



16 June 1995

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 239 (1995) 349–353

Spatial structure in low-temperature amorphous phases of water

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Received 7 March 1995

Abstract

The spatial (local) structure in liquid water at ambient conditions has been recently determined in computer simulation and neutron diffraction studies using the spatial distribution functions between atoms. The spatial distribution functions of oxygen atoms are analyzed for the low-temperature amorphous phases of water obtained in MD simulations with the TIP4P potential. These structural data reveal the important role played by the nontetrahedral, interstitial coordination of H₂O molecules in phase transitions of low-temperature water.

1. Introduction

Recently, a direct approach to the study of liquid state structure has been put forward [1–4] which relies upon the spatial distribution function (SDF) between atoms, $g(r, \Omega)$. Traditionally, the microscopic structure in liquids has been characterized with the radial distribution function (RDF), $g(r)$, which is routinely available through X-ray/neutron diffraction experiments or from computer simulations [5]. Unfortunately, the RDF represents an average over the orientations of the central molecule and hence its ability to provide information on the spatial correlations in the liquid state is limited. Unlike the one-dimensional RDFs, the SDFs span both the radial and angular coordinates of the interatomic separation vector, thereby providing a complete picture of the local three-dimensional packing of molecules. In Refs. [1,3,4] the SDFs for oxygen and hydrogen atoms have been used to describe the local three-dimensional structure in liquid water under normal conditions.

In this Letter, we focus upon low-temperature water. We have recently performed molecular dynamics (MD) simulations of ice nucleation induced by a homogeneous electric field and have characterized the microscopic structure of the polar ice emerging from this crystallization of liquid water [6]. By changing the thermodynamic conditions in these applied-field simulations we have also succeeded in generating an amorphous ice whose molecular structure remained largely unexplored. Our goal here is to use spatial distribution functions to characterize the local structure in amorphous ices obtained in computer simulations. In the recent MD simulation studies of Poole et al. [7,8] they have suggested that low-temperature water exhibits a critical point above which the two metastable amorphous phases of solid water (usually referred to as low- and high-density amorphous ice, hereafter LDA and HDA) become indistinguishable; these states were previously shown to be separated by a line of first-order transition. Poole et al. [7,8] based their conclusions on studies of solid water samples obtained by a simple quench-

ing of liquid configurations. Here we investigate the spatial structure in these quenched liquid configurations and that of HDA and compare them with the local structure in a low-density amorphous ice obtained by applying an electric field to a supercooled liquid. Our observations are based upon molecular dynamics simulations with the TIP4P model for water [9]. Technical details regarding our simulation methodology can be found in Refs. [1,6,10].

2. Results

An initial sample of supercooled liquid water was prepared by taking a well-equilibrated configuration of TIP4P water at the density of 0.9 g/cm^3 at 298 K and slowly cooling it to a temperature of 250 K where it was equilibrated for a further 200 ps. A homogeneous static electric field of 0.5 V/\AA was then applied to this liquid sample. After 200 ps the temperature was decreased (within 20 ps) to 100 K and the electric field removed. Figs. 1a and 1b display, respectively, the RDF, $g(r)$, and the SDF, $g(r, \Omega)$, of oxygen atoms in the resulting amorphous solid. We recall [1,2] that $\Omega = (\theta, \phi)$ represents the angular coordinates of the separation vector where θ denotes the angle between the dipole axis of the central water molecule and the oxygen–oxygen separation vector and ϕ is the angle away from the plane of the molecule. O...O correlations essentially perpendicular to the plane of the central molecule, corresponding to $\phi \approx 90^\circ$, are plotted in Fig. 1b. We point out that the application of this electric field to a supercooled liquid with a slightly higher density ($0.94\text{--}0.96 \text{ g/cm}^3$) induces nucleation of cubic ice. This field-induced crystallization of TIP4P water has been examined elsewhere [6].

Fig. 1b clearly exhibits features consistent with local tetrahedral order, the peaks due to the first, the second and the third hydrogen(H)-bonded neighbors (marked, respectively, as 1, 2 and 3) being well resolved. The spatial structure beyond the third neighbor is less pronounced, which is also reflected in the rather featureless tail of the RDF beyond about 5 \AA (see Fig. 1a). Careful visual inspection of configurations of the amorphous solid whose average structure is depicted in Fig. 1 reveals a packing structure consisting essentially of stacked molecular

