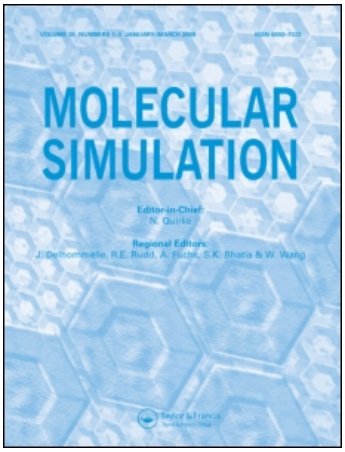

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Quantized Water Clusters Around Apolar Molecules

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QUANTIZED WATER CLUSTERS AROUND APOLAR MOLECULES

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In order to understand the mechanism of gas hydrate kinetics and to explore the existance of other new cavities in the hydrate structure, we have used Molecular Dynamics (MD) simulation to study a system comprising two Lennard-Jones particles and 214 water molecules. Equilibrium structure and properties of twelve cases have been investigated. Our findings were as follows:

- Apolar molecules promote spherical liquid water clusters in a hydrate-like labile cavity.
- The size of the cavity and the coordination number is dependent upon the size of the apolar molecule.
- The coordination number of water molecules is quantized in jumps of four.
- Similarities are observed between the labile cavities and cavities in solid hydrates and in other chemical structures such as Buckminsterfullerene.
- Such a simulation procedure suggests the possibility of other clusters which may exist in yet-to-be-found hydrates. A separate question involves whether such suggested cavities can be combined with other cavities into a space-filling crystal.

I INTRODUCTION

The hydration structure and dynamics of apolar molecules in water is of special importance in understanding the mechanism of hydrate Kinetics [1]. The interactions between water and apolar molecules are directly related to the structure and, function of biochemical molecules. The intriguing richness of solution behavior of apolar molecules in water is summarized under the terms "hydrophobic hydration" and "hydrophobic interaction" [2, 3].

A gas hydrate is a special type of clathrate compound formed by the physical combination of water with light gases and/or volatile liquids. The three common cavities, shown in Figure 1, were determined to form two normal structures in the 1950's [1, 4, 5, 6]. These solid compounds cause serious problems by blocking flow channels in oil/gas completion, production, and processing [7]. Thermodynamic inhibition of hydrate formation is not always the best choice from either operational, economical, or environmental viewpoints. A new approach, called-kinetic inhibition, has been proposed, in which the system is operated within the thermodynamic stability regime, but large crystal aggregates are prevented [8]. An understanding of hydrate formation kinetics holds the key for such inhibition techniques.

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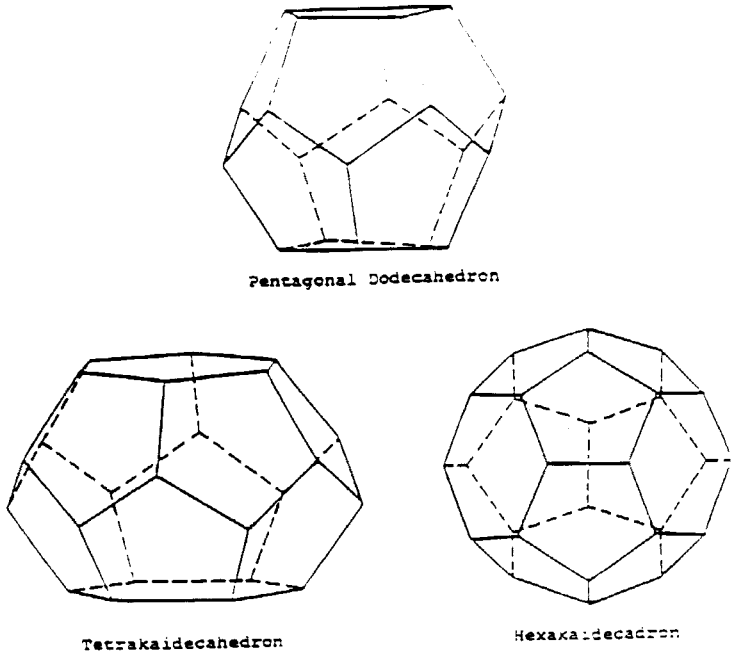

Figure 1 Basic Cage Structures For Structure I and Structure II Hydrates (Reference 1).

Recently, almost a half century after the discovery of the older structures, Ripmeester *et al.* [9] used NMR spectroscopy to determine a new hydrate, structure *H* in 1987. With this new discovery came the question, "Are there other hydrate structures or cavities which await discovery, perhaps using modern, sophisticated tools?" The recent discovery of a multitude of similar cavities in the carbon fullerene "family" [10] indicated that fullerene cavities have possible analogs in hydrates, because both types of cavities obey the geometric rules of Leonhard Euler, e.g. all cavities have twelve pentagonal faces and any number of hexagonal faces, except one. The geometric analogies to known hydrate cavities motivated us to perform a computer simulation to determine whether other hydrate cavities were possible.

During the initial period of hydrate formation, the primary nucleation process is predominant. Such a process is a microscopic phenomenon involving tens or hundreds of molecules. The clustering of water around an apolar molecule might be considered a precussor for nucleation [11, 12]. Molecular simulation has proved to be one probe of such phenomena. [12, 13]

II LITERATURE REVIEW

Over the years, quite few studies of hydrophobic effects have been carried out by different research groups. Early studies in this area were comprehensively reviewed in *water: A Comprehensive Treatise* series edited by Frank [14].

