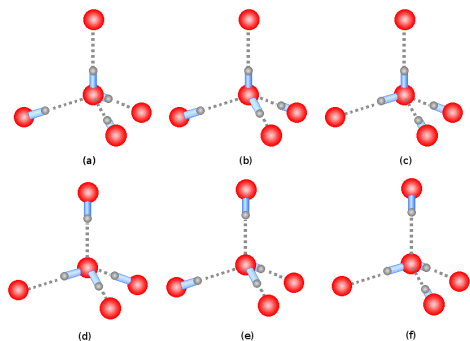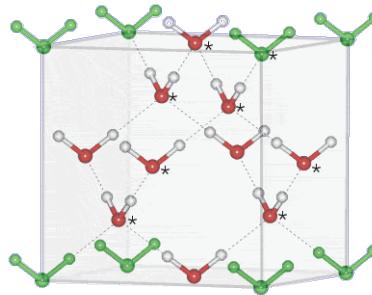

Figure 2: An example of an ordered hydrogen atom positioning on a cubic lattice. All water molecules in the same type of site have the same orientation [4].

Figure 3: The tetrahedral bond structure allows six possible orientations of the water molecule [5].

We observe that phase transitions that occur at a pressure dependent phase boundary happen by a structural re-ordering of oxygen atoms from one state to another; contrarily, the phase transitions that occur at a temperature boundary do not structurally re-order the oxygen lattice, but are a transition from an ordered to disordered hydrogen state. For example, the phase transition between ice VII and VIII or cubic ice (I_c) and ice IX occur at a temperature boundary, and Fig. 2 shows an example of the type of ordering scheme found in these structures. The phase transition between ice VI and VII occur at a pressure boundary so the hydrogen placement between bonds will be in a disordered state. This is illustated in Fig. 3; all six orientations equally

likely.

The structures of ice VI and VII have been identified through the experimental work of Kamb [6] and then later through the work of Kuhs [7]. Both experiments found ice VI to be a member of space group $P4_2/nmc$ and ice VII a member of space group $Pn3m$, determining the form of the coordinates for the basis oxygen atoms, which are shown in Table 1. The positions of oxygen atoms are listed; the hydrogen atom locations are disordered. There are four hydrogen atoms around every oxygen making a tetrahedral bonding structure. Fig. 4 shows an ideal tetrahedral bonding scheme, with hydrogen bonds linking oxygen atoms.
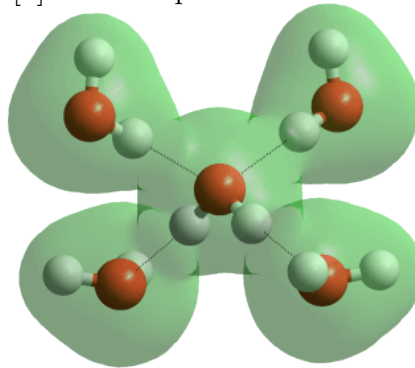

Figure 4: Ideal tetrahedral bond structure shown with water molecules [5].

Because of the hydrogen bonding, the hydrogens must obey the "**ice rules**," which are the two constraints:

1. *There is precisely one hydrogen atom on each hydrogen bond.*

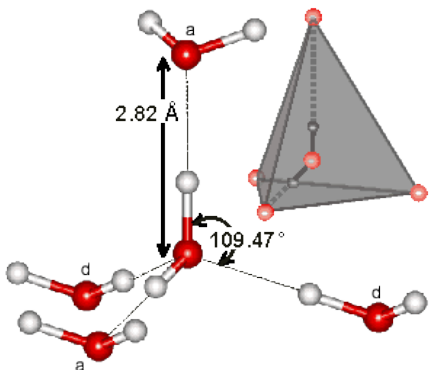2. *There are precisely two hydrogen atoms near each oxygen atom.*

Figure 5: Ideal tetrahedral bond angle shown with water molecules. The ideal bond angle is $\theta_o = 109.47°$ [5].

Violation of the first rule (known as Bjerrum L and D defects [8]) happens when either none or two protons are located between bonds. An ionic defect is a violation of the second rule where three protons are located near one oxygen atom. These defects are energetically unfavorable so they rarely occur. The first rule is estimated to have one defect per five million bonds at approximately 263 K. The number of defects goes down considerably with decreasing temperature, and there are even less ionic defects

since they are even more energetically unfavorable [8]. Even though these defects are energetically unfavorable, they will need to be considered in a model.

The unit cell of ice VI is a body-centered tetragonal (bct) Bravais lattice with tetragonal dimensions $a = 6.27 \pm 0.01$ Å and $c = 5.79 \pm 0.01$ Å. Very similarly, ice VII is defined with a face-centered cubic (fcc) Bravais lattice with cubic dimensions of $a_c = 3.30 \pm 0.01$ Å. Another interesting feature is that both ice structures of interest contain two sublattices (notated A and B in Table I) where the atoms on an A sublattice connect only with other A atoms on the sublattice, and the atoms on the B sublattice only connect with atoms on the other B sublattice. The sublattices do not interconnect, yet they do interpenetrate. Therefore, the complete structure is considered "self-clathrate" [6].

2 Building a Model

This project focuses on the structural phase transition between ice VI and VII and how this transition might occur. We first utilized the Jmol applet [9] for three dimensional viewing of ice VI and VII structures in different orientations in space. The challenge was to construct a simulation cell of adequate size that could represent both structures in a common coordinate system. Because of the large number of possibilities, the visualization of small sample cells helped to build a model which contained the possible structures. Figure 6 shows snapshots of some of the structures created in Jmol. The circles indicate the position of the oxygen atoms positions, not the bonds or location of the hydrogen atoms. We let the lighter shade atoms be the A sublattices of ice VI and VII. It was this visualization tool that aided the ideas for the proposed simulation cell.

After visualizing and comparing coordinate systems, we decided on a simulation cell that contains two units cells of Ice VI (see Fig. 6 (a)) and one unit cell of Ice VII (see Fig. 6 (d)). The simulation cell shown in Fig. 7 is a projection diagram on the xy plane showing potential lattice sites.

The idea is to throw twenty oxygen atoms into the simulation cell and let the atoms

Ice VI		Ice VII	
A	B	A	B
a:[0 0 0]	a:$\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]$	a:$\left[\frac{1}{2}\frac{1}{2}\frac{1}{2}\right]$	a: [0 0 0]
d: $\left[\frac{1}{2}\frac{1}{2}0\right]$ $\left[0\frac{1}{2}\frac{1}{2}\right]$ $\left[\frac{1}{2}0\frac{1}{2}\right]$	d:$\left[00\frac{1}{2}\right]$ $\left[\frac{1}{2}00\right]$ $\left[0\frac{1}{2}0\right]$	disappears	disappears
b:$\left[\frac{1}{4}\frac{1}{4}\frac{1}{4}\right]$ $\left[\frac{3}{4},\frac{3}{4},\frac{1}{4}\right]$ $\left[\frac{3}{4},\frac{1}{4},\frac{3}{4}\right]$ $\left[\frac{1}{4},\frac{3}{4},\frac{3}{4}\right]$		g: $\left[\frac{1}{2},\frac{1}{2}+x,\frac{1}{2}+\overline{z}\right]$ $\left[\frac{1}{2},\frac{1}{2}+\overline{x},\frac{1}{2}+\overline{z}\right]$ $\left[\frac{1}{2}+x,\frac{1}{2},\frac{1}{2}+z\right]$ $\left[\frac{1}{2}+\overline{x},\frac{1}{2},\frac{1}{2}+z\right]$	
	c:$\left[\frac{3}{4}\frac{3}{4}\frac{3}{4}\right]$ $\left[\frac{1}{4}\frac{1}{4}\frac{3}{4}\right]$ $\left[\frac{1}{4}\frac{3}{4}\frac{1}{4}\right]$ $\left[\frac{3}{4}\frac{1}{4}\frac{1}{4}\right]$		$\left[0\ x\ z\right]$ $\left[0\ \overline{x}\ z\right]$ $\left[x\ 0\ \overline{z}\right]$ $\left[\overline{x}\ 0\ \overline{z}\right]$

Table 1: Coordinates of the oxygen basis atoms in ice VI and VII. Following the group theory convention, positions are shown as fractions of the Bravais lattice dimensions; a and c for body-centered tetragonal ice VI and a_c for face-centered cubic ice VII. The bars indicate negative fractions.