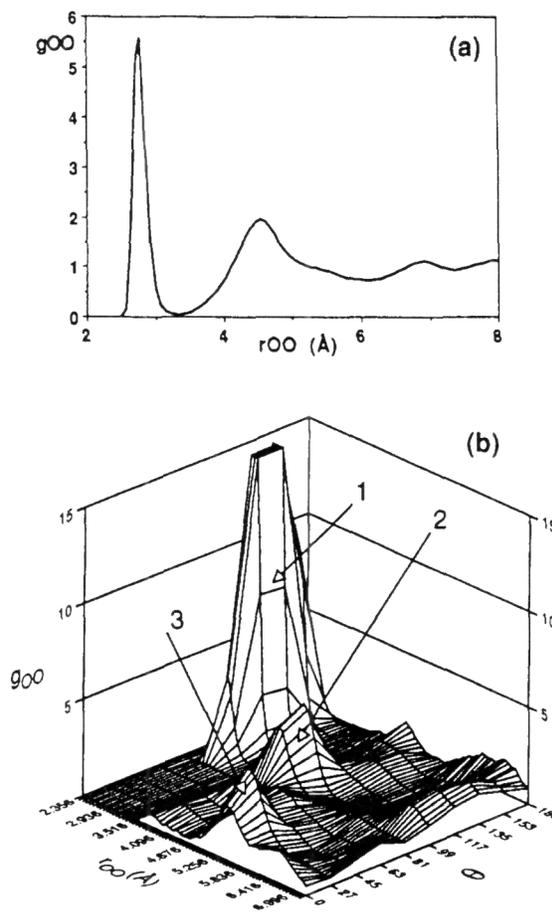


Fig. 1. The structure of low-density amorphous ice at 100 K formed from supercooled liquid TIP4P water under a field of 0.5 V/\AA . (a) The radial distribution function of oxygen atoms and (b) the spatial distribution function of oxygen atoms for $\phi \approx 90^\circ$. θ denotes the angle between the dipole axis of the central water molecule and the oxygen–oxygen separation vector. 1, 2 and 3 identify, respectively, the first, the second and the third tetrahedrally bonded neighbors of the continuous H-bond network. In (b) the nearest-neighbor peak (labeled 1) was truncated, its actual height being about 41.

layers with numerous planar defects and long-range disorder within the layers. The SDF in Fig. 1b does not exhibit features due to interstitial, nontetrahedral coordination peculiar to the local structure in liquid water [1,3] or high-density amorphous ice [11,12]. Hence, we identify this amorphous solid as low-density amorphous ice. In the SDF for liquid water the interstitial, nontetrahedral coordination appears as a local maximum at approximately $3.3\text{--}3.9 \text{ \AA}$ (see

Fig. 3 in Ref. [1]); in the orientationally averaged RDF for liquid water the interstitial coordination accounts for the elevated pair-density in the region of its first minimum at about 3.5 Å. We conclude that the application of the electric field helps to eliminate the interstitial coordination in low-temperature water, thus inducing its transformation, depending upon the density of the system, into amorphous or crystalline ice.

To gain a more detailed microscopic understanding of the structural transformations of low-temperature water we have analyzed the spatial structure in the high-density amorphous ice obtained by an isothermal compression of our field-induced low-density amorphous ice. An LDA–HDA transformation was previously observed in MD simulations by Tse and Klein [11] and Poole et al. [7,8]. In the present MD study we essentially follow the methodology described in Refs. [7,8] in compressing our water samples. The RDFs of oxygen atoms for our high-density amorphous ice at densities of 1.2 and 1.3 g/cm³ are displayed in Fig. 2a. These RDFs closely resemble the RDFs obtained by Tse and Klein [11], who described them as ‘featureless’ (beyond the first peak) with ‘no evidence of coordination shells’. However, an inspection of the SDF in Fig. 2b for this high-density amorphous ice reveals that the local tetrahedral hydrogen-bond coordination in HDA extends beyond the nearest neighbors. Our results consistently indicate that the peak due to second H-bonded neighbors (peak 2 in Fig. 2b) persists in the SDF for amorphous solid water over a wide range of densities. It is also evident from Fig. 2b that the interstitial coordination (marked as A), which was absent in our LDA, reappears in HDA at separations of about 3.2–3.9 Å. Clearly, emergence of this broad interstitial peak, which is distinct from the peaks due to H-bonded neighbors in the angle-dependent SDF in Fig. 2b, makes it very difficult to distinguish any structural features beyond the first maximum in the orientationally averaged RDFs shown in Fig. 2a.

We now focus upon on the local structure in amorphous phases of solid water obtained by a simple quenching (no applied field) of liquid water configurations. These amorphous phases have been extensively examined in MD simulations by Poole et al. [7,8] in an attempt to determine the spinodal