Stillinger etc. [15, 16] described water (based on molecular dynamics simulations)

as a "microscopically connected [3-dimensional] random network of hydrogen bonds, with frequent strained and broken bonds, that is continually undergoing topological reformation." Stillinger and Rahman [17, 18] demonstrated that the most common structures of a water molecular network were five and six member polygons which form the faces of hydrate cavities. Geiger, Stillinger, and Rahman [19] carried out computer simulations of dissolved apolar solutes in water. They found out that the water network rearranges to form a clathrate-type cage around the apolar solute. The initial molecular dynamics work on gas hydrates was performed by Tse, Klein and McDonald [20]. Mountain *et al.* applied molecular dynamics to hydrate solids, using the SPC potential model [21]. Marchi and Mountaion [22] employed constant pressure molecular dynamics to study the thermal expansion of structure II hydrates.

Chen and Plummer studied the molecular dynamics of eight possible networks of five water molecules [23], and of the 5^{12} cavity[2] [24]. They found that the most stable pentamer is the ring structure, at temperatures below 305K, and that the 5^{12} cavity is very stable. In another molecular dynamic (MD) comparison of the 5^{12} cavity and of 8 nitrogens dissolved in 192 water molecules, Dang [25] found a hydration number of 17, which approaches the coordination number of 20 for the 5^{12} cavity in the hydrate structure. In Monte Carlo studies Owicki *et al.* [26] determined that the average coordination number of water molecules around dissolved methane was 23, while Swaminathan *et al.* [27] showed that the value approximated 20. Similar results were obtained in studies conducted by Nakanishi *et al.* [28, 29] for a system of 63 water molecules and one apolar molecule.

The low solubility of apolar molecules in water is caused by a negative entropy of hydration, which also is the source of most of the unusally high solution heat-capacity [3]. It is believed that those large entropy effects are very important in clathrate-hydrate formation, micelle formation, and other fields [3, 30, 31]. Such clustering may also be one of the principle driving forces of hydrate primary nucleation. Recently Smith and Haymet [32] reported a computer simulation of the free energy of association for hydrophobic solutes. The Smith and Haymet calculation determined that the entropy causes an attraction between the solutes at separations less than 5.5 Å, which is very close to the guest-guest distance in the hydrate structure. Further reviews on hydrophobic effects may be found in Ben-Naim's monographs [2, 3].

III METHOD OF SIMULATION

To study the equilibrium structures and properties of water with dissolved apolar molecules, a computer program for pure water developed by Mountain [33] was used as a starting point. The program was modified to increase the number of particles from 108 to 216 water molecules. Beeman's algorithm [34] was used in the program and the simulation was carried out at constant pressure. Starting with a pure water simulation, the equilibrium properties of bulk water, such as density, temperature, total energy, and radial distribution functions, were favorably compared with literature values, as indicated in the results section.

In the simulation we used the SPC water model. This is a rigid, three-site model,

[2]This nomenclature indicates twelve pentagonal faces.

which predicts acceptable thermodynamic and structural properties for bulk water over a wide range of temperature and pressure [35, 36]. The model has a positive charge site at the location of each hydrogen atom and a virtual negative charge site on oxygen atom. The values of the charges are denoted by q_i. The Ewald Sam was incorporated into the simulation to account for long-range Coulombic interactions. There is also a Lennard-Jones (LJ) site centered on the oxygen atom on each water molecule. The real space part of EWALD sum was cut off when the distance between sites is greater than half of the box. The Ewald configuration space term was cut off after 514 vectors. Thus the functional form of the water-water interaction potential is given by the sum of eletrostatic and van der Waals forces as in equation [1].

$$\epsilon_{mn} = \sum_{i}^{on\ m} \sum_{j}^{on\ n} \frac{q_i q_j e^2}{r^2} + \frac{A}{r_{oo}^{12}} - \frac{C}{r_{oo}^{6}} \tag{1}$$

where q_i and q_j refer to charges on different sites for m and n water molecules respectively, and ϵ and σ are Lennard-Jones potential parameters. The parameters for SPC model are collected in Table 1. [36]

The water-apolar and apolar-apolar potentials are

$$\Phi_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{2}$$

Where i and j stand for different molecules. The cross interaction potential between water and apolar molecules were obtained by using classical combining rules as follows.

Table 1 SPC Potential Parameters for Water Monomer.

Name	$r_{(x)}$, (Å)	<*HOH*, deg.	$A \times 10^{-3}$, *Kcal Å/Mol*	*C*, *kcal Å⁶/Mol*	*q(O)*	*q(H)*	ϵ_1(*Kcal/Mol*)	σ(Å)
SPC	10	109.47	629.4	625.5	−0.82	0.41	71.8	3.16

Table 2 Lennard-Jones Potential Parameters of Apolar Molecules.

Name	*Size Ratio (APOLAR:H2O)*	*Size,(Å)*	*Molecule*	*Size,(Å)*
H2O	1.0:1.0	3.16	H2O	3.16
A	1.0:1.0	3.16	Ne	2.97
B	1.125:1.0	3.56	Ar	3.80
C	1.25:1.0	3.95	Kr	4.00
D	1.50:1.0	4.74	CH4	4.36
E	1.65:1.0	5.21	Xe	4.58
F	1.80:1.0	5.69	H2S	4.58
G	2.00:1.00	6.32	CO2	5.12
H	2.25:1.0	7.11	C2H6	5.50
I	2.40:1.00	7.58	c-C3H6	5.80
J	2.5:1.0	7.90	C3H8	6.28
K	2.80:1.0	8.85	i-C4H10	6.50
L	3.0:1.0	9.48	n-C4H10	7.10
M	3.5:1.0	11.06		

$$\epsilon_{ij} = \sqrt{(\epsilon_i \epsilon_j)} \tag{3a}$$

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{3b}$$

The parameters for cases studied are listed in Table 2. In our simulation, we chose the energy parameter of the apolar molecules to be a constant equal to the Lennard-Jones energy parameters in the water. The simulation cube edge box length of periodicity was about 18 Å and the pressure was set to a value providing a density of 1.0 g/cm^3 for pure water. For the Lennard-Jones potential a cut-off distance $R_c = 9$ Å was chosen, beyond which interactions were disregarded.

