

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

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

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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 paper, Jhon and Eyring successfully explained 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^{1,3} the structure of ice and vapor have been known as described in the following.

Ice is known to form a tetrahedral arrangement^{1,2} of H₂O molecules in which the⁴ 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°⁵

However, to elucidate the structure of liquid

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water, and to explain the abnormal properties of the water, a number of models have been proposed without complete success in the past year⁶⁻¹¹

Common to most of these theories is the assumption that water mainly consists of a variety of different kinds of clusters^{8,9,10,11} and also hydrogen bonds in water may be bent to some degree⁶

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 bond¹² 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^{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^{13,14}

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 2.767 Å 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-Schroeder¹² is used.

$$V_{HB} = D \left\{ 1 - \exp \left(-n(r-r_0)^2/2r \right) \right\} - D^* \exp \left\{ -n^*(R-r-r_0)^2/2(R-r) \right\} + \frac{n^* D^*}{2} \left\{ 1 - \left(\frac{r_0^*}{R-r} \right)^2 \right\} \exp \left\{ -n^*(R_0-r-r_0^*)^2/2(R_0-r) \right\} \exp(-bR) - \frac{1}{2} \left(\frac{R_0}{R} \right)^m \exp(-bR_0) \frac{1}{\left(b - \frac{1}{2R_0} \right) \exp(-bR_0)} \quad (1)$$

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 I. Constants for the hydrogen bonding O-H...O

D , Kcal/mole	118.0	r_0 , Å	0.97
D^* Kcal/mole	81.3	r_0^* , Å	0.97
$n \cdot 10^{-6}$, cm ⁻¹	9.18	$10^{-6}b$, cm ⁻¹	4.80
$n \cdot 10^{-8}$, cm ⁻¹	13.32	m	6.0

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

$$V_{\text{polar}}=U_0\left\{\left(\frac{r_0'}{r'}\right)^{12}-2\left(\frac{r_0'}{r'}\right)^6-\frac{\mu^2}{r'^3}g\right\} \quad (2)$$

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/mole¹⁶ and μ , dipole moment of water molecules as 1.834 D; r' and r_0' is the distance between interacting molecules and its equilibrium distance respectfully. And $g=2 \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos(\phi_b - \phi_a)$ ¹⁷ is a function of the angles θ_a and θ_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 $\theta_b - \theta_a$ 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 eq. (2), if we consider all sums to the all molecules belong to the same group, the total interaction energy can be evaluated respectively.

$$V_{v,d}=\sum_j U_0\left\{\left(\frac{r_0'}{r_{ij}}\right)^{12}-2\left(\frac{r_0'}{r_{ij}}\right)^6-\frac{\mu^2}{r_{ij}^3}g_{ij}\right\} \quad (3)$$

here \sum indicate the sum to the 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 Nth group from the centered molecule will be given by Eqs. (1) and (3)

$$V_N=4 V_{H,B}+\sum_j^N V_{v,d} \quad (4)$$

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, $\sum_j g_{ij}$ becomes zero as

Table II. Potential energies in ice, Kcal/mole

Group order	No. of molecule in a group	relative ^b distance	$V_{v,d}^c$	V_N^d
1	4	1.0000	-1.32682	-14.22137
2	12	1.6330	-0.40251	-14.62388
3	12	1.9149	-0.15737	-14.78125
4	6	2.3094	-0.02574	-14.80699
5	12	2.5166	-0.03079	-14.83778
6	24	2.8284	-0.03058	-14.86836
7	16	3.0000	-0.01432	-14.88268
8	12	3.2660	-0.00645	-14.88913
9	24	3.4157	-0.00987	-14.89900
10	12	3.7859	-0.00266	-14.90166
11	12	4.1231	-0.00159	-13.90325

a) in eq. (4), $4V_{H,B}=-12.8945$

b) relative distance=distance/distance of nearest neighbor. The distance of nearest neighbor is 2.767 Å

c) by eq. (3)

d) by eq. (4)

previously pointed out. And, the value of $V_{V,D}^i$ is negative, and the contribution of $V_{V,D}^i$ 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, $\angle\alpha = \frac{1}{2} \angle \text{O} \begin{matrix} \text{H} \\ \diagup \\ \diagdown \\ \text{H} \end{matrix} = \frac{1}{2} \cdot 104.5^\circ$ and

$\angle\beta = \frac{1}{2} \cdot \angle \text{O} \begin{matrix} \text{H-O} \\ \diagup \\ \diagdown \\ \text{H-O} \end{matrix} > 109.46^\circ$

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

θ_1 Group order	4.7		5.2		5.6	
	$V_{V,D}^i$	V_N	$V_{V,D}^i$	V_N	$V_{V,D}^i$	V_N
1	-1.3191	-16.3257	-1.1728	-16.3532	-1.0519	-16.3590
2	-0.4665	-16.7922	-0.4351	-16.7882	-0.4081	-16.7671
3	-0.1467	-16.9389	-0.1595	-16.9477	-0.1695	-16.9366
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	0.0183	-16.9691	0.0365	-16.9432
7	0.0148	-16.9622	0.0117	-16.9573	0.0095	-16.9338
8	0.0067	-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 θ	Distance ^a (Å)	Molar Volume ^b (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	-16.9821
5.10	2.6654	17.56	47	-16.9866
5.20	2.6634	17.52	47	-16.9873
5.40	2.6594	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. (5)

b. assumed the tetrahedral structure

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

According to the calculation of V^N upon varying the θ 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 θ 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 temperature¹⁰.

