Domain Structure of Liquid Water According to the Theory of Intermolecular Forces

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(Received April 20, 1972)

Abstract: In the past years, a number of theories have been published to elucidate the structure of liquid water.

Common to most of these theories is that water mainly consist of several different kinds of clusters and also hydrogen bonds in water may be bent to some degree. Recently, in a series of papers, Jhon and Eyring successfully explained the thermodynamic, dielectric, surface and transport properties of water, assuming that it contains small domains of about 46 molecules.

According to the theory, the cluster size does not change with temperature, but the cluster concentration changes. In this paper, the potential energy of the domain has been calculated by means of the Lippincott-Schroeder empirical potential function for the hydrogen bond, the dispersion energy and dipole-dipole interaction terms.

The calculated results show that the domain of nearly 46 molecules is energetically most probable, and its size is independent of temperature. And also, we evaluated the effect of angle variation of the bent hydrogen bond.

In addition, the relaxation energy difference for ice and water is also explained by this method.

Introduction

According to previous findings by infra-red or X-ray spectroscopy\textsuperscript{1,2} the structure of ice and vapor have been known as described in the following.

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Ice is known to form a tetrahedral arrangement\textsuperscript{1,2} of H\textsubscript{2}O molecules in which the length between nearest molecules is 2.767 Å and the HOH angle is practically the same as the tetrahedral angle. On the other hand, the HOH angle for vapor molecules is close to 104.5°\textsuperscript{6}.

However, to elucidate the structure of liquid
water, and to explain the abnormal properties of the water, a number of models have been proposed without complete success in the past year.\textsuperscript{6-13}

Common to most of these theories is the assumption that water mainly consists of a variety of different kinds of clusters\textsuperscript{8,9,10,11} and also hydrogen bonds in water may be bent to some degree.\textsuperscript{6}

Recently, in a series of papers, Jhon and Eyring successfully explained thermodynamic, dielectric, surface and transport properties of water, assuming that liquid water is mainly made up of small domains of about 46 molecules.

According to the theory, the cluster size does not appreciably change with temperature, but the cluster concentration changes. In this paper, we calculated the potential energy of the domain by means of the Lippincott-Schroeder empirical potential function for the hydrogen bond\textsuperscript{12} the dispersion energy and dipole-dipole interaction terms.

The calculated results indicate that the domain of nearly 46 molecules is energetically most probable, and its size is independent of temperature. And we also calculated the effect of angle variation of a bent hydrogen bond.

A few alternative attempts to obtain the cluster of water molecules has been reported\textsuperscript{13,15}

**Calculation Scheme**

As discussed previously, the HOH angle for the vapor is 104.5°, while the H···O···H angle is 110-120° from the quantum mechanical calculation.\textsuperscript{15,14}

The angle HOH for ice is retained as tetrahedral. However, upon melting of ice, water is assumed to have the bent-hydrogen bond keeping the O-O distance rather smaller than 2.767Å in ice.

Now, suppose that the shape of the water molecule is a sphere for simplicity and consider the interaction energy between the specified water molecule and the surrounding water molecules.

The hydrogen bonding energy can be calculated only for the nearest neighbor interaction since this may be treated as a short range force. However, we have to consider both the dispersion force and the dipole-dipole interaction to be long range force.

To evaluate the hydrogen bonding energy, the following potential function developed by Lippincott-Schroeder\textsuperscript{12} is used:

\[
V_{hb}=D\left(1-\exp\left(-n\left(r-r_0^d/2R\right)\right)\right)-D^* \\
\exp\left(-n^*\left(R-r-r_0^d/2(2-R-r)\right)\right) \\
+\frac{n^*D^*}{2}\left\{1-\left(\frac{R^*}{R-r}\right)^2\right\} \\
\exp\left(-n^*\left(R_0-r-r_0^d/2(2R_0-r)\right)\right) \\
\exp\left(-bR-\frac{1}{2}\left(R/\left(\frac{R^*}{b}\right)\right)^n\exp(-bR_0)\right)
\]

(1)

Here \(r\) is the internuclear distance of the O-H bond, \(r_0\) the corresponding equilibrium value in the absence of a hydrogen bond, \(D\) the dissociation energy of the O-H bond, and \(n\) a parameter, \(r^*, r_0^*, D^*,\) and \(n^*\) having the same significance in relation to the H···O bond, \(R\) is the internuclear distance, \(R_0\) is the corresponding equilibrium distance, and \(m\) and \(b\) are parameters.