The time step τ for the numerical integration of the dynamic equations was $\tau = 6.5 \times 10^{-15}$ sec for both pure water and water with apolar molecules. Due to the potential cutoff and small round off errors, the errors, the momenta of the system were rescaled every 1000 steps to avoid any convection shifting. The resulting system is a close approximation to the (N, P, H) ensemble first proposed by Andersen [37].

After, the equilibrium configuration was obtained for 216 water molecules, two molecules were randomly chosen and changed to Lennard-Jones particles. This change is accomplished through calculation of coordinates, Euler angles, and charges of the oxygen and hydrogen atoms of SPC water via the center of mass coordinates. Then two random particles were changed to spherical particles without charge. Thus we obtained a system with 214 water molecules and 2 apolar molecules.

Throughout the simulation, the water in the hydration shell, bulk water and apolar molecular structures and properties were calculated. These included radial distribution functions, angular distribution functions, coordination numbers around apolar molecules, temperature, energy and mean square displacement etc. Our major interests were directed to microstructural and microdynamic properties in the hydration shell around apolar molecules.

IV SIMULATION RESULTS AND DISCUSSION

A *Bulk Water Structures and Properties*

This part of the study serves two purposes:

1. To compare our pure bulk water results with literature values from both experimental and computer simulation results of SPC water, and
2. To set up the equilibrium configuration of 216 water molecules for futher clustering studies.

The thermodynamic property comparisons between our constant pressure simulation results and Monte Carlo NPT simulations are within 10%. The densities of water for our MD and Monte Calo simulations are 1.010 g/cm^3 at 26.8°C and 0.971 g/cm^3 at 20°C respectively. The small discrepancy is attributed to slightly different temperature and pressure conditions. In the constant pressure simulation algorithm, the pressure must be relatively higher than the experimental value, if we require a realistic water density.

The radial distribution functions for different sites are shown in Figure 2. The solid line represents the results from Jorgensen [36] MC simulation at 25°C and 1 atmosphere in the NPT ensemble. The dashed line of the oxygen-oxygen radial distribution function represents the results of X-ray experiments. The dotted line in

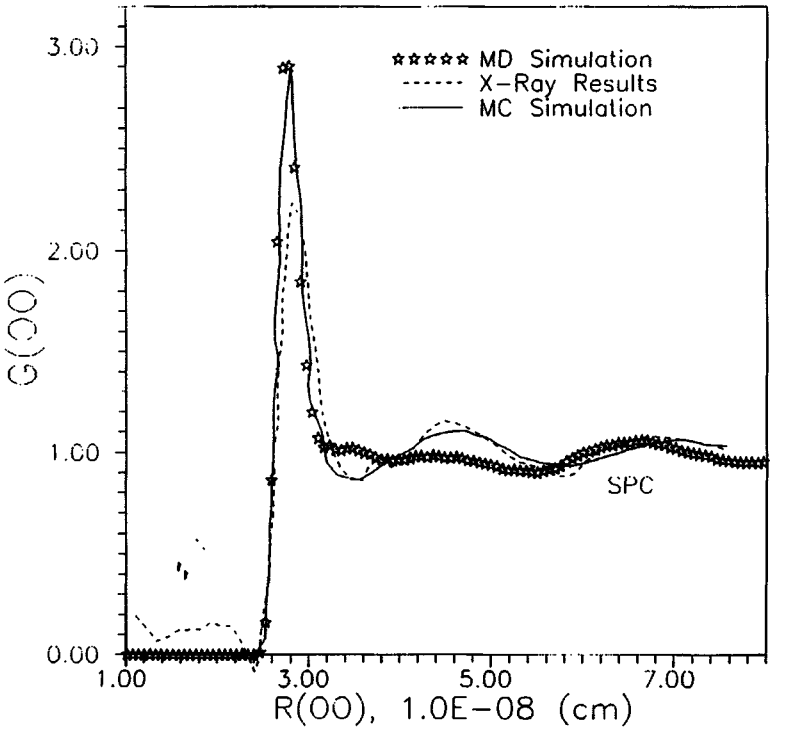

Figure 2(a) OO Radial Distribution Functions.

