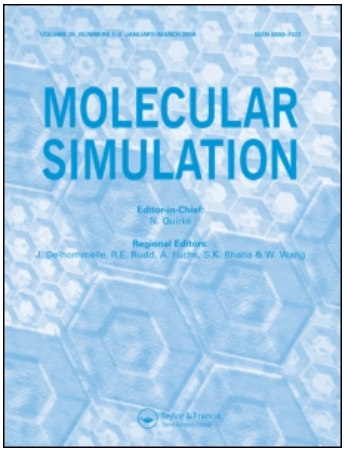

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POTENTIAL SURFACE ANALYSIS AND LOW TEMPERATURE DYNAMICS OF WATER

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Collective motions in liquid water are investigated by examining potential surfaces of an assembly of water molecules in its liquid state. It is found that coarse-graining of the quenched structures and low temperature dynamics provide information on their hierarchal structures. The distribution of the potential energy minimum structures in configuration space is examined is detail and is compared with those of methanol. The strong and fragile nature of liquid water is discussed.

KEY WORDS: Water, methanol, potential surface, quench, coarse-graining.

1 INTRODUCTION

Water is the most ubiquitous substance and is known to have various anomalous properties. Much effort has been devoted to account for those anomalies from the microscopic point of view. We have made a variety of analyses on the potential energy surface of liquid water assembly and the collective motions on that surface [1–4]. Information obtained by those analyses is useful to understand water dynamics; the energy barrier between two adjacent quenched structures, the transition pattern, etc. However, there remains a lot to be answered on the dynamics of liquid water. In particular, frequent transitions among those potential minimum structures makes an analysis complicated. The two dimensional plot of the distance matrix in our previous study [3, 5], suggests that a collection of the minimum structures belonging to the same group can be represented by a single structure. This suggests a hierarchal structure of the potential surface of water.

The anomalous properties are enhanced in lower temperature region. Those properties observed in lower temperature region have been so far accounted for by two ideas; one is due to Speedy and Angell [6–8] on the basis of stability-limit conjecture, another is proposed by Poole *et al.* based on the observation in molecular dynamics simulation [9–11]. The microscopic explanation of the divergent properties was made by Sasai [12] and Sastry *et al.* [13].

In normal supercooled region, water is seemingly fragile while it has a characteristics of strong liquid near the glass transition in hypercooled state suggesting a new phase, called "water II" [14–16]. The potential of free energy surface of

glass forming liquid has been conjectured and was shown schematically in a simplified way [16]. The distribution of the minimum potential energy in configuration space is rather uniform for a strong liquid while that of a fragile liquid has shallow minima as well as well deeper minima in which the system is trapped in near the glass transition temperature. The observed temperature dependence of the viscosity seems to be easily related by molecular dynamics simulation and by quenching technique to its potential minimum in configuration space.

We explore, in this study, the potential surfaces of liquid water at a room temperature and at a temperature near the glass transition in order to delineate a mechanism of the fragile-strong transition. A hierarchal structure of potential surface in water is examined and temperature dependence of the potential energy surface is compared with that of water.

2 MODEL AND METHODS

The water-water interaction is modeled by the TIP4P potential [17], which is simple and is capable of reproducing most of measured properties in the framework of rigid rotors. The methanol interaction used in the present study is described by the OPLS potential [18]. Molecular dynamics simulations are carried out for water and methanol. The temperatures are set to 300 and 160 K for both water and methanol systems. The time step for integration of equations of motion is 4×10^{-16} s. for water at 300 K, 8×10^{-16} s. for water at 160 K, 8×10^{-16} s. for methanol at 300 K, 1.6×10^{-15} s. for methanol at 160 K. The pair interaction potential is truncated at the half of the cell length. The number of molecules is 64, which are confined in a periodic cubic cell. The obtained instantaneous structures are quenched to the corresponding local potential minimum structures [2, 5, 19–21]. Those structures are used to generate coarse-grained structures. The coarse-graining consists of two steps; the averaging the successive instantaneous structures over 0.4 ps and the subsequent quenching. The average process is performed according to

$$\bar{r}_i(t) = \frac{1}{\Delta t} \int_{-\Delta t/2}^{\Delta t/2} r_i(t+\tau) d\tau \tag{1}$$

where $r_i(t)$ is the coordinate (both translational and orientational) of ith molecule at time t and $\bar{r}_i(t)$ is the averaged coordinate over $\Delta t (= 0.4$ ps). Care must be taken when the averaging of the orientational parameters is made: The Euler angles representing orientations in quenching process are converted to the quaternion parameters and the averaging is made according to Equation (1). Then, a normalization of quaternion to satisfy the condition,

$$\eta_i^2 + \zeta_i^2 + \chi_i^2 + \xi_i^2 = 1 \tag{2}$$

is required before converting back to Euler angles.