randomly choose one of the many the possible configurations; and then, via a Monte Carlo algorithm, simulate movement of the atoms from ice VI to one of the possible configurations of ice VII, or vice versa. For example, Figs. 8 and 9 contain three of the possible crystal structures the simulation cell can represent. Figures 8 (a) and (b) show in projection two of the possible realizations of ice VI and Figs. 9 (a) and (b) show one possible realization ice VII with two of sublattices A and B projected seperately. Each realization of an ideal ice VI or VII structure has its own energy, but the degeneracy of each of these perfect states is different.
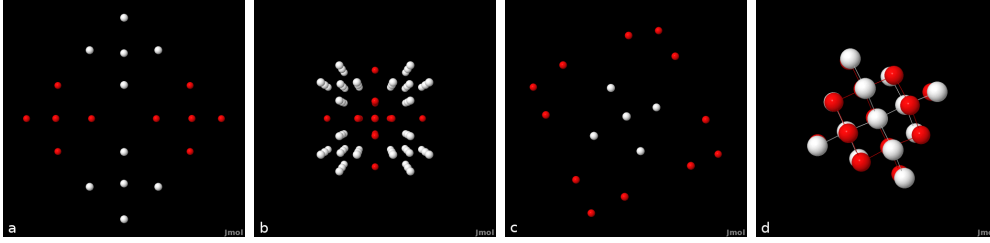
Figure 6: a,b, and c are snapshots of ice VI. All snapshots are a projection on the $xy-$plane, and the lighter shades are the A sublattices. It should be remembered the oxygen atoms exist at different heights in z. One unit cell of ice VI contains one A and a one B sublattice, so the visualizations contain different numbers of atoms. d is a snapshot of the unit cell of ice VII with the a sublattice being the lighter shade.

This should appear through the entropy when the transition is modeled in a simulation.

3   Future Work

As seen with some of the previous examples, real world crystal systems have many degrees of freedom. Our eventual goal is to model the ice VI-VII phase transition using a lattice gas model. A lattice gas model can represent a large number of fixed particles confined to a lattice but allowed to move throughout the lattice to different lattice sites. Most importantly, the model may include specific interactions between

Figure 7: Each circle in the xy plane represent atoms at heights $z = 0, 2, 3, 4$ (large circles) and $z = 1, 3, 5, 7$ (small circles). The dimensions of the unit cell are $\frac{\sqrt{2}}{8}a \times \frac{\sqrt{2}}{8}a \times \frac{c}{8}$, where a and c are the lattice constants of ice VI. For ice VII, $a_c = \sqrt{2}a = c$.

particles, such as interaction energies and collisions. A particular lattice will contain N sites, with $\rho = \frac{n}{N}$ being the fraction of particles occupying the lattice [8]. For the special case of the lattice gas Ising model the particles must satisfy the following rules (as given
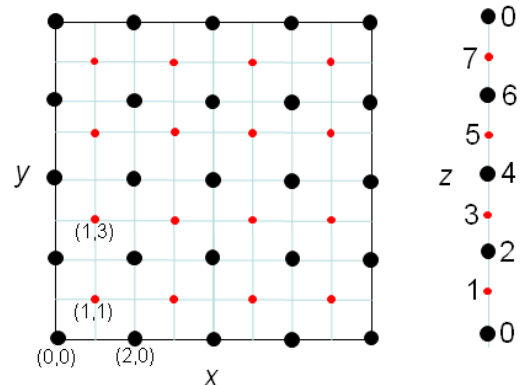
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by Newman [8]):

1. *"The total number of particles is fixed, so that if a particle disappears from one site it must reappear at another. (Equivalently, we could say that the particle density ρ is constant.)"*

2. *"A lattice site can be occupied by at most one particle at any time. This "site exclusion" rule has a similar effect to the hard-sphere repulsion seen in real systems, which is the result primarily of Pauli exclusion."*

3. *"If two particles occupy nearest-neighbor sites on the lattice, they feel an attraction with fixed energy ϵ. This rule mimics the effect of the attractive forces between molecules."* [8]

With these assumptions, a certain fraction of particles ρ (i.e., the twenty oxygens in ice VI) could be placed at random, and a Monte Carlo simulation, such as the Metropolis or continuous time algorithm, could be performed. Remembering that the atoms have freedom to move in the model, as the thermodynamic variables (e.g., temperature T and pressure P) of the system change, the system may undergo a phase transition. Ice VI should evolve into an ice VII structure through random Monte Carlo moves. We are not at this point in the project yet, so we discuss instead steps in building a lattice gas model, starting with the creation of a Hamiltonian.