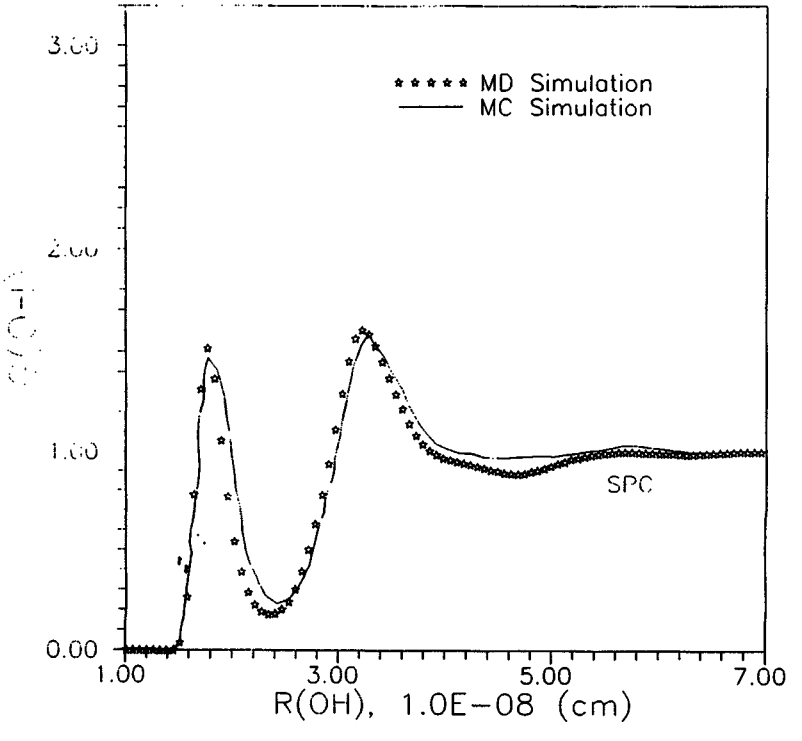

Figure 2(b) OH Radial Distribution Functions.

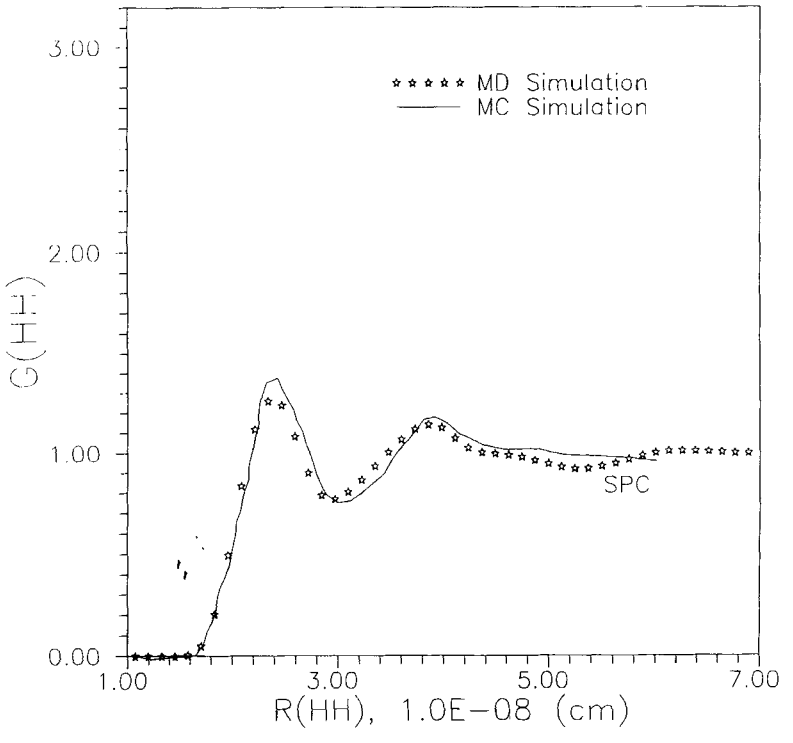

Figure 2(c) HH Radial Distribution Functions.

Figure 2 gives our MD simulation results in NPH ensemble, seem to be in good agreement with both experimental and Monte Carlo simulation results.

B *Distribution Functions of Water in Water-Apolar Mixtures*

Three radial distribution functions (RDF) of water were calculated with two apolar molecules dissolved in bulk water: those for oxygen-oxygen, hydrogen-oxygen, and hydrogen-hydrogen, with results shown in Figure 3. There are not many differences between the RDF of bulk pure water and water with two apolar solutes. Since the concentration of apolar molecules is so small, they produced no significant influence on the bulk water structure.

The structure of the water molecules adjacent to apolar molecules exhibited substantial change from the pure water structure. The oxygen-apolar, the hydrogen-apolar radial distribution functions were computed with only two obvious peaks, as shown in Figure 4. The positions of the two initial peaks are slightly greater than the effective diameter of the apolar molecules. The starting point at which the radial distribution function differs from zero for both distribution functions are almost equal, implying that the water molecules are in a preferred orientation.

The most interesting observations concern the water molecular orientation distribution functions or angular distribution functions. For these studies the center of apolar molecule was taken as the origin. The angle between apolar-oxygen-hydrogen was deteremined by its cosine value. The typical results are shown in Figure 5. There are two peaks in the results: one peak corresponds to an angle of 180° at

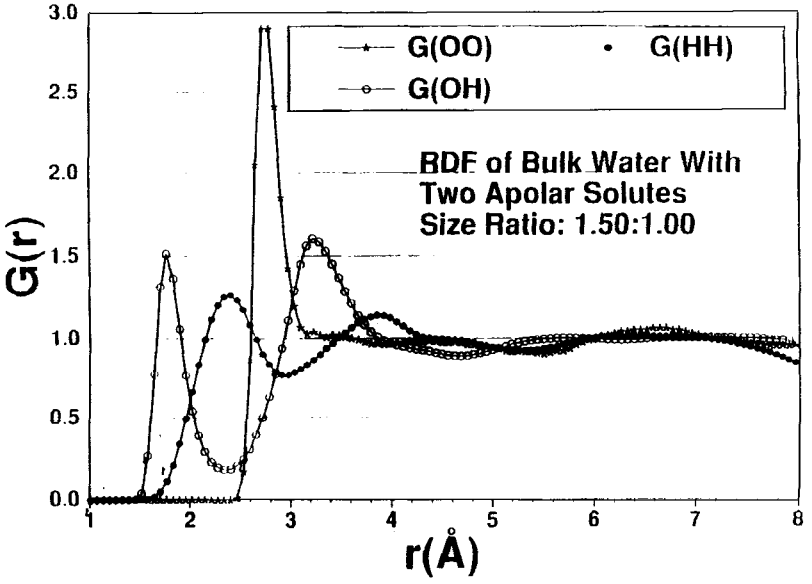

Figure 3 Radial Distribution Functions of Bulk Water With Two Apolar Solutes.

