

Fluctuation of Local Order and Connectivity of Water Molecules in Two Phases of Supercooled Water

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We investigate the fluctuations of coordination numbers and the spatial correlations of imperfectly coordinated water molecules in two phases of supercooled water. It is found, although the average coordination numbers are 4 in local energy minimum structures of both phases, that the magnitude of the fluctuation differs significantly between two phases. Connectivity of water molecules whose first and second neighbors are also perfectly (four-) coordinated is examined. It is revealed that such locally ordered water molecules spread over the entire system in the low density liquid phase whereas those molecules form only small size clusters in the high density liquid water phase. [S0031-9007(97)04925-9]

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Water occupies a unique position among various liquids because of many anomalous properties such as the appearance of temperature of maximum density [1]. Above all, the divergence of heat capacity and other thermodynamic response functions on approaching the temperature 228 K in supercooled state is the most notable one [2,3]. Recently, the anomalies have been accounted for by existence of a second critical point from which a phase boundary of the low and high density liquid (LDL and HDL) phases appear [4,5] or by LDL-HDL phase transition [6,7]. LDL is a lower energy phase than HDL, which is similar to the fact that an ordered ice phase has a lower density (and also energy) than liquid water. Two amorphous ices have been indeed observed experimentally at high pressure [8,9]. Although it is still controversial where the critical point locates in phase diagram, we can understand in the broad sense the origin of the unique properties of water in terms of the critical behavior and/or the associated spinodal instability [10,11].

We have shown that various properties of TIP4P water [12] below the temperature 213 K at atmospheric pressure are significantly different from those above that temperature [6,7]. It may, however, not be generally accepted that there is a first order phase transition at atmospheric pressure among many computational studies. The location of the second critical point seems to depend seriously on intermolecular interaction, boundary condition, treatment of long range intermolecular interaction, simulation time, ensemble, and so on. In this Letter, we will not discuss the relation between the simulated and experimental pressures, from which the exact location of the second critical point is deduced, but will investigate structural difference between two phases in order to obtain an insight into the origin of the transition in network forming substances such as water, silica, silicon, etc. [13].

The most important issue at present is to address why two phases exist in one component liquid state and what is the most noticeable difference in structure between them. Structures of two liquid phases and their hydrogen bond

network patterns are, however, far from clear. Here, structural difference between two liquid states will be accounted for in terms of the fluctuation of local order and the network pattern among the ordered water molecules. The local order is well characterized by hydrogen bonds. The number of water molecules hydrogen bonded with four neighbors increases drastically upon the transition from the high to the low density liquid for any reasonable choice of hydrogen bond criterion [7]. The local order of LDL is much enhanced compared with HDL. However, the hydrogen bond number itself depends seriously on the criterion [7]. Therefore, the coordination number is more preferable rather than the hydrogen bond number in discussing the connectivity of the network structure since we have a more definite criterion to define it than the hydrogen bond; the coordination number can be defined quite reasonably by the number of other molecules (oxygen atoms) within the first minimum distance of the corresponding radial distribution function, $g(r)$. The running coordination number, $n(r)$, is given as

$$n(r) = \rho \int_0^r g(r') dr', \quad (1)$$

where r is the molecular separation and ρ stands for the number density.

The experimental coordination number at room temperature is 4.4 according to the above definition with a molecular separation r_m at which $g(r)$ takes the first minimum [1]. This value is not expected to change significantly upon temperature decrease: at most it approaches the limiting value 4 (in ice). Instead, a difference appears in its fluctuation and species-4 decreases with increasing temperature (species- j is a water molecule to which other j molecules are coordinated). We will examine a difference in coordination number fluctuation and its spatial correlation to show that the phase transition is associated with the percolation transition of a kind of locally ordered clusters [14].

Molecular dynamics simulations for 1728 TIP4P water molecules [12] are performed with a fixed pressure of 0.1 MPa at several temperatures using Nosé-Andersen's

constant temperature-pressure method [15,16]. Since a large gap in thermodynamic properties at atmospheric pressure has been found around 213 K, the temperatures, T cover the higher and lower states than that temperature, setting to 233 and 193 K together with the room temperature, 298 K. The simulation time ranges from 0.2 (298 K) to 5 ns (233 and 193 K). We examine the coordination number, its fluctuation, and the connectivity of species-4 from the present configurations. The minimum energy structures called quenched structures [17] are obtained, which provide information on fundamental structure without thermal excitation [18].