First, a Hamiltonian must be constructed to represent the state of the solid being modeled. Here we define a set of variables δ_i to represent n lattice sites in the simulation cell (e.g., for our problem Fig. 7), such that δ_i is 0 if the lattice site is unoccupied by an atom, or 1 if it is occupied. Mathematically, it can be expressed as

$$\sum_{i=1}^{N} \delta_i = \rho N = n \tag{1}$$

For the Ising model, by rule two, the pairs of nearest-neighbor particles contribute an energy $-\epsilon$ to the system. This can be written as

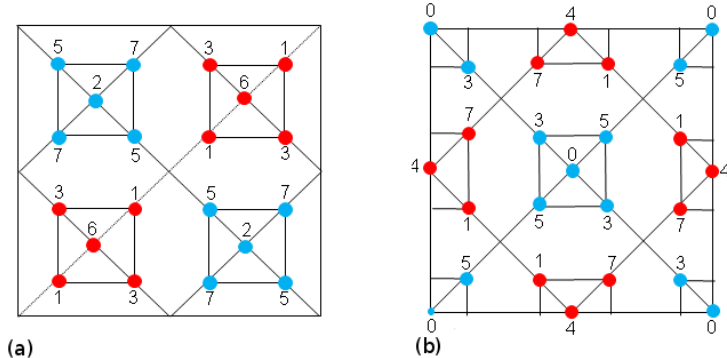$$H = -\epsilon \sum_{i,j} \delta_i \, \delta_j, \tag{2}$$

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Figure 8: a,b are two projection diagrams on the xy-plane of possible ice VI configurations. The numbering represents the heights in z on a scale of $\frac{c}{8}$. Each of the configurations have four different degenerate states found by permuting z coordinates of center and corner positions.

where i, j are nearest neighbor sites. We can add to the model by specifying different energy parameters for interactions between first and higher order neighbors; or by putting in anisotropy, making the x and y directions different than z; or by codifying the physics of ice rules, putting in energetics to select for tetrahedral bonds. A very simple way to do this is a strain term,

$$E = \frac{1}{2}E_a \sum_{(i,j,k)} (\theta_{ijk} - \theta_o)^2, \tag{3}$$

where $\theta_o \approx 109.47°$ is the ideal angle of a perfect tetrahedron, i, j, k represent neighboring sites, and θ_{ijk} represents the bond angle between the three sites. If the energy parameter E_a for the angle is positive, smaller and larger angles than the perfect tetrahedral of Fig. 4 will have larger energies. When the dimensions of the simulation cell are set so that it is a cube, a 16-atom structure for ice VI has the lowest energy state (zero). This model will give an idea of differences in energy states through distortions of the perfect tetrahedron to imperfect ones.

Understanding the mechanism behind this phase transition, the way these structures distort, break bonds and migrate, is the goal of this research. In this project we developed a simulation cell to model the phase transition, and mathematically described a simple
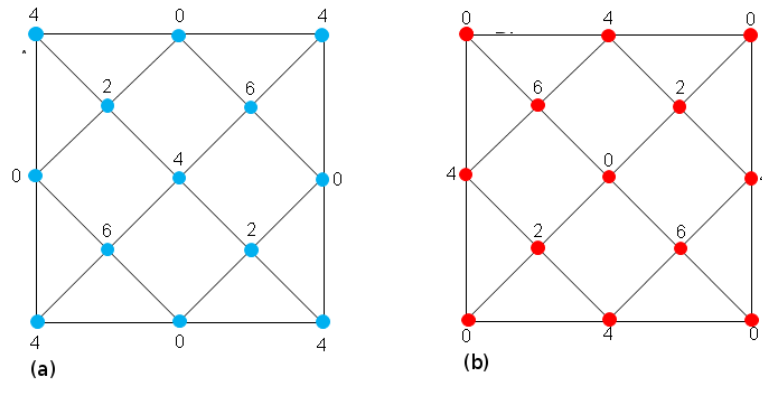
Figure 9: a and b are projection diagrams into the xy-plane of sublattices A and B for one potential ice VII configuration. The numbering represents the heights in z on a scale of $\frac{c}{8}$. Their are two equivalent permutations in this configuration.

strain model. The last step will be to create a phenomenological Ising-like spin model of the system to capture the energetics of the transition, and then to use either molecular dynamics or Monte Carlo simulations to carry out the study of the transition.

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