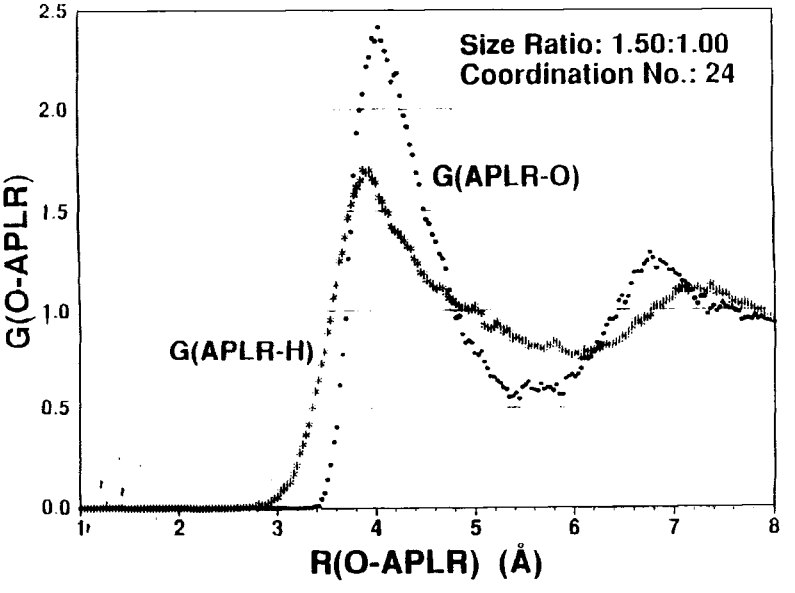

Figure 4 Radial Distribution Functions of Apolar-Oxygen, Apolar-Hydrogen.

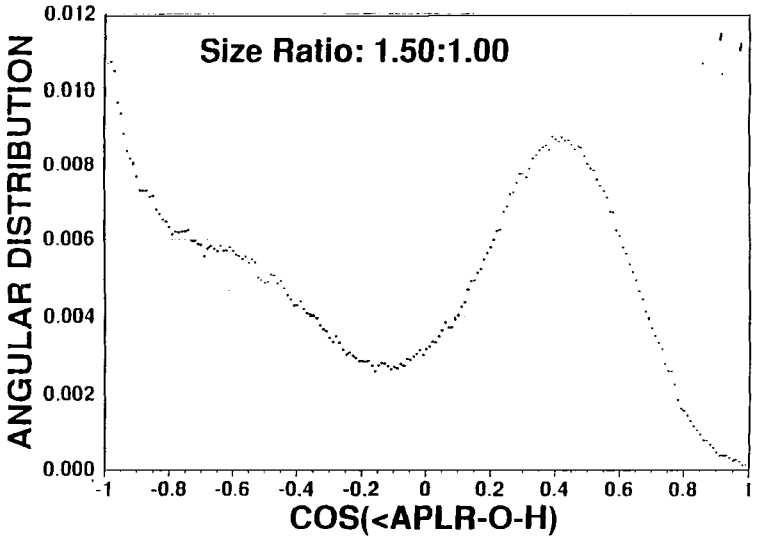

Figure 5 Angular Distribution of Apolar-Oxygen-Hydrogen.

$\cos(\theta) = -1.0$, and the other peak approximates an angle of 55°–60°. The area under the second peak is approximately twice as big as the first one. This indicates that majority of the hydrogen atoms approximate a sphere with a diameter slightly larger than diameter of apolar molecules. The remainder of hydrogen atoms at 180° point away from the apolar molecules. In contrast, the orientation of water molecules in the bulk water did not demonstrate such orientations, but their hydrogen atoms point either inward or outward from certain water molecules, as a function of hydrogen bonding.

In Structure I and II hydrates, there are three different types of cavities. The small cavity consists of 20 water molecules with 30 of its 40 hydrogen atoms aligned along the cavity surface. The remaining 10 hydrogens point away from the cavity center. The other two cavities have similar hydrogen alignments. For hydrogen atoms on the cavity surface, the angle formed by imaginary lines between guest-oxygen-hydrogen atoms are about 55° to 60°.

Such angular distributions can be explained in terms of the van der Waals repulsive forces acting between water and apolar molecules. These forces direct the oxygen or water positions and exclude hydrogens from pointing toward the center of each cavity. Since there is no interaction between hydrogen and apolar molecules, the orientation of the hydrogen atoms are determined by surrounding water molecules.

C *Dynamic properties of the system*

The system was divided into three different regions, namely, bulk water, water in hydration shell, and apolar molecules. The schematic in Figure 6 shows the distinction between different regions of the system.

