Using a Theoretical Model for the Energy of Ice VI and VII

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Abstract

Solid water, ice, is found in at least ten different crystalline forms as a function of temperature and pressure. My research was to study the transition between Ice VI and Ice VII, building upon a former REU student's framework and the Sillinger-Weber model of Monoatomic water, developed by Molinero and Moore. The previous student, Dawn King, had shown that the experimental Ice VI and VII crystalline structures could be represented on one lattice structure, the "King" lattice. Using this lattice I used the Stillinger-Weber model to calculate the energy of the two forms of ice. I explored how the energy changed as a function of internal parameters, but was unsuccessful in finding believable trends when the dimensions of the unit cell were varied. Further work needs to be done on the ability to do statistical calculations by using the Monte Carlo simulation.

1. Introduction

Ice exist in at least 10 different crystalline forms. The basis of this research was to find out, in general, more about the process in when ice goes from one state to the other by varying the temperature or the pressure. After I mastered the basic condensed matter concepts (e.g., Lennard-Jones potential, Bravais lattice and basis, Space groups…), then the real challenge came as to find out why and how Ice VI goes to Ice VII just by raising the pressure. Both Ice VI and VII are self-clathrate, meaning that there are sub-lattices within the crystal structure which penetrate each other but never touch. Using Dawn King's framework of both Ice forms I can, by using Fortran, study the energetics of both forms.

1) There is precisely one hydrogen atom on each hydrogen bond.
2) There are precisely two hydrogen atoms near each oxygen atom.

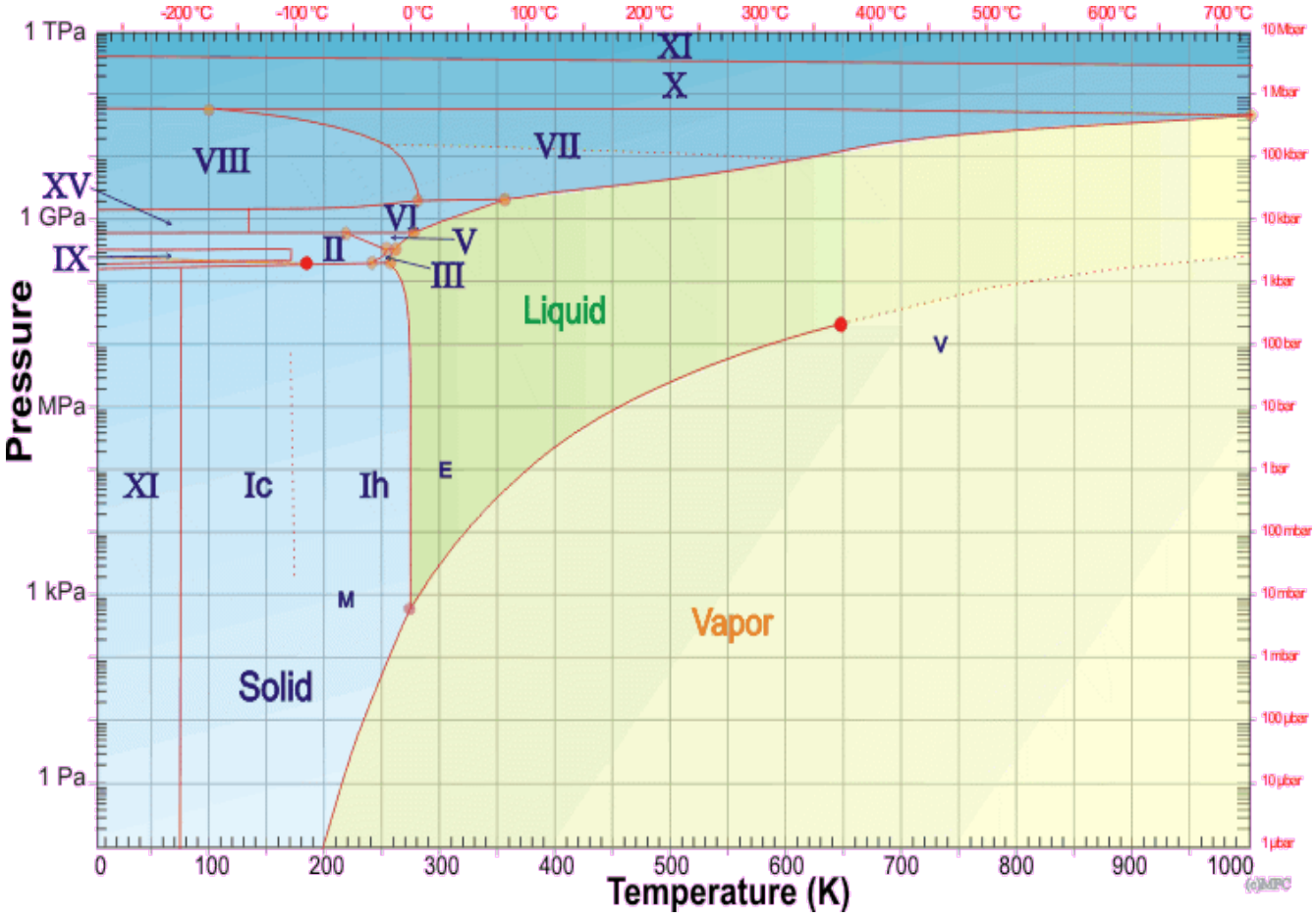


Figure 1: A phase diagram of water. There are at least 16 known states of solid states. “E”, “M”, and “V” represent the standard temperature and pressure of Earth, Mars, and Venus. [3]

2. The King Model for the Ice VI and VI Structures

King noticed that it was possible to represent Ice VI and VII (see Figs. 2 and 3, respectively) on one underlying lattice of 4X4X8 points. Two unit cells of Ice VI fit on this lattice, compared with 1 unit cell for Ice VII. Each water molecule is represented by a point; in Fig. 2, there are 20 molecules, compared with 16 in Ice VI.

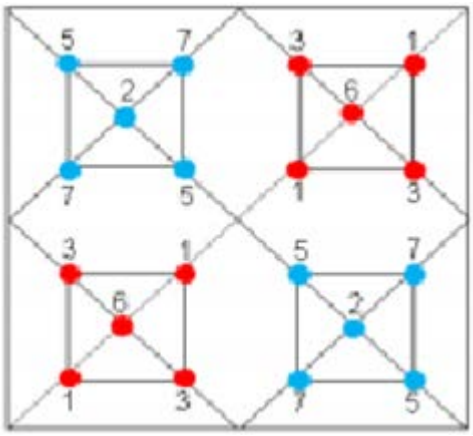


Figure 2: Is a projection on the xy-plane, of possible Ice VI configurations. The number represents the heights in z-axis on a scale of c/8. Each configurations has 4 degenerate states and 4 nearest-neighbors.

Ice VI has two distinguishable groups that never touch each other but penetrate each other along the xy axis, and form chains along the z-axis. The lattice unit cell of Ice VI is a body-centered tetragonal (bct) Bravais lattice with dimensions a = 6.27 ± 0.01 Å and c = 5.79 ± 0.01 Å.

Ice VII, like Ice VI, has two distinct groups that never touch; but instead of being separated on the xy-plane they overlap each other into one, periodic, lattice structure. It has a face-centered cubic (fcc) Bravais lattice of dimensions a = 3.30 ± 0.01 Å. It is the fact that we do not know why, when adding pressure, Ice VI goes into this unique form that is Ice VI, which drives the basis of this research.

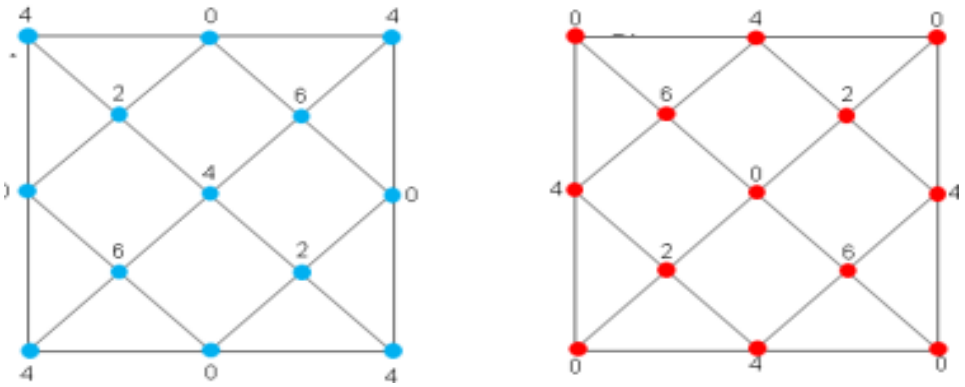


Figure: 3 shows the two groups that overlap each other but never touch (self-clathrate). This is a projection of the sub-lattices on the xy-plane. The numbers represent the heights on the z-axis on a scale of c/8.

3. **The Energy**

The SW potential was developed for semiconductors with tetrahedral bonding.

It contains both 2- and 3-body terms, where λ is a parameter that tunes the tetrahedral penalty.

Molinero and Moore realized that ice networks could be understood in terms of tetrahedral bonding and adapted the SW potential for "Monoatomic Water." Their model represents water molecules as points, as was done by Dawn King for the King lattice.

$$E = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\varphi_2(r) = A\varepsilon\left[B\left(\frac{\sigma}{r}\right)^p - \left(\frac{\sigma}{r}\right)^q\right]\exp\left(\frac{\sigma}{r - a\sigma}\right)$$

$$\varphi_3(r, s, \theta) = \lambda\varepsilon[\cos\theta - \cos\theta_o]^2\exp\left(\frac{\gamma\sigma}{r - a\sigma}\right)\exp\left(\frac{\gamma\sigma}{s - a\sigma}\right)$$

The equation above represents the Stillinger-Weber Potential [2], where λ is a parameter that tunes the tetrahedral penalty. In other words, the higher lambda is, the more tetrahedral the structure is. The Stillinger-Weber potential is great to use when wanting to apply the Monte Carlo simulation between Si-Ge phase transition[4]. Now we want to take this potential and try to apply the same Monte Carlo simulation to this phase transition, but first the potential must be compared to experimental results.

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

Table I: Space group positions for Ice VI and Ice VII. The units are (a,a,c) for body-centered tetragonal VI and (a,a,a) for face-centered cubic VII and internal parameters *x=0.21* and *z= -0.1*.

4. Results

Using Dawn's Model we set up the structure, using Fortran, and calculate the nearest-neighbor energies using the Stillinger-Weber model.

For Ice VI we hold 'a' and 'c' constant at values:

a = 8.87 Angstroms [1]

c = 5.79 Angstroms [1]

then we vary 'x' and 'z' to obtain the values, **Fig. 5 and Fig.6**, which give the minimum energy (these are the values you see in the caption of Figure 4).

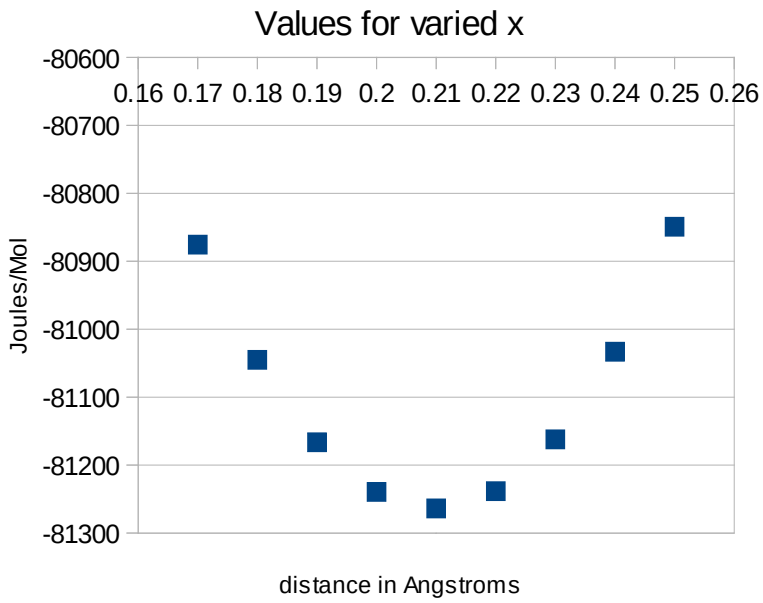
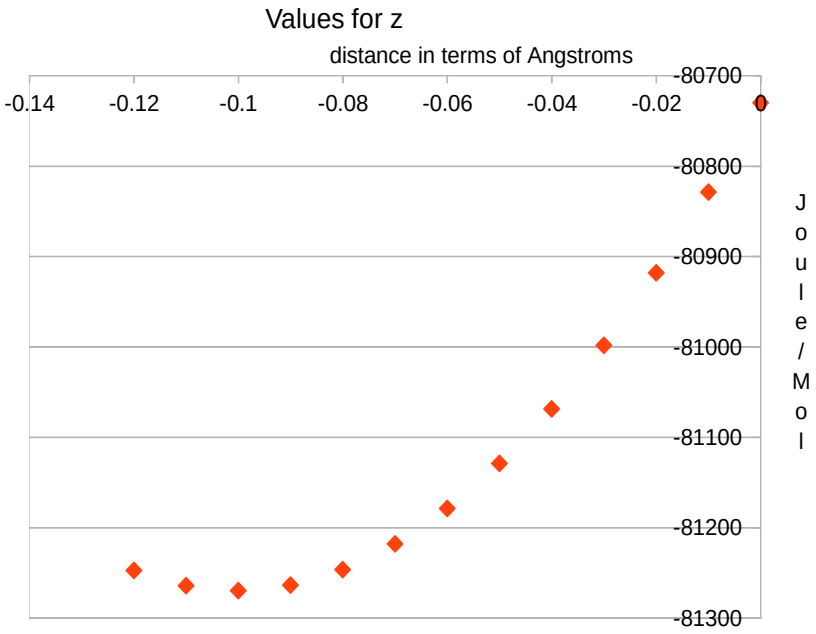
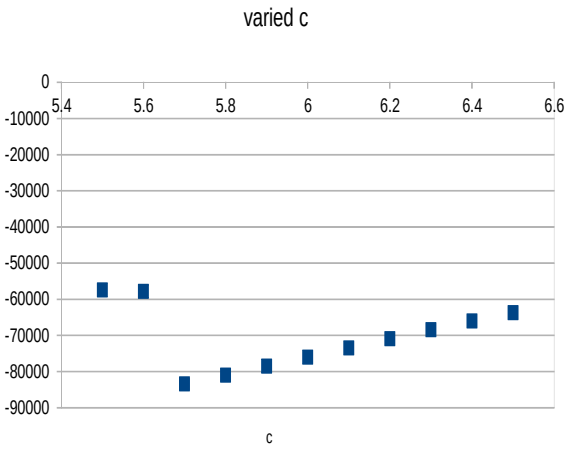


Figure 5: The Graph shows the Minimum of the internal parameter 'x' value found by the Stilinger-Weber Model.


Values for z
distance in terms of Angstroms
-0.14
-0.12
-0.1
-0.08
-0.06
-0.04
-0.02
0
-80700
-80800
-80900
-81000
-81100
-81200
-81300
Joule/Mol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0
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-30000
-40000
-50000
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-70000
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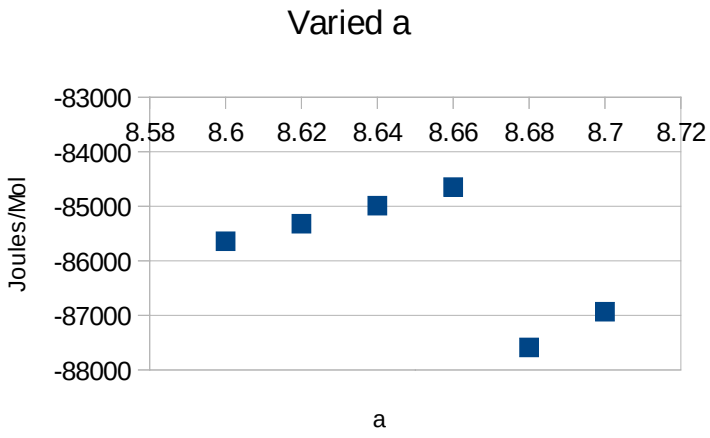
5.8
6
6.2
6.4
6.6
c


Varied a
-83000
-84000
-85000
-86000
-87000
-88000
8.58
8.6
8.62
8.64
8.66
8.68
8.7
8.72
Joules/Mol
a

Is there a mistake in the Fortran code? Or are we seeing a limitation in the Stillinger-Weber model for ice? Without knowing the answer to these questions, we cannot determine whether this model works for these structures and whether future researcher can use the Monte Carlo method to study trajectories and see how the Ice VI structure changes to Ice VII.

[1] http://physics.nd.edu/assets/25212/king_dawn_modeling_phase_trans.pdf

[2] V. Molinero and E.B. Moore, "Water Modeled As an Intermediate Element between Carbon and Silicon," J.Phys. Chem B113, 4008-4016 (2009).

[3] http://www.btinternet.com/~martin.chaplin/phase.html .

[4] M. Laradji and D.P. Landau," Structural Properties of Si, Ge alloys: A Monte Carlo simulation with the Stillinger-Weber potential," Phy. Rev. B 51,8 (1995).