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 Eyring⁹.

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 $\text{O} \begin{cases} \text{H}\cdots\text{O} \\ \text{H}\cdots\text{O} \end{cases}$ plane.

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

$$\begin{aligned} \vec{u}_1 &= (\sin \alpha, 0, \cos \alpha) \\ \vec{u}_2 &= (-\sin \alpha, 0, \cos \alpha) \\ \vec{u}_3 &= (0, \sin \beta, -\cos \beta) \\ \vec{u}_4 &= (0, -\sin \beta, -\cos \beta) \end{aligned} \quad (\text{A-1})$$

$$\begin{aligned} \vec{v}_1 &= (0, \sin \alpha, \cos \alpha) \\ \vec{v}_2 &= (0, -\sin \alpha, \cos \alpha) \\ \vec{v}_3 &= (\sin \beta, 0, -\cos \beta) \\ \vec{v}_4 &= (-\sin \beta, 0, -\cos \beta) \end{aligned} \quad (\text{A-2})$$

here O-H \cdots O distance is taken as unity, α , and β 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.

$$\begin{aligned} \text{Group 2, } & \vec{u}_1 + \vec{v}_1 \left(\sqrt{\frac{8}{3}} \right) \\ \text{Group 5, } & \vec{u}_1 + \vec{v}_1 + \vec{u}_1 \left(\sqrt{\frac{19}{3}} \right) \end{aligned}$$

$$\text{Group 7, } \vec{u}_1 + \vec{v}_1 + \vec{u}_2 + \vec{v}_2 + \vec{u}_1 \quad (A-3)$$

$$\text{Group 10, } \vec{u}_1 + \vec{v}_1 + \vec{u}_1 + \vec{v}_1 + \vec{u}_1 \left(\sqrt{\frac{43}{3}} \right)$$

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

For liquid water, $\alpha = \frac{1}{2}(104.5^\circ)$ and $\beta > \frac{1}{2}(109.46^\circ)$. 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

$$\text{Group 5, } \vec{u}_1 + R_1 \vec{v}_1 + R_3 R_1 \vec{u}_1 \quad (R_1 R_3 R_1) \quad (A-4)$$

$$\text{Group 10, } \vec{u}_1 + R_1 \vec{v}_1 + R_3 R_1 \vec{u}_1 + R_1 R_3 R_1 \vec{v}_3 \\ + R_1 R_1 R_1 R_1 \vec{u}_1 \quad (R_1 R_1 R_1 R_3 R_1)$$

here

$$R_1 = \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix}$$

$$R_2 = \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{pmatrix}$$

$$R_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix} \text{ etc,}$$

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

Then,

$$\theta_2 = \theta_1 \\ \phi_2 = \frac{\pi}{2} \quad (A-5)$$

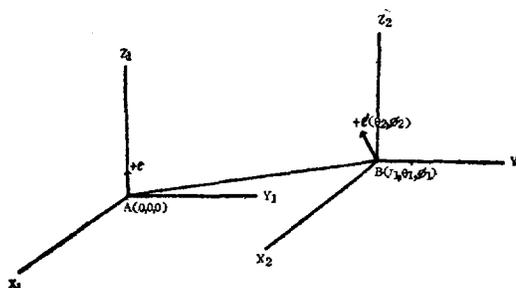


Figure 1. Original coordinate system. The coordinate system indexing 2 is taken to be parallel to coordinate system indexing 1 at (r_1, θ_1, ϕ_1)

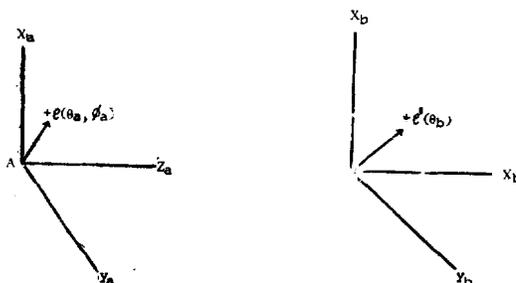


Figure 2. Transformed coordinate system. The coordinate system indexing b is taken to be parallel to system a and the each Z-component is in same line.

and

$$\cos \theta_b = \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) + \cos \theta_1 \cos \theta_2 \\ \sin \theta_b \sin \phi_b = \sin \theta_1 \cos \theta_2 - \cos \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \\ \sin \theta_b \cos \phi_b = -\sin \theta_2 \sin(\phi_1 - \phi_2)$$

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