These values are summarized in Table I. In

<table>
<thead>
<tr>
<th>Table I.</th>
<th>Constants for the hydrogen bonding O-H···O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D, \text{Kcal/mole} )</td>
<td>118.0</td>
</tr>
<tr>
<td>(D^*, \text{Kcal/mole} )</td>
<td>81.3</td>
</tr>
<tr>
<td>(n10^4, \text{cm}^{-1} )</td>
<td>9.18</td>
</tr>
<tr>
<td>(n10^4, \text{cm}^{-1} )</td>
<td>13.32</td>
</tr>
</tbody>
</table>

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In this paper, the relation \( r = r_0 = r^* = r_0^* \) is assumed. The second term to represent the dispersion interaction for an isolated pair of polar molecules is represented by

\[
V_{\text{disp}} = U_0 \left( \frac{r_0}{r'^*} \right)^2 - \frac{\mu^2}{r^2} g \tag{2}
\]

In eq. (2), the dipole-dipole interaction energy in addition to the Lennard-Jones potential is included. Here \( U_0 \), dissociation energy of the water molecules, is taken as 0.332 Kcal/mole and \( g \), dipole moment of water molecules as 1.834 D: \( r' \) and \( r^* \) is the distance between interacting molecules and its equilibrium distance respectively. And \( g = 2 \cos \theta_a \cos \theta_b \sin \theta_c \cos (\phi_a - \phi_b) \) is a function of the angles \( \theta_a \) and \( \theta_b \) formed by the a and b dipoles with the line joining their centres when the dipoles line in the same plane, and the angle \( \theta_a - \theta_b \) between the planes passing through the line joining the centres of the dipoles and their axis (See Appendix II).

First of all, the coordinates of each molecules must be known and the calculation scheme can be described in Appendix I.

Now, we can classify the groups in which each molecules have the same distance from the centered molecule as follows: 1—4—12—12—6—12—24—16—12—... In eqs. (2), if we consider all sums to the all molecules belong to the same group, the total interaction energy can be evaluated respectively.

\[
V_{r,i} = \sum_{j} \left( \frac{r_{ij}}{r^*_{ij}} \right)^{12} - 2 \left( \frac{r_{ij}}{r^*_{ij}} \right)^6 - \frac{\mu^2}{r_{ij}} g_{ij} \tag{3}
\]

Here \( \sum \) indicate the sum to all molecules to the \( i \) th group, and \( g_{ij} \) can be evaluated as shown in Appendix II. Hence, the total potential energy to the \( j \) th group from the centered molecule will be given by Eqs. (1) and (3).

\[
V_j = 4V_{N,i} + \sum \sum_{k} V_{r,k} \tag{4}
\]

In eq. (3), the value of \( \sum g_{ij} \) for ice is zero as pointed out in Appendix I and each \( r_{ij} \) value is equal for different \( j \), while those values for water have slight different values.

**Calculation and Result**

For ice structure, \( \sum g_{ij} \) becomes zero as
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previously pointed out. And, the value of $V_{1,0}$ is negative, and the contribution of $V_{1,0}$ is negligibly small as $N$ becomes large.

Hence, for various $N$, the value in Eq. (4) indicate no minimum point or no converging trend. This results up to the values of $N=11$ are summarized in Table II.

However, for liquid water, we obtained the minimum point on the potential energy curve upon varying the angle value of $\theta = \angle \beta - \angle \gamma$.

Here, $\angle \alpha = \frac{1}{2} \angle O_H^\cap = \frac{1}{2} \cdot 104.5^\circ$ and

$\angle \beta = \frac{1}{2} \cdot \angle O_H^\cap - \beta > 109.46^\circ$

In this calculation, the distance between nearest neighbor for liquid water is assumed