3 RESULTS AND ANALYSES

3.1 Thermodynamic Properties

A series of quenched structures of water are obtained: 800 structures from MD simulation at 300 K, each separated by 10 fs, 4000 structures at 160 K, each separated by 80 fs. The potential energies are tabulated in Table. 1. The potential energy at higher temperature is higher in instantaneous structure by 4.2 kJ mol^{-1} removing the harmonic contribution, which is a function of only the temperature and the number of degrees of freedom for any classical harmonic system. This difference is separated into two origins; the anharmonic nature of the potential energy surface and the depth of the potential well, both of which may depend on the temperature. The anharmonic contributions to the potential energy are 2.3 kJ mol^{-1} at 300 K and 0.3 kJ mol^{-1} at 160 K. The potential energy difference between the lower and higher temperature systems still remains in the local minimum structures after removing thermal fluctuation; the difference is approximately 2.2 kJ mol^{-1}. This indicates that liquid water is not strong liquid and the potential energy surface visited by the system is dependent largely on the temperature. The difference in pure methanol liquid is 1.0 kJ mol^{-1}, which is smaller than that of water but may be large enough to belong to a fragile liquid. The potential energy fluctuation in quenched water at the lower temperature is small, 0.1 kJ mol^{-1}, which should be compared with that at the higher temperature, 0.4 kJ mol^{-1}. The potential energies

Table 1 Potential energy and mean square deviation of water and methanol in instantaneous (I), quenched (Q) and coarse-grained (C) structures. Energy is in kJ/mol. C20 and C50 indicate that the coarse-grained structure are obtained by repeating 20 and 50 cycles of the procedures given in the text.

	I	*Q*	*C*20	*C*50
		$\Delta t =$	0.4 *ps*	
	water	(300 K)		
energy	−42.08	−51.83	−52.70	−52.88
deviation	0.45	0.48	0.36	0.28
		$\Delta t =$	1 ps	
energy	−42.08	−51.83	−52.81	−52.93
deviation	0.45	0.48	0.44	0.41
	water	(160 K)		
energy	−49.75	−53.99		
deviation	0.24	0.08		
	methanol	(300 K)		
energy	−35.00	−43.01		
deviation	0.39	0.25		
	methanol	(160 K)		
energy	−39.65	−43.97		
deviation	0.23	0.16		

of quenched water are plotted in Figure 1. The frequent change of the potential energy indicates that the sampled time is long compared with the relaxation time of the local structure and the system is well equilibrated. The fluctuation of the potential energy for methanol at lower temperature is larger than that for water as listed in Table 1. Methanol has a character of fragile liquid as is manifested by this larger potential fluctuation and no transformation from fragile to strong liquid seems to take place. On the other hand, the potential surfaces of water at lower temperature is rather uniform. This is an evidence that water at lower temperature has a strong character.

A question as to how the potential energy is lowered by lowering the temperature should be addressed. The potential surface at room temperature seems to be complicated and transitions from one minimum to another take place frequently. As has been shown in our previous study [3,5], a set of local minimum structures are close together in configurational space. The distances between successive structures in configuration space are small. This indicates that those structures may constitute a group. The representative structure of this group is indeed obtained by the coarse-graining of a series of quenched structures in a similar way as was made in realization of V-structure [22,23]. This process is repeated for 50 cycles. The potential energy is also shown in Figure 1. There are only 113 independent structures, while there exist 523 structures with a simple quenching process. The potential energy of those representative structures are almost always lower than the simply quenched structures. This means that the coarse-graining procedure eliminates higher potential energy structures from temporal equilibrium positions in the same sense that the V-structure is obtained by eliminating large distortions. A group of quenched structures seem to have a hierarchal structure in configuration space and can be

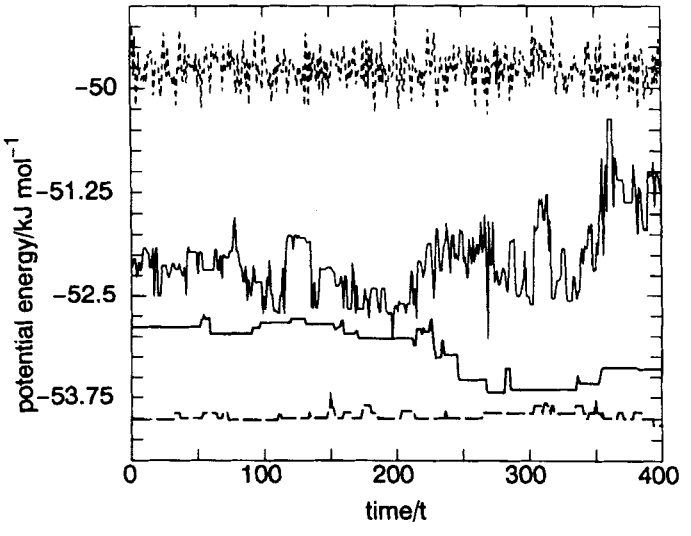

Figure 1 Potential energy of water over 400 configurations. Solid line; quenched structure, heavy solid line; coarse-grained structure at 300 K with time interval of 10 fs. Dotted line; instantaneous structure, heavy dashed line; quenched structure at 160 K with time interval of 80 fs.

represented by the coarse-grained structure, which is closer to what we called "overall inherent structures" in the previous study [3, 5]. the simplest way to examine the tetrahedral coordination of each water molecule is to evaluate the contributions of the potential energy separately; a term arising from the coulombic interaction and a term from the Lennard-Jones part. The former can be a measure of tetrahedrality. If the latter term contributes heavily, the structure is that of the simple liquid. Those two terms for water systems are listed in Table 2. As the total energy decreases, the Lennard-Jones part increases and the tetrahedral coordination is enhanced sacrificing the oxygen-oxygen repulsive interaction.

3.2 Structure of Water

The structure of water, represented by the radial distribution functions (RDFs) are obtained for instantaneous, quenched and coarse-grained structures. The RDFs for oxygen pair of water molecules at 160 and 300 K are shown in Figure 2. The first minimum at 160 K is very low and the second peak at around 4.5 Å is also pronounced, which is one of the indications of tetrahedral coordinations of water molecules. The RDFs of water for the quenched and the coarse-grained structures at 300 K are plotted in Figure 3 together with that of the quenched structure at 160 K. The structure is indeed enhanced by the coarse-graining. This may again suggest that hierarchal structure of the potential energy surface exists in liquid water. We have performed another simulation in which spherical molecules are confined in the same size of the basic cell as used for water. The pair interaction potential was invented in order to mimic the arrangement of oxygen atoms in liquid water; its RDF has a similar characteristics to that of the oxygen pair of water [24]. Although the location of the first peak is slightly shifted toward longer distance region, the whole shape is similar to that of water as shown in Figure 4. The distance to the first peak becomes smaller upon quenching because of the strong interaction among water molecules while the reverse is seen in the spherical molecules. Coarse-grained structures are also obtained in the same method as used for water system. In Figure 4, the RDF for the coarse-grained structure of this spherical molecule is also drawn but no appreciable change is seen from the simply quenched structure. The coarse-graining does not make any difference in the RDF of spherical molecules.

Table 2 Potential energy components of water in instantaneous (I), quenched (Q) and coarse-grained (C) structures. Potential energy (in kJ/mol) is divided into Coulombic and Lennard-Jones (LJ) terms.

	I	*Q*	*C50*
		T = 300 K	
Coulomb	−51.21	−63.32	−65.33
LJ	+9.13	+11.48	+12.45
		T = 160 K	
Coulomb	−63.66	−68.64	
LJ	+13.71	+14.26	

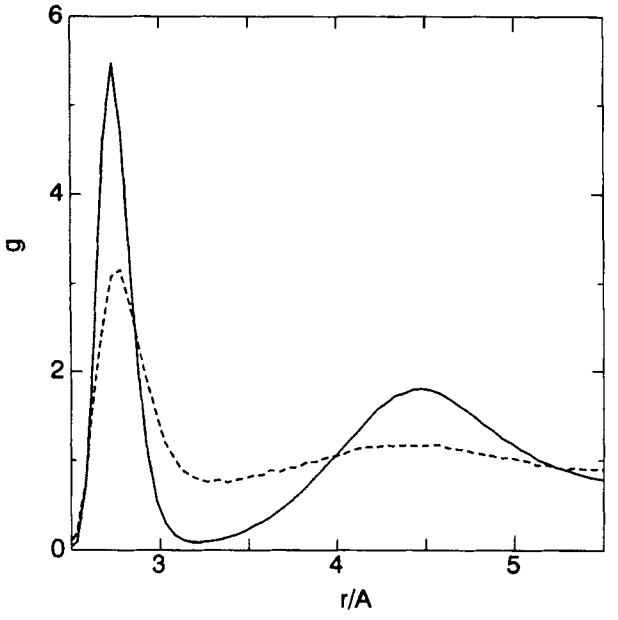

Figure 2 Radial distribution functions for oxygen pair of instantaneous structure at temperature 300 K (dotted line) and 160 K (solid line).

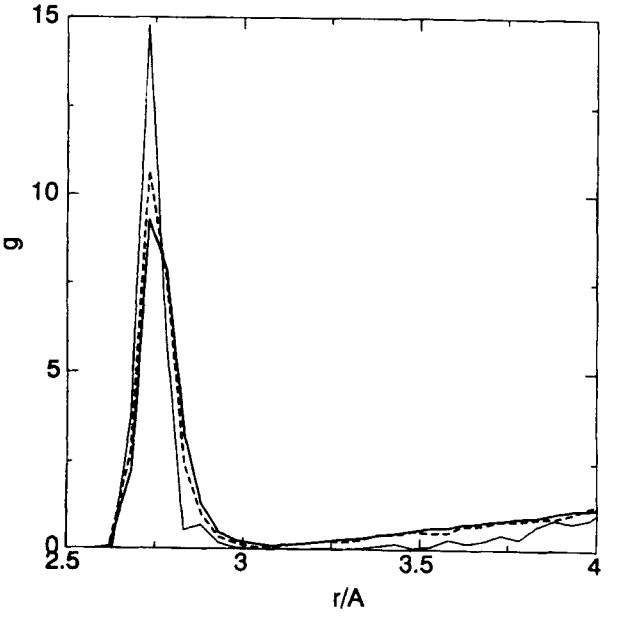

Figure 3 Radial distribution functions for oxygen pair of quenched structure (heavy solid line) and coarse-grained structure (heavy dotted line) at temperature 300 K and of quenched structure (thin solid line) at 160 K.

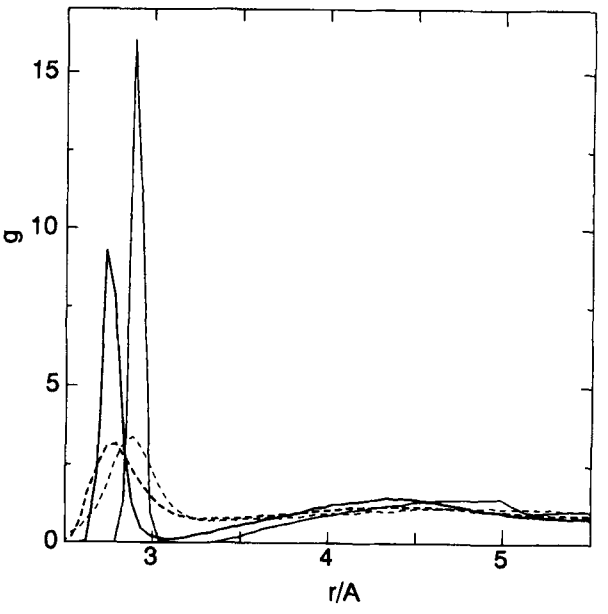

Figure 4 Radial distribution functions for oxygen pair of instantaneous structure (heavy dotted line) and quenched structure (heavy solid line) at temperature 300 K and for spherical molecules of instantaneous structure (dotted line), quenched structure (solid line) and coarse-grained structure (dash-dot line). The radial distribution function for the coarse-grained structure overlaps almost completely with that for the quenched structure.