We have measured mean square displacement (MSD) as a function of time for the above three regions. The center of mass (approximately the same as the oxygen

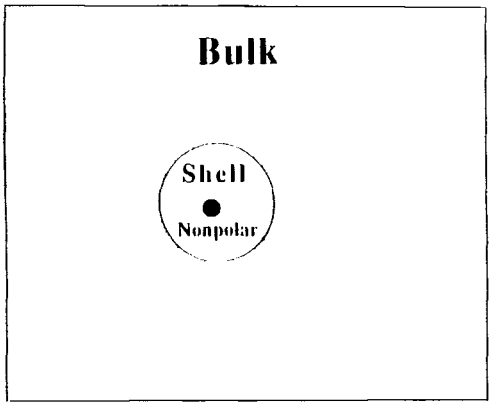

Figure 6 Schematic Diagram of the System.

position) is used to label the position of each water molecule. The number of molecules in the hydration shell, which ranges from 15 to 70 for one apolar molecule, is a strong function of the size of apolar molecule. To avoid the diffusion of water molecules out of the hydration shell during the observation period, the MSD calculation was restarted every 1000 steps for the molecules in each respective region. At every 1000 steps, the water molecules are labeled according to region, and positions of the center of mass were recorded as $\bar{R}_j(t_0)$. The molecules were then traced for another 999 steps. There are 12 sets of MSD over the 12,000 simulation steps. The final mean square displacement was obtained by averaging values for the 12 sets. The equation determining the MSD is:

$$[\Delta\bar{R}_j(t)]^2 = \{\bar{R}_j\ (t_0 + t) - \bar{R}_j(t_0)\}^2$$

Figure 7 shows the detailed behavior of MSD for small apolar molecules and Figure 8 demonstrated the properties of MSD for large apolar molecules. From both figures one can see that the motion of water molecules is retarded by the presence of apolar molecules in the system. The bulk water molecules move more freely than those in the hydration shell. The MSD for apolar molecules depends upon the size ratio between the apolar molecule and the cavities. When the ratio is small, the MSD is large for long periods of time. This observation implies that apolar molecules have more free space to move inside the cavity. If the ratio is relatively large, the apolar molecules have less space available to move inside the cavity. In latter case, the MSD of the apolar molecule is very similar to the MSD of water in the hydration shell. The results showed that the statistics for both bulk water and water in the hydration shell are satisfactory, but the statistics for apolar molecules are poor due to the very small number of molecules.

From the discussion in this and the previous section, one may tentatively conclude that the water molecules form a hydrogen-bonded cluster around apolar molecules. The motion of the water is restricted to some degree by the presence of apolar molecules. The structure of the cluster has some characteristics of hydrate cavities, such as water molecule orientation.

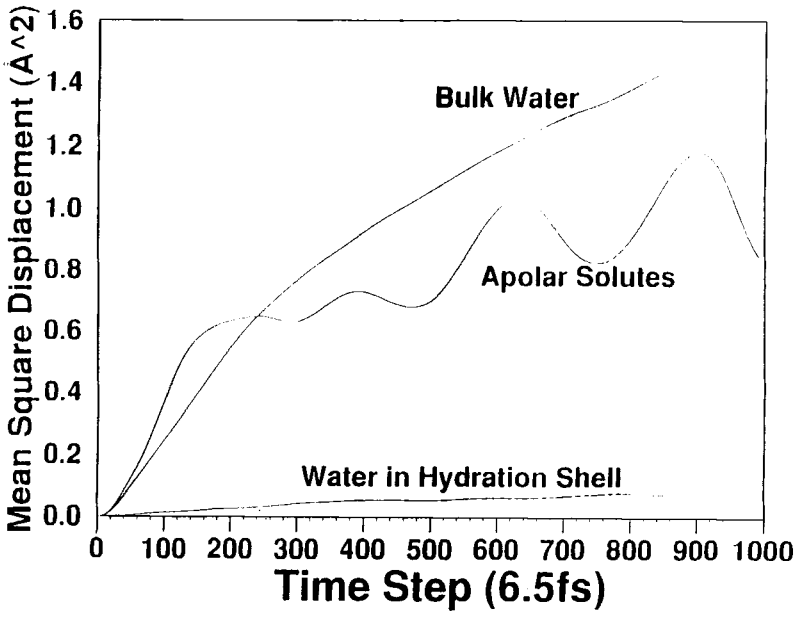

Figure 7 Mean Square Displacement of the System with Small Apolar Solutes.

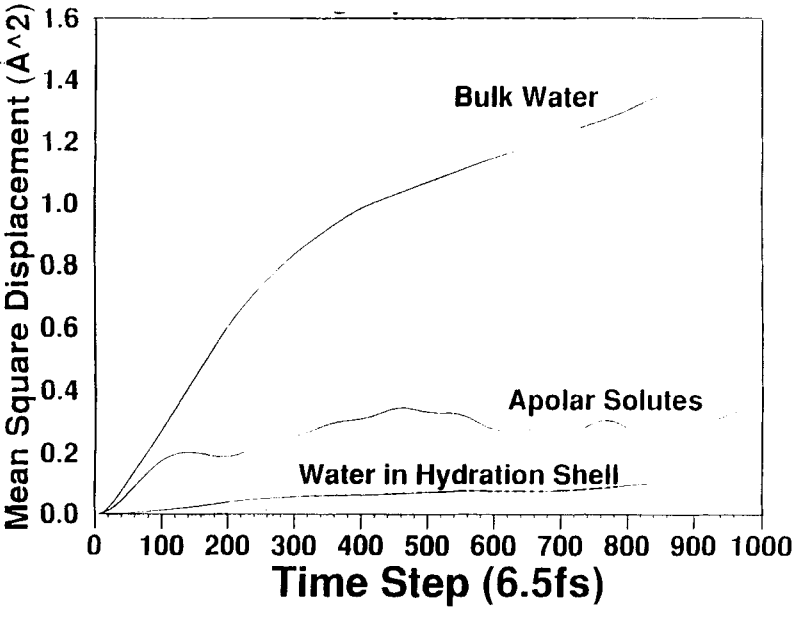

Figure 8 Mean Square Displacement of the System with Large Apolar Solutes.

D *Coordination number and Size Dependence of Clusters and Cavities upon Apolar Molecules*

The coordination number was determined from the oxygen-apolar radial distribution function, as the total number of water molecules between zero and the first minimum. The coordination number can be calculated in either of two ways. The first way is to calculate the coordination number directly from the simulation every step for every molecule; then the final value may be obtained by averaging over the total steps and total number of molecules. The second calculation method is to integrate the radial distribution function to the first minimum. In this work, we used primarily the first method, with the use of second method to check our results.

The coordination number and the size of the cavities were tabulated in Table 3. Both coordination number and size are strong functions of apolar molecular sizes. As the size of the apolar molecule increases, the density of the system decreases from 1.13 g/cm^3 to 0.92g/cm^3. This shows that the large apolar molecule creates more void space in the system than the smaller ones. The system with a small apolar apolar molecules is more dense than the system with a large apolar molecule at the same pressure.

Table 3 also shows the coordination number of apolar molecule does not increase continuously as the size of apolar molecule increases. When the apolar molecule is lest than 2.5 times of water molecule diameter, the coordination number appears to be quantized in jumps of 4 as shown in Figure 9. Beyond the size difference of a factor of 2.5, the number seems to increase by an even number. During the duration of simulation, the number of water molecules inside the hydration does not differ from the average coordination number by $+/-1$ as shown in Table 3. A larger diviation in the number of water molecules around apolar molecules were not observed in the simulation over 1000 steps. The depiction of water clusters around apolar molecules are shown in Figure 10. The hydrate-like liable cavity was observed around an apolar molecule (red ball).

The quantized behavior, may be due to the special feature of water molecules which cause them to maximize their hydrogen bonds by forming a tetrahedral angle network, as shown in Figure 11. By maximizing the hydrogen bonds, each water will lower its potential energy through associating with four other water molecules.

Table 3 The coordination Number and Cavity Sizes.

Name	*Size Ratio (APOLAR: H2O)*	*Coordination Number*	*Cavity Size (1.0E-08 cm)*
H2O	1.0:1.0	N/A	N/A
A	1.0:1.0	15.5 +/− 1.	4.49
B	1.125:1.0	19.5 +/− 1.	5.02
C	1.25:1.0	19.98 +/− 1.	5.09
D	1.50:1.0	24.1 +/− 1.	5.53
E	1.65:1.0	28.6 +/− 1.	5.69
F	1.80:1.0	28.6 +/− 1.	5.85
G	2.00:1.00	36.2 +/− 1.	6.45
H	2.25:1.0	40 +/− 1.	6.70
I	2.40:1.00	43.7 +/− 1.	6.98
J	2.5:1.0	47.6 +/− 1.	7.33
K	2.80:1.0	53.9 +/− 1.	7.62
L	3.0:1.0	57.7 +/− 1.	8.09
M	3.5:1.0	74.47 +/− 1.	8.94

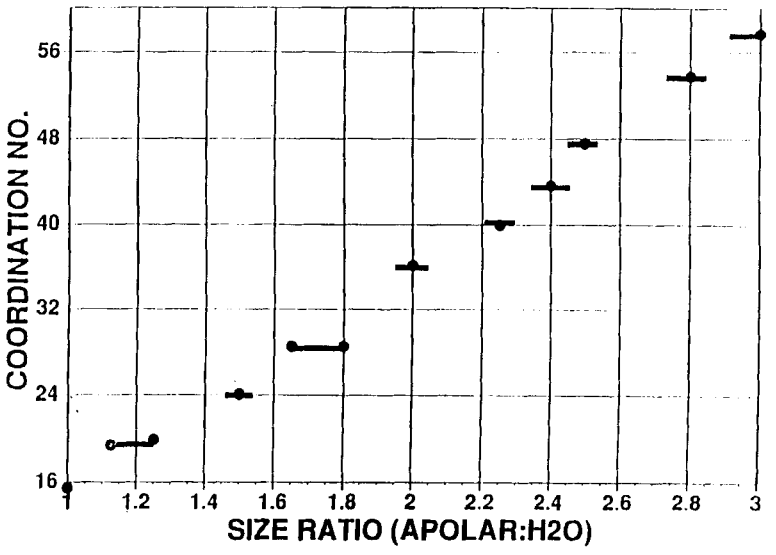

Figure 9 Coordination Number vs. Size Ratio.