| Table III. Potential energies in liquid water by angle variation, Kcal/mole |
|----------------------------------|-----------|-----------|-----------|
| $\theta$ Group order | $4V_{\theta}^H s^a$ | $-15.0055$ | $-15.1803$ | $-15.3071$ |
| $V_{1,0}$ | $V_N$ | $V_{1,0}$ | $V_N$ | $V_{1,0}$ | $V_N$ |
| 1 | -1.3191 | -18.9257 | -1.1728 | -16.3532 | -1.0519 | -18.3590 |
| 2 | -0.4665 | -15.7922 | -0.4351 | -16.7882 | -0.4081 | -15.7671 |
| 3 | -01457 | -15.9389 | -0.1595 | -16.9477 | -0.1695 | -15.9366 |
| 4 | -0.0085 | -16.9474 | -0.0300 | -16.9777 | -0.0476 | -16.9843 |
| 5 | -0.0264 | -16.9738 | -0.0096 | -16.9873 | 0.0045 | -16.9798 |
| 6 | -0.0033 | -16.9770 | 0.0138 | -16.9691 | 0.0365 | -16.9432 |
| 7 | 0.0148 | -16.9622 | 0.017 | -16.9573 | 0.0095 | -16.9338 |
| 8 | 0.0007 | -16.9555 | 0.0146 | -16.9428 | 0.0213 | -16.9124 |
| 9 | 0.0218 | -16.9337 | 0.0315 | -16.9113 | 0.0400 | -16.8724 |
| 10 | 0.0092 | -16.9245 | 0.0173 | -16.8940 | 0.0241 | -16.8483 |
| 11 | 0.0087 | -16.9157 | 0.0139 | -16.8801 | 0.0184 | -16.8299 |

*a) by eq. (4)

| Table IV. Minimum potential energies in liquid water by angle variation, Kcal/mole |
|----------------------------------|-----------|-----------|
| Angle $\theta$ | Distance* (Å) | Molar Volume* (cc) | Domain Size | $V_N$ |
| 3.10 | 2.7054 | 18.36 | 147 | -16.8567 |
| 3.30 | 2.7014 | 18.28 | 147 | -16.8769 |
| 3.50 | 2.6974 | 18.20 | 71 | -16.9006 |
| 4.00 | 2.6874 | 17.99 | 71 | -16.9475 |
| 4.50 | 2.6774 | 17.80 | 71 | -16.9732 |
| 4.70 | 2.6734 | 17.72 | 71 | -16.9770 |
| 4.90 | 2.6694 | 17.64 | 47 | -16.9832 |
| 5.10 | 2.6654 | 17.56 | 47 | -16.9866 |
| 5.20 | 2.6634 | 17.52 | 47 | -16.9873 |
| 5.40 | 2.6604 | 17.44 | 47 | -16.9843 |
| 5.60 | 2.6554 | 17.36 | 35 | -16.9736 |
| 6.00 | 2.6474 | 17.20 | 35 | -16.8946 |
| 6.80 | 2.6314 | 16.89 | 35 | -16.9946 |
| 8.00 | 2.6074 | 16.44 | 35 | -16.6060 |

*a. by eq. (6)

b. assumed the tetrahedral structure

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to be decreased as $r=2.767-0.02 \text{\AA}$, here 2.767\text{\AA} is that for ice structure.

According to the calculation of $V^m$ upon varying the $\theta$ value, the following minimum range is obtained; $N=11$ up to $\theta=3.3^\circ$, $N=6$ up to $\theta=4.7^\circ$, $N=5$ up to $\theta=5.4^\circ$, and $N=4$ beyond $\theta=5.4^\circ$.

In Table III, we listed the potential energies in liquid water domain by angle variation $\theta$ for each group respectively.

In Table IV, only minimum values for specified $N$ up to $N=11$ is shown.

Discussion

Judging from Table II and Table IV, one can see the structure difference between ice and liquid water. Ice is supposed to extend to have the infinite tetrahedral structure, while water has the probable domain size ranging from 71 to 35. Among them, the domain size of 47 molecules is the most favorable energetically.

It is very interesting to know that the estimated molar volume for liquid water by simple calculation is 17.5 ml/mole. In the past, many authors tried to explain the abnormal properties of water assuming that water is consist of a several sizes of clusters (or domain). Some authors assumed that the size of the cluster is dependent upon temperature.

However, according to the calculated result in this paper, the size of 47 molecular domain is most energetically probable and is independent of temperature. This fact support the previous finding by Jhon and Eyring.

Appendix I

Directions of the dipole moment of the molecules in ice structure tend to be parallel and the molecules are held together in a tetrahedral arrangement. However, the directions of dipole moments in liquid water is a little deviated from the parallel trends.

Here, we will show how to obtain the coordinates of each molecules, both the distance and the angles between molecules. For ice, the direction of the water dipole is taken to be parallel along $Z$ axis, i.e., perpendicular to $XY$ plane, and the hydrogen bonding with the nearest neighbors is also taken to be perpendicular to $X$ axis or $Y$ axis.

Now if we represent the bondings to nearest neighbors from the centered molecule as vector, we have two class of vectors $\vec{u}$ and $\vec{v}$, i.e. $\vec{u}$ or $\vec{v}$ is defined as the vector perpendicular to the $Y$ axis or $X$ axis for $O\cdots H\cdots O$ plane.

Then, four each vectors for $\vec{u}$ and $\vec{v}$ will be given as

$$\vec{u}_1=(\sin \alpha, 0, \cos \alpha)$$
$$\vec{u}_2=(-\sin \alpha, 0, \cos \alpha)$$
$$\vec{u}_3=(0, \sin \beta, -\cos \beta)$$
$$\vec{u}_4=(0, -\sin \beta, -\cos \beta)$$

(A-1)

$$\vec{v}_1=(0, \sin \alpha, \cos \alpha)$$
$$\vec{v}_2=(0, -\sin \alpha, \cos \alpha)$$
$$\vec{v}_3=(\sin \beta, 0, -\cos \beta)$$
$$\vec{v}_4=(-\sin \beta, 0, -\cos \beta)$$

(A-2)

Here $O\cdots H\cdots O$ distance is taken as unity, $\alpha$, and $\beta$ are previously defined.

For ice, $\alpha=\beta=\frac{1}{2} (109.46^\circ)$

Now, we classify the groups in which molecule is in a same distance from the centred molecule, and express the coordinate of the molecule by the vector notation in (A-1) and (A-2).

The followings are some examples.

Group 2. $\vec{u}_1 \pm \vec{v}_1 \left( \frac{\sqrt{3}}{3} \right)$

Group 5. $\vec{u}_1 \pm \vec{v}_1 \pm \vec{u}_1 \left( \frac{\sqrt{3}}{3} \right)$
Group 7. \( \vec{u}_1 + \vec{v}_1 + \vec{w}_1 + \vec{y}_1 \) (3)

Group 10. \( \vec{u}_1 + \vec{v}_1 + \vec{w}_1 + \vec{y}_1 \left( \sqrt{3} \right) \)

here the values in ( ) is the distance from the centered molecule.

For liquid water, \( \alpha = \frac{1}{3} (104.5\degree) \) and \( \beta \geq \frac{1}{2} \) (109.46\degree). Since the dipole directions between nearest neighbors are not parallel each other, we have to introduce the rotors to get the coordinates of the molecules.

The followings are some examples

\[
\begin{align*}
\text{Group 5,} & \quad \vec{u}_1 + R_1 \vec{v}_1 + R_2 \vec{R}_1 \vec{u}_1 \ (R_1 R_2 R_1) \ (A-4) \\
\text{Group 10,} & \quad \vec{u}_1 + R_1 \vec{v}_1 + R_2 \vec{R}_1 \vec{u}_1 + R_3 \vec{R}_1 \vec{v}_3 + R_4 \vec{R}_2 \vec{R}_1 \vec{v}_3 \ (R_1 R_2 R_1) \\
\end{align*}
\]

here

\[
\begin{align*}
R_1 &= \begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{pmatrix} \\
R_2 &= \begin{pmatrix}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-\sin \theta & 0 & \cos \theta
\end{pmatrix} \\
R_3 &= \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{pmatrix}
\end{align*}
\]

and third row value in ( ) in (A-4) express the dipole direction.

**Appendix II**

In Fig. 1, the relation between the centered molecule (A) and the neighbor molecule (B) having separated distance \( r \) from A is shown.

If we transform the coordinate the new one in Fig. 2, one can calculate the values of \( g_{ij} \) (12) in Eq. (3).

Then,

\[ \theta_s = \theta_3 \]

\[ \phi_s = \frac{\pi}{2} \]  

(A-5)

\[
\begin{align*}
\text{Figure 1. Original coordinate system.} \\
\text{The coordinate system indexing 2 is taken to be parallel to coordinate system indexing 1 at} (r_1, \theta_1, \phi_1)
\end{align*}
\]

\[
\begin{align*}
\text{Figure 2. Transformed coordinate system.} \\
\text{The coordinate system indexing b is taken to be parallel to system a and the each Z-component is in same line.}
\end{align*}
\]

\[
\begin{align*}
\cos \theta_1 = \sin \theta_1 \sin \phi_2 - \cos \theta_1 \cos \theta_2 \\
\sin \theta_1 \sin \phi_2 = \sin \theta_1 \cos \theta_1 - \cos \theta_1 \sin \theta_2 \cos \phi_1 + \sin \phi_1 \cos \phi_2 \\
\sin \phi_1 = -\sin \theta_1 \sin (\phi_1 - \phi_2)
\end{align*}
\]

**References**

1. J. D. Bernal and R. H. Fowler; *J. Chem. Phys.*, 1, 515 (1933)
Domain Structure of Liquid Water According to the Theory of Intermolecular Forces