As plotted in Fig. 1(a), no significant difference is seen in running coordination number for structures generated by molecular dynamics simulations. The coordination numbers lie in the range from 4.1 (193 K) to 4.8 (298 K) at the corresponding inflection points (the minimum in the radial distribution function) due to a partial collapse of ice structure and a thermal excitation in water. Quenched structures are, however, preferable rather than structures generated by molecular dynamics simulation in calculating the coordination numbers because we are interested in purely structural properties. The coordination numbers at three temperatures are all reduced to approximately 4.0 as shown in Fig. 1(b). The local structure (within $r_m = 3 \text{ \AA}$) after removing thermal energy remains unchanged *on average* in liquid water.

This does not mean all the water molecules participate in icelike structure. The percentages of various species are given in Table I. The species-4 is the most dominant one in HDL at 298 and 233 K. In water, its population increases drastically upon transition from the high to the low density liquid, which is reconfirmation of what we found in the analysis of hydrogen bond number distributions [7]. Although the number of each species is sensitive to temperature, their mean values, approximately 4, at all three temperatures are rather insensitive.

A new quantity, fluctuation of the coordination number, is defined by

$$\Delta n(r) = \langle [N(r) - n(r)]^2 \rangle^{1/2}, \quad (2)$$

where $N(r)$ is the coordination number for a given molecule at a given instant and $\langle \dots \rangle$ stands for average taken over all generated configurations. The fluctuations of coordination number are shown in Fig. 2. The fluctuation in $\Delta n(r)$ becomes the smallest around the minimum of the radial distribution function. This fact justifies the choice of r_m to define a coordination number. To visualize how small the fluctuation is, we consider a body-centered cubic lattice model. The half of the sites are regularly occupied in cubic ice where the coordination number is 4 and its fluctuation is 0. If molecules are randomly distributed and half of the sites are occupied, its fluctuation is very large [$\Delta n(r_m) = 2^{1/2}$]. In water, its magnitude is 0.45 for HDL while 0.25 for LDL.

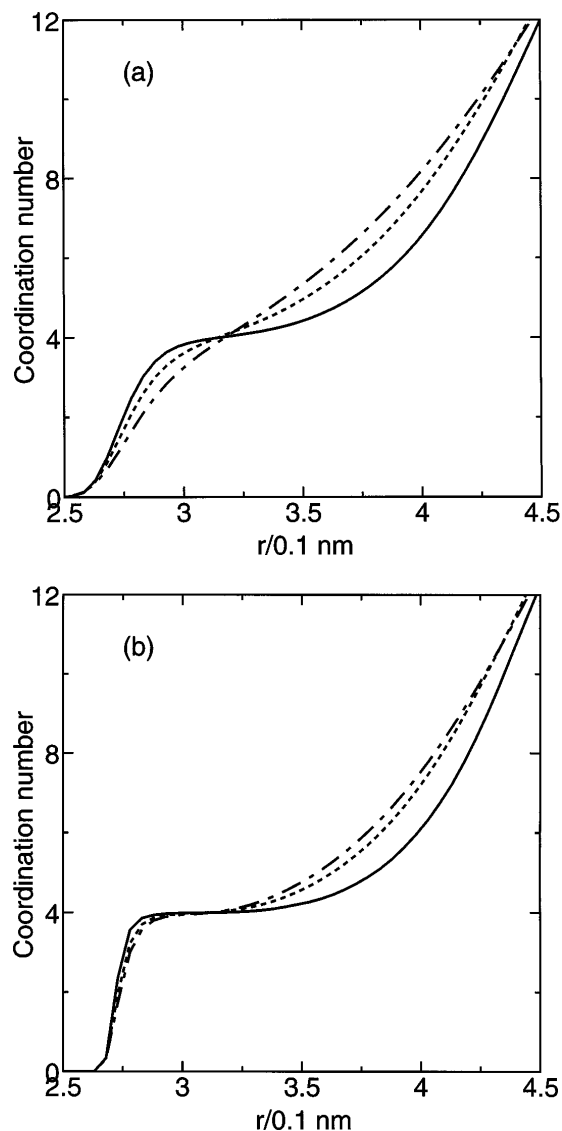


FIG. 1. Running coordination number as a function of distance from a central molecule. (a) Instantaneous (generated by molecular dynamics simulation) structure; (b) quenched structure. Solid line, water at 193 K (LDL); dotted line, water at 233 K (HDL); and dash-dotted line, water at 298 K (HDL).

Although species-5 has lower energy than species-4, its mobility (as well as that of species-3) is higher than that of species-4 [19]. Thus, species-3 and -5 can be regarded as defects. The number of defects (molecules other than species-4) are greatly reduced in real water at ambient temperature compared with a randomly occupied case and the transition gives rise to further reduction of defects. A question is raised as to how those defects are spatially correlated with each other. We define a probability distribution g_{ij} for a molecule next to a central one having j neighbor molecules on the condition that the central molecule has i neighbors. The probability is also given in Table I. Clearly, defects are correlated such that species-3 molecules repel each other

TABLE I. Coordination number distribution p_i (%) having i neighbors and probability distribution g_{ij} (%) for a molecule next to a central one having j neighbor molecules on the condition that the central molecule has i neighbors at temperature T (K) and 0.1 MPa. The cutoff length for coordination number is 3 Å.

$T \setminus i$	2	3	4	5	6
298	1	18	74	7	0
233	1	11	83	5	0
193	0	3	95	2	0

$i \setminus j$	3	4	5
$T = 298$			
3	10	75	14
4	14	77	8
5	22	73	4
$T = 233$			
3	4	80	15
4	7	86	7
5	15	82	3
$T = 193$			
3	1	87	11
4	2	96	2
5	11	89	0

(so do species-5 molecules) while a species-3 molecule attracts a species-5.

It has been recognized that water in ambient temperature is a transient gel that hydrogen bonds form an infinite size of cluster [14]. Even when we consider a site percolation of only species-4 water at room temperature, water is percolated as is clear from Table I. The site per-

colation threshold for those systems is as low as that of diamond structure, 0.4 (see below [20]), which should be compared with 0.74 for water. This suggests that a larger correlation unit of species-4 should be considered in order to distinguish LDL from HDL. Next, we impose a further condition; a central species-4 has four neighboring species-4. This procedure is repeated up to the third neighbors and ratios of the perfectly coordinated water molecules are given in Table II. We found a large difference between two liquid phases when a spatial correlation up to the second neighbors is taken into account. Since we are considering site percolation, the percolation threshold p_s is related empirically to the packing fraction, η as

$$p_s \eta \approx 0.16 \quad (3)$$

for three dimensional system [21]. The packing fraction is calculated by

$$\eta = \pi \rho r_m^3 / 6. \quad (4)$$

Hence, the threshold value p_s is approximately 0.34 (similar to the diamond structure), which implies that water at 193 K is percolated while water at 233 K or higher is not.

Water molecules whose first and second neighbors are all species-4 form various sizes of clusters, which are called hard core patch [14]. We obtain a hard core patch size distribution which is plotted in Fig. 3. It is evident that the largest hard core patch size is about 1000 and the patch spreads over the entire system at 193 K while the maximum size of hard core patch is limited to 100 at 233 K. This indicates that a correlation length of the hard core patch becomes infinite upon the transition from the high to the low density liquid. To examine whether there exists a special correlation of species-4, let us assume random distribution of species-4. The probability that the first neighbors are all species-4 is given by $(p_4)^4$. For the perfect first and second neighbors, it is $(p_4)^{16}$. (For the third neighbors, it is impossible to apply a simple enumeration because of formation of pentagonal and hexagonal rings, the latter of which is only a constituent of low pressure ice.) Those probabilities are given in parentheses. The observed ratio is only slightly larger than that of the random distribution. No special correlation seems to exist.

We may consider a further local order of species-4 and the corresponding percolation transition. However, this is

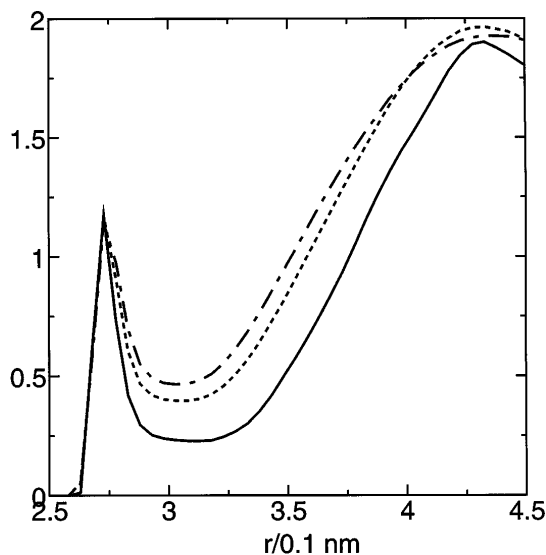


FIG. 2. Fluctuation of the running coordination number. Solid line, water at 193 K (LDL); dotted line, water at 233 K (HDL); and dash-dotted line, water at 298 K (HDL).

TABLE II. Probability (%) of water molecules which have only species-4 up to i th neighbors. The probability of random distribution of species-4 is given in parentheses.

$T \setminus i$	0	1	2	3
298	74	26 (30)	1 (1)	0
233	83	44 (47)	8 (5)	0
193	95	80 (81)	50 (44)	20

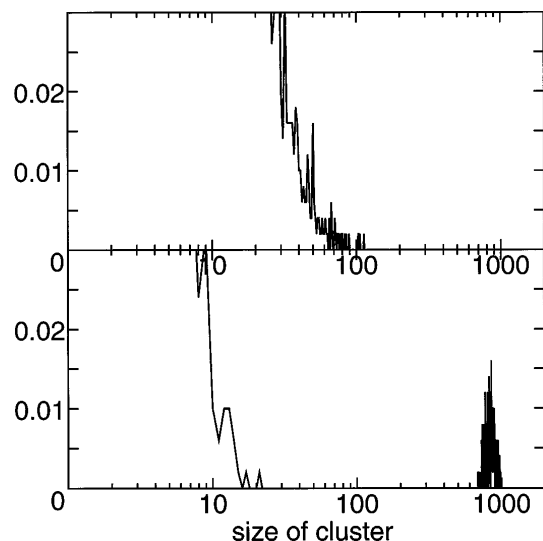


FIG. 3. Distribution of the cluster size composed of the water molecules having first and second neighbors of species-4; top, 233 K, bottom, 193 K.

unlikely to occur since a further local ordering necessarily gives rise to the correlation of ring species and thus leads probably to ice with some defects. The percolation of this higher order correlation (up to the third neighbors) is not observed in either the high or the low density liquid phase (even at 193 K, its population does not exceed the threshold value).

In summary, we find the following differences between two liquid phases. Liquid water has on average four neighbors in quenched structures. Both phases contain defect species-3 and -5. The population of each defect species differs between two phases. The like-species repels each other and the unlike species attracts one another. Those water molecules having first and second perfectly ordered (four-coordinated) neighbors form various sizes of clusters. The clusters are disconnected in high density phase whereas the largest cluster in low density phase is connected and spreads over the entire system. A further ordering, percolation of the perfectly coordinated clusters up to the third neighbors, may lead to mostly ring structures and seems to result in ice, whereby exceeding the limiting size of ice nucleus.

An appropriate order parameter to describe the phase equilibrium is the density difference between two liquid phases. In order to understand the phase behavior of supercooled water in terms of the pressure dependence of density, let us consider the simplest lattice model where some of the body-centered cubic lattice sites are occupied by water molecules while others are left unoccupied. If all the sites are occupied in this model, the coordination

number is 8. Even if the occupation ratio is less than $1/2$, the average coordination number of 4 is realized by a spatial fluctuation of various species- j analogous to the critical fluctuation. That is, it is conceivable that the density may change by changing magnitude of the fluctuation on the condition that a water molecule has four neighbor molecules on average. The occupation ratio of the lattice sites in high density liquid is expected to increase with increasing pressure (it cannot exceed $1/2$ in order for the average coordination number to be kept a constant value, 4), while the fluctuation is gradually suppressed. The degree of the spatial correlation for unlike defect pairs may depend heavily on pressure. This will be examined in detail in future work.

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- [1] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, London, 1969).
- [2] R.J. Speedy and C.A. Angell, *J. Chem. Phys.* **65**, 851 (1976).
- [3] C.A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Vol. 7, Chap. 1.
- [4] P.H. Poole, F. Sciortino, U. Essmann, and H.E. Stanley, *Nature (London)* **360**, 324 (1992).
- [5] P.H. Poole, F. Sciortino, U. Essmann, and H.E. Stanley, *Phys. Rev. E* **48**, 3799 (1993).
- [6] H. Tanaka, *Nature (London)* **380**, 328 (1996).
- [7] H. Tanaka, *J. Chem. Phys.* **105**, 5099 (1996).
- [8] O. Mishima, L.D. Colvert, and E. Whalley, *Nature (London)* **310**, 393 (1984).
- [9] O. Mishima, *J. Chem. Phys.* **100**, 5910 (1994).
- [10] R.J. Speedy, *J. Phys. Chem.* **96**, 2322 (1992).
- [11] F. Sciortino, P.H. Poole, U. Essmann, and H.E. Stanley, *Phys. Rev. E* **55**, 727 (1997).
- [12] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, and M.L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- [13] C.A. Angell, *Science* **267**, 1924 (1995).
- [14] H.E. Stanley and J. Teixeira, *J. Chem. Phys.* **73**, 3404 (1980).
- [15] S. Nosé, *Mol. Phys.* **52**, 255 (1984).
- [16] H.C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- [17] I. Ohmine and H. Tanaka, *Chem. Rev.* **93**, 2545 (1993).
- [18] F.H. Stillinger and T.A. Weber, *J. Phys. Chem.* **87**, 2833 (1983).
- [19] F. Sciortino, A. Geiger, and H.E. Stanley, *Nature (London)* **354**, 218 (1991).
- [20] D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, Philadelphia, 1985).
- [21] H. Scher and R. Zallen, *J. Chem. Phys.* **53**, 1421 (1970).