Coordination number is a direct measure of the tetrahedral structure of water. Any water molecule is regarded as a coordinated one if its distance from the central molecule is less than 3.2 Å. Distributions of coordination number are given in Table 3. Even after removing thermal fluctuations, one fourth of water molecules are not tetrahedrally-coordinated. With coarse-graining procedure, a tetrahedral network is considerably enhanced. However, 18 % of water molecules still have defects. Those defects are remarkably reduced by lowering the temperature. The structure of water at very low temperature seems to be different qualitatively from that at room temperature.

3.3 Collective Motions near Potential Well

We compare the density of state for intermolecular vibrational motions by performing a normal mode analysis. Those for instantaneous and quenched structures at 300 K are given in Figure 5 and those at 160 K in Figure 6. In the case of instantaneous structures, there exist some imaginary frequency modes. The density of imaginary modes is plotted in negative region of the figure. The number of imaginary modes is approximately 40 out of 381 total modes at 300 K. The number is reduced remarkably and is approximately 7 at 160 K; instantaneous structures are

Table 3 Coordination number distributions (%) of water in instantaneous (I), quenched (Q) and coarse-grained (C) structures.

Coordination number	*0*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
instantaneous		T	=	300	K				
	0	0.2	4.1	27.7	52.1	19.3	2.3	0.2	0
quenched		T	=	300	K				
	0	0	0.4	12.7	74.8	11.6	0.4	0	0
coarse-grained		T	=	300	K				
	0	0	0.1	8.3	82.1	9.1	0	0	0
instantaneous		T	=	160	K				
	0	0	0.1	3.6	92.0	4.3	0.1	0	0
quenched		T	=	160	K				
	0	0	0	2.6	94.4	3.0	0	0	0

stable for most of the displacements and only 1.8 % of total modes are unstable. The shape of mode density for the coarse-grained structure shown in Figure 7 is not so different from that for quenched structure although shifted slightly to higher frequency. Those density distributions depend seriously on the temperature as shown in Figure 8. The density of state at lower temperature looks like that of low density hexagonal ice (ice Ih), both of which have a gap between translational and rotational modes.

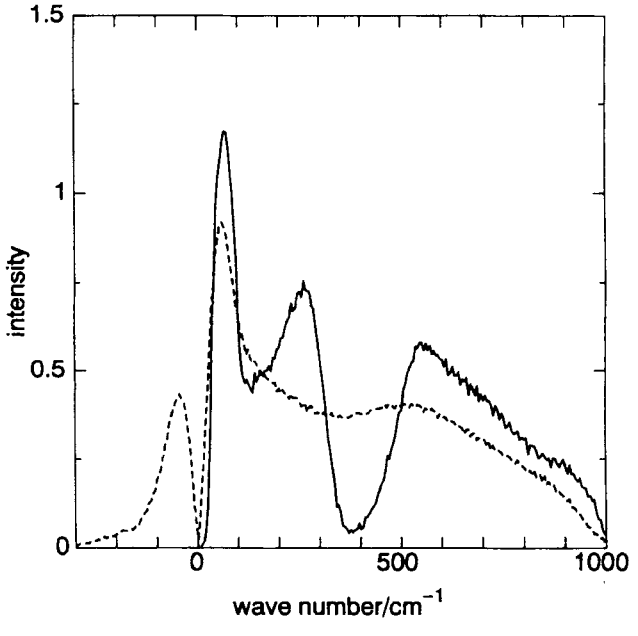

Figure 5 Density of state of intermolecular vibrational motions for quenched structure of water (solid line) and for instantaneous structure (dotted line) at 300 K.

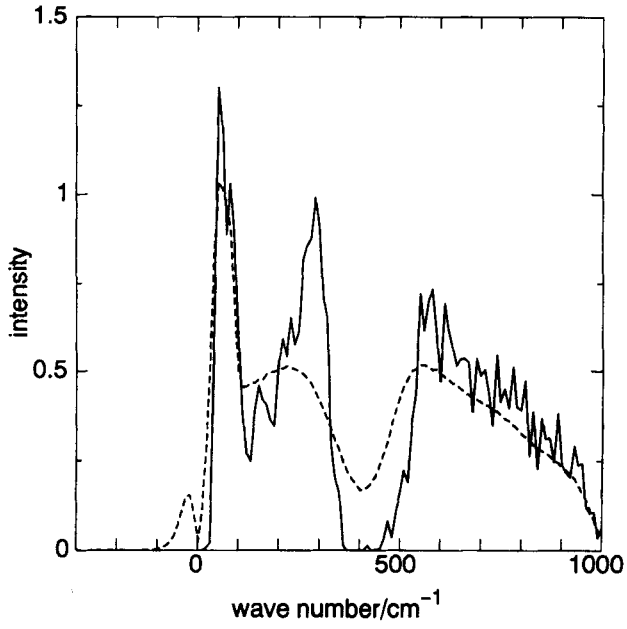

Figure 6 Density of state of intermolecular vibrational motions for quenched structure of water (solid line) and for instantaneous structure (dotted line) at 160 K.

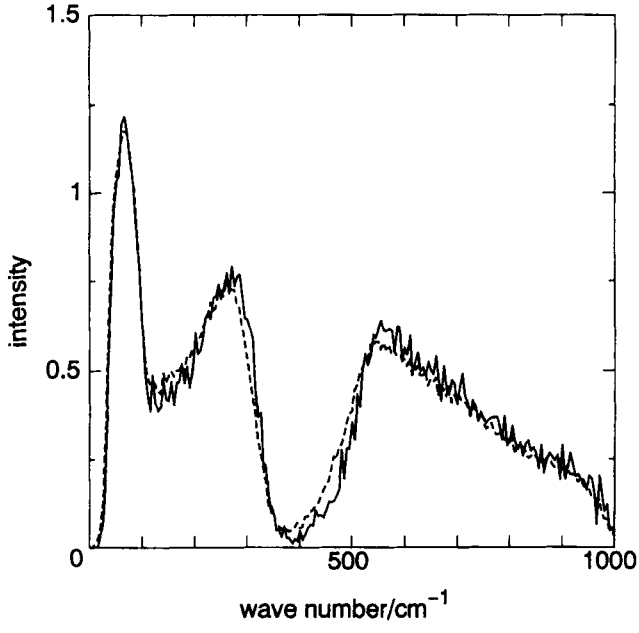

Figure 7 Density of state of intermolecular vibrational motions for quenched structure of water (dotted line) and for coarse-grained structure (solid line) at 300 K.

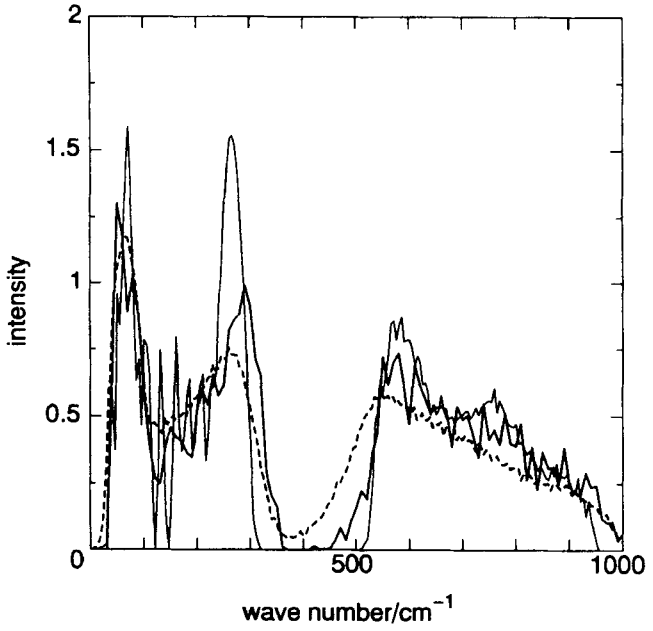

Figure 8 Density of state of intermolecular vibrational motions for quenched structures of water at 300 K (heavy dotted line) and at 160 K (heavy solid line) and for ice 1h (thin solid line).

4 CONCLUSION

Collective motions in liquid water are investigated by examining potential surfaces of an assembly of water molecules in its liquid state. It is found that coarse-graining of the quenched structures and low temperature dynamics provide information on their hierarchal structures. The distribution of the potential energy minimum structures in configuration space is examined in detail and is compared with those of methanol. Methanol has a character of fragile liquid as is manifested by the larger potential fluctuation in quenched structure and no transformation from fragile to strong liquid seems to take place. The potential surface of water along the quenched trajectory is irregular at higher temperature and the standard deviation in the minimum potential energy is large. On the other hand, the standard deviation is small at lower temperature and the potential surface seems to be rather regular. This suggests that water at lower temperature has a characteristics of strong liquid.

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