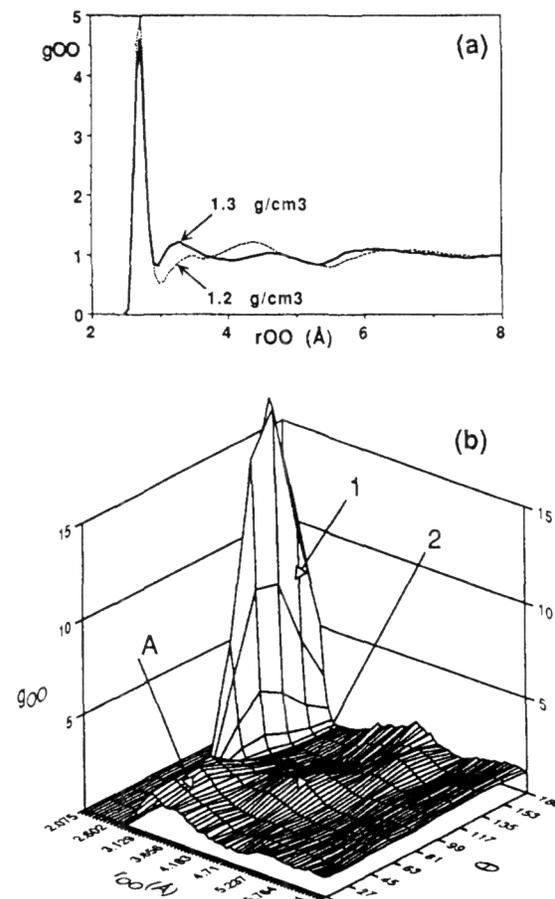


Fig. 2. The structure of high-density amorphous ice at 100 K obtained by isothermal compression of low-density amorphous ice. (a) The radial distribution function of oxygen atoms at the densities of (-----) 1.2 g/cm³ and (—) 1.3 g/cm³ and (b) the spatial distribution function of oxygen atoms for $\phi \approx 90^\circ$ at the density of 1.2 g/cm³. The angle θ and features 1 and 2 are defined as in Fig. 1, while A represents additional nontetrahedral coordination.

behavior of low-temperature water. It has been argued that deeply supercooled water does not exhibit a reentrant spinodal as previously thought (Angel and Speedy [13]); rather a new critical point for low-temperature water was suggested by these simulations.

Following the prescriptions of Poole et al. [8] we have prepared a sample of solid TIP4P water at a density of 0.9 g/cm³ at 100 K by cooling a liquid water configuration, originally at 250 K, at a rate of 1.5 deg/ps. The resulting structure is displayed in

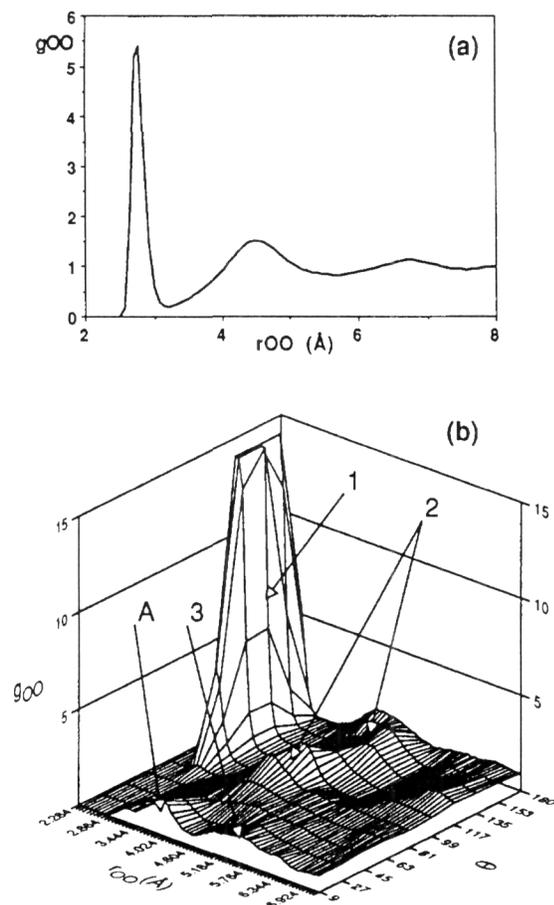


Fig. 3. The structure of amorphous solid water at 100 K obtained by quenching of liquid TIP4P water. (a) The radial distribution function of oxygen atoms and (b) the spatial distribution function of oxygen atoms for $\phi \approx 90^\circ$. The angle θ and features 1, 2, 3 and A are defined as in Figs. 1 and 2. In (b) the nearest-neighbor peak (labeled 1) was truncated, its actual height being about 32.

Fig. 3. We find a striking similarity between the spatial structure in this amorphous solid at 100 K obtained by quenching (see Fig. 3b) and the spatial structure in the original supercooled liquid at 250 K (see Fig. 2a in Ref. [6]). In both cases the interstitial coordination persists in the local structure. In addition, the second and the third H-bonded neighbors do not form distinct peaks in the spatial distribution functions as can be seen in Fig. 3b. We recall that the amorphous ice emerging from supercooled liquid water under an applied electric field does not exhibit the nontetrahedral, interstitial coordination, and both

the second and the third H-bonded neighbors appear as well-defined maxima in the SDF for this amorphous solid (see Fig. 1b).

3. Concluding remarks

Many experimental investigations [12,14–16] have consistently indicated that low-density amorphous ice (independent of the method of its preparation) does not feature interstitially coordinated water molecules. In this work we have attempted to demonstrate that by applying an electric field to a supercooled water sample one can prepare in a computer simulation an amorphous material without interstitial neighbors in its local structure. In contrast, configurations of solid water obtained by simple quenching of a liquid water sample were found to contain these nontetrahedrally coordinated molecules. