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Studies on aperiodic and quasiperiodic crystals

Mertz, John Edward, Ph.D.

University of Illinois at Urbana-Champaign, 1988

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

V. A MODEL FOR QUASIPERIODIC SOLID WATER

A. Introduction

In their original paper Bernel and Fowler[1] discuss how the internal structure of water influences some of its macroscopic properties. Since that time legions of investigators[2] have explored the structure-property relationships in H_2O over its entire phase diagram. In this chapter we also intend to examine some of these relationships, but we will confine ourselves to the supercooled water and amorphous ice regions of the phase diagram.

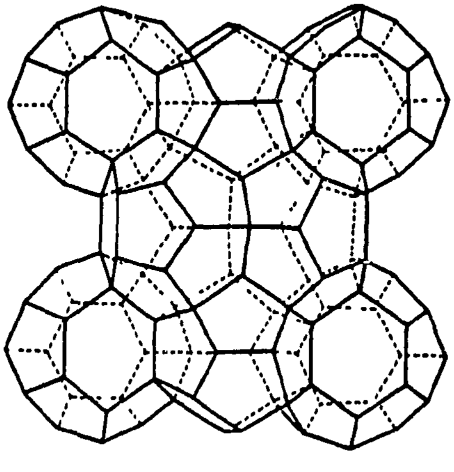
As water is cooled through its density maximum at 4°C into the supercooled region, its responses to temperature and pressure become increasingly more anomalous. For instance, the heat capacity[3] and isothermal compressibility[4] increase rapidly as water is supercooled to lower and lower temperatures. Extrapolation of experimental data predicts these response functions to be infinite at $T_s = -46^\circ$ C. Unfortunately this catastrophe has never been observed because all attempts to reach this temperature have resulted in crystalline ice.[5] Speedy has put forth a structural model that may explain some of this behavior[6]. He suggests that the concentration of pentagonal rings of hydrogen-bonded water molecules increases as the temperature is lowered. He postulates that the cooperation between pentagonal clusters and the cavities associated with these clusters play a dominant role in the anomalous behavior of the thermodynamic response functions.

Amorphous ice also exhibits peculiar behavior. One remarkable property it has is the ability to adsorb large amounts of gas. It has recently been found that amorphous ice can trap up to 3.3 times as much argon as the amount of ice itself.[7] Other studies show that adsorption isotherms predict the low density form of amorphous ice ($0.91\ g/cm^3 \leq \rho \leq 0.94\ g/cm^3$) to be a microporous solid.[8] Micropores are defined as pores of < 20 Å.[9] These voids seem unphysically large when compared to the average oxygen-oxygen distance of 2.75 Å.[10] The density predicted from the microporous volume is too low , $\rho \cong 0.81\ g/cm^3$.

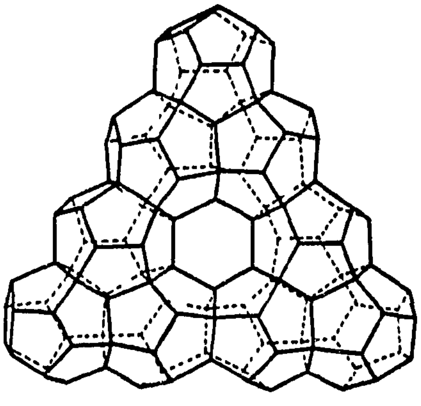
The widely accepted random network model of amorphous ice[11] neither has pores this large nor the free volume necessary to adsorb this amount of gas. It is not surprising that in light of these adsorption isotherms ideas of clathrate structures are mentioned in favor of the random network model.

The appearance of significant structures such as the pentagon and the clathrate polyhedra are reminiscent of the geometric themes present in metallic crystals and glasses. The connection between metallic systems and the clathrate hydrates lies in the polyhedra comprising each system. The polyhedra found in the type I and type II clathrate hydrates[12], Figure (5.1), are geometric duals to the coordinating polyhedra of some metallic alloys. The polyhedra and their respective duals are shown in

Figure (5.1). The polyhedral packings present in two types of clathrate hydrates.



Type I



Type II

Figure (5.2).

This dual relationship can be demonstrated through the icosahedron and the dodecahedron. A dodecahedron can be formed by placing a point in the center of each tetraheda in the icosahedron. The angle between adjacent edges in the dodecahedron is 108.00°: Very close to the ideal tetrahedral angle of 109.47°. In this chapter we will use this transformation to develop a model of quasicrystalline ice.

B. Generation of the Model

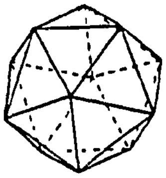
In the second chapter of this thesis we proposed a binary decoration of the quasicrystal that was structurally similar to the $Mg_{32}(Al,Zn)_{49}$ crystal. The polyhedra in this crystal are exactly those mentioned in the introduction of this chapter. Therefore, we should be able to transform the polyhedra within the binary decoration into their corresponding duals to obtain a lattice capable of accommodating water molecules.

We accomplished this by searching through the lattice for tetrahedra. Once a tetrahedron was located, a point, P_D ,was placed in the center according to the formula,

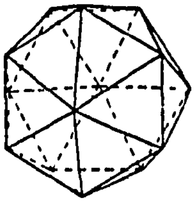
$$P_D = \frac{1}{4}\left[V_T^1 + V_T^2 + V_T^3 + V_T^4 \right]$$

where P_D is the new point belonging to the dual lattice and V_T^i is

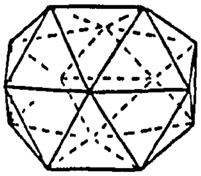
<u>Figure (5.2)</u>. The n-hedra composed of tetrahedra, (a) 12-hedron, (b) 14-hedron, (c) 15-hedron, (d) 16-hedron and their tetrahedrally-coordinated counterparts.



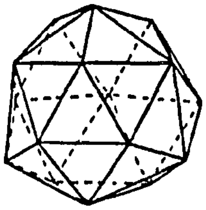
(a)



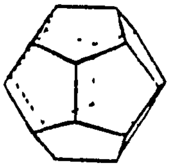
(b)



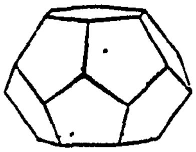
(c)



(d)



(e)



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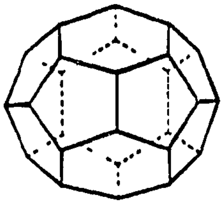
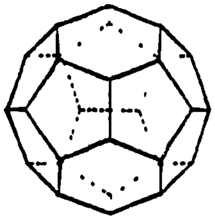


(g)



(h)

the i^{th} vertex of the tetrahedron. The lattice that results from this procedure is shown in Figure (5.3). In this picture the oxygens are located at the endpoints of the lines and the lines represent hydrogen bonds between pairs of water molecules.

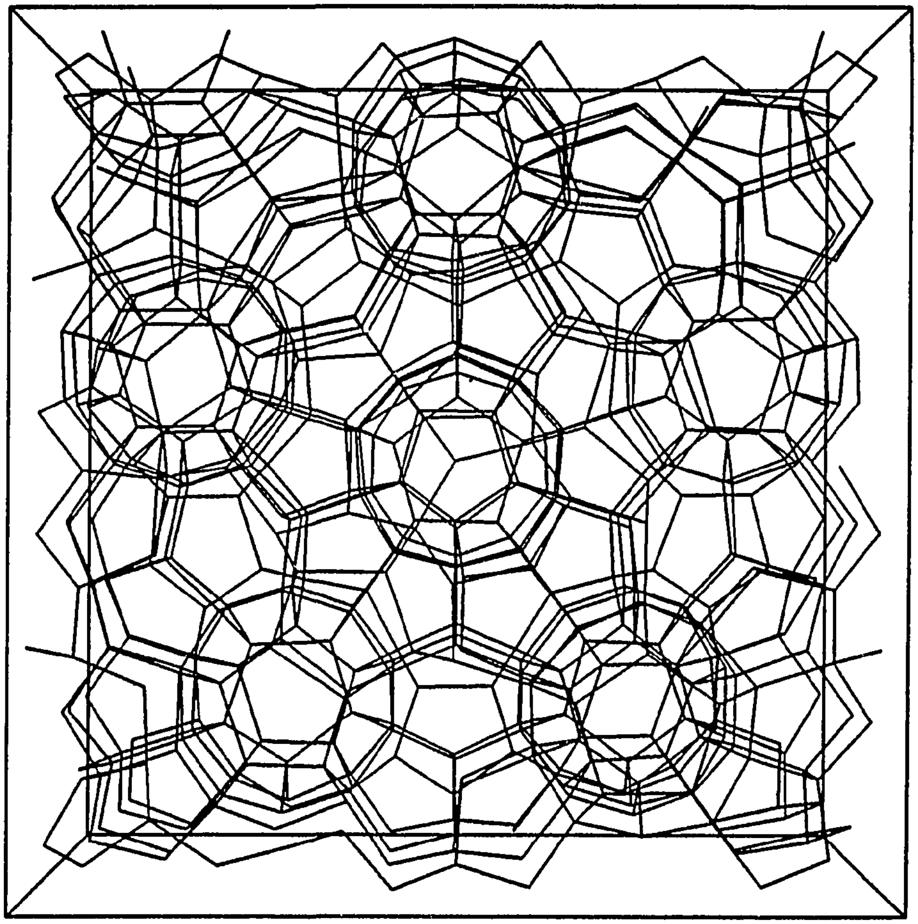
Our final version of the model includes the set of original vertices, $\{V_T\}$, and the new set of points resulting from the dual transformation procedure. From this model we get the following results. The density of the lattice is, $\rho = 0.917 \pm 0.003$ g/cm^3, the nearest neighbor O-O distance is, 2.74 ± 0.18 Å, and the angle between three oxygens, O-O-O , $109.3^\circ \pm 4.71^\circ$. All of these compare well with the experimental data. The average distance between the O-O pairs is slightly shorter than what is experimentally observed, 2.75 Å, but the relaxation of the lattice could lengthen it. We also find a ratio of pentagons to hexagons in our lattice to be approximately 10:1.

C. Computer Simulation Methods and Results

We use the ST2 water potential.[13] This potential has four point charges that are oreintated toward the corners of the tetrahedron. It has been demonstrated that it can describe some of the properties in liquid water well[14] and also predict a reasonable melting temperature for ice I.[15]

The surface effects are handled in a way similar to the methods employed in chapter two of this thesis. We use a

Figure (5.3). The inner-core sample of water molecules used in the simulation. Lines represent hydrogen-bonds between two water molecules. The lattice is orientated so that the view is along the five-fold symmetry axis. The box is included for depth perception.



stationary outer-shell that provides a static potential for the inner-core water molecules that will move. In addition, we divide the outer-shell into two parts. The water molecules that are closest to the inner-core adjust their proton positions to the motion of the water molecules in the inner-core while their oxygen postions stay fixed. This was done to increase the hydrogen bonding between the inner- and outer-cores. The remaining water molecules in the outer-shell have both their proton and oxygen positions fixed.

Because there is a degree of randomness concerning the initial proton positions we first relaxed the proton positions of the water molecules, while holding all the oxygens fixed. The next step in the simulation was moving the entire water molecule in the inner-core. After the inner core had relaxed for approximately 0.5 ps we again relaxed the proton positons. This was done to help stabilize the lattice by increasing hydrogen-bonding between the water molecules.After the proton positions relaxed the inner-core was again relaxed for another 0.5 ps.

We continued through this successive procedure of relaxing the inner-core and then relaxing just the protons. We found that that no matter how mildly we relaxed the system, it would not stablize; the water molecules continued to move until the lattice was completely disrupted.

This instability could be intrinsic to the lattice or maybe an artifact of the ST2 potential. Inspection of the system at various intervals revealed that the hexagons in the sample were the first species to break up. The O-O-O angles in the hexagon conformation are considerably larger than the ideal tetrahedral angle. Because the ST2 potential is known to overemphasize the tetrahedral nature of water,[16] it could account for the instability of the hexagon conformations.

The only way to separate these possibilites is to carry out another simulation with a softer, less rigid potential. Unfortunatly, at the present time we are unable to do this.

LIST OF REFERENCES

1. J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
2. F. Franks, Ed., Water-A Comprehensive Treatise, Vols. 1-7 (Plenum Press, New York 1973).
3. C. A. Angell, W. J. Sichina, and M. Oguni, J. Phys. Chem. **86**, 992 (1982).
4. R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).
5. C. A. Angell in Water-A Comprehensive Treatise, Vol. 7, F. Franks, Ed. (Plenum Press, New York 1983).
6. R. J. Speedy, J. Phys. Chem. **88**, 3364 (1984).
7. A. Bar-Nun, J. Dror, E. Kochavi, and D. Laufer, Phys. Rev. B **35**, 2427 (1987).
8. E. Mayer and Rudolf Pletzer, Nature **319**, 298 (1986).
9. D. H. Everett, Pure Appl. Chem. **31**, 579 (1972).
10. A. H. Narten, C. G. Venkatesh, and S. A. Rice, J. Chem. Phys. **64**, 1106 (1976).
11. S. A. Rice and M. G. Sceats, J. Phys. Chem. **85**, 1108 (1981).
12. L. Pauling in The Nature of the Chemical Bond, 3rd ed.,(Cornell Univ. Press, Ithaca, New York 1960).
13. F. H. Stillinger and A. Rahman, J. Chem. Phys. **60**, 1546 (1974).
14. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impley, and M. Klein, J. Chem. Phys. **79**, 926 (1983).
15. T. A. Weber and F. H. Stillinger, J. Phys. Chem. **87**, 4277

(1983).

16. M. D. Morse and S. A. Rice, J. Chem. Phys. **76**, 650 (1982).