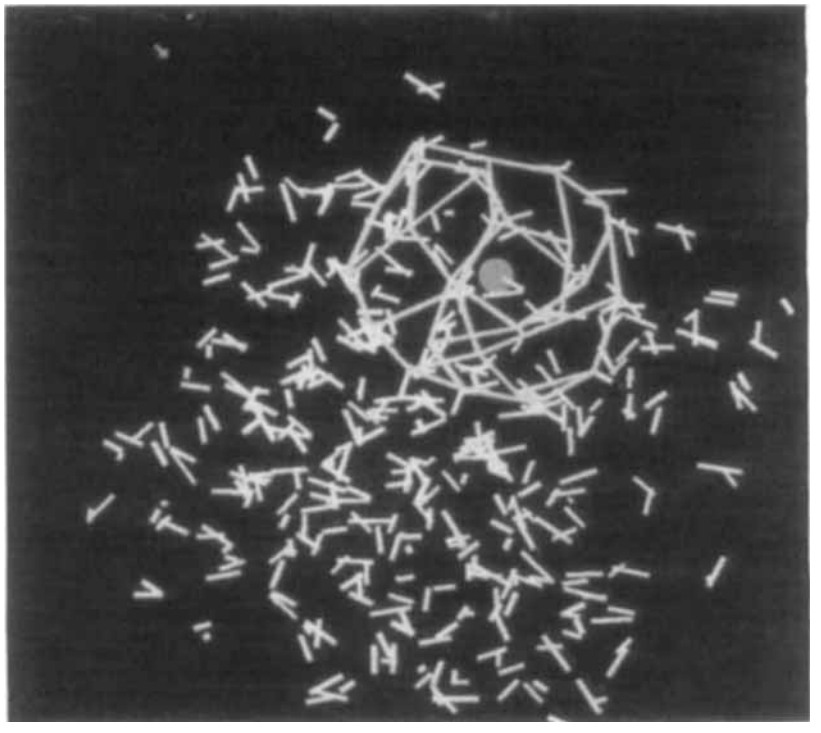

Figure 10 Clusters of Water Around Apolar Molecules. (see colour plates).

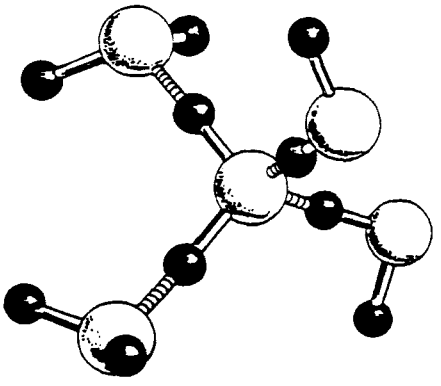

Figure 11 Hydrogen-Bonded Water Molecules (Frank, 1973 (14)).

As Stillinger (1979) pointed out, tetrahedral coordination represents the most feasible way of packing molecules about a central water molecule to permit fully-developed hydrogen bonds. The energy associated with such packing is most favorable to form pentagonal and hexagonal faces, which are the building blocks for convex polyhedra. The resulting effect is that water molecules easily form different convex polyhedra, caused by repulsive force between water and apolar molecules, and attractive forces between water molecules. The repulsive forces between water and apolar molecules were found to support the hydrate structures by Rogers [39].

V *Comparison with the Fullerene Family*

The carbon fullerene "family" [10] provides a striking comparison with the water clusters from our simulations. For example, the coordination numbers for both structures are even integers. The carbon numbers of fullerene family have been determined at C_{24}, C_{28}, C_{32}, C_{50}, C_{60}, C_{70}, C_{84}, C_{90}, C_{96}, C_{240}, C_{300}, and C_{540} etc. Hydrate structures composed of apolar molecules as quests and water molecules as hosts have the following water coordination numbers: Structure I, 20 and 24; Structure II, 20 and 28; Structure *H*, 20 and 36. Another proposed hydrate structure by Dyadin *et al.* [27] has a coordination number of 32. Both the carbon fullerene family and hydrate structures are convex polyhedra which obey Euler's theorem.

$$F \times V = E + 2$$

where F, V, and E represent numbers of faces, vertices, and edges, respectively.

The major structural differences between fullerene solids and water clusters in clathrate-type cavities are as follows:

1. Fullerene solids are composed of carbon clusters which are connected by carbon-carbon covalent bonds, while water clusters are hydrogen bonded. The bond length of C—C in fullerene solids is about 1.4Å, while the length of the hydrogen bond in clathrate structures is about 2.76Å.
2. Fullerene solids are self-stable as individual clusters which may or may not trap other guests into their cavities while water clusters are unstable without a substantial number of the cavities filled with guest molecules.

3. Fullerene individual clusters are stable, while the individual water clusters cannot form repeating unit crystals. Clusters must combine with other cluster sizes to form space-filling solid hydrates structures.

From the nature of chemical bonds, we know that the covalent bonds are an order of magnitude stronger than hydrogen bonds. Hydrogen bonds are more flexible than covalent bonds. Thus hydrogen bonded structures should have substantial ability to absorb small strains, either from within or without the cavities.

VI CONCLUSIONS

In conclusion, apolar molecules promote short lived ($t > 6.5$ ps) spherical water clusters in a hydrate-like labile cavity. The size of the cavity and the coordination number is dependent upon the size of the apolar molecule. The repulsive forces between oxygen and apolar molecules appear responsible for preventing the collapse of this cage base on the simulation and the model. Similar studies of solid hydrates conducted by Rodger [39, 40] found that the repulsive forces support the hydrate cavities. The coordination number of water molecules around small apolar molecules is quantized in jumps of approximately four, below a guest:water ratio of 2.5. This quanta is always an even number.

The water molecule prefers the tetrahedral configuration with others waters, and this preference is the principal reason for existance of such geometrical structures. Water is one of the best candidates to form tetrahedral angles with an angle between H—O—H of about 105°, which is very close to the tetrahedral angle (109.5°).

Our simulation was carried out for more than 24 000 steps around temperature of 250K. This system was stable over the simulation period. The labile cavities are stable and geometrically similar to the cavities in hydrate structures and other solid materials such as fullerene "family". The simulation and comparison with other solid materials suggest the possibility of other new clusters or cavities which may exist in hydrate structures yet to be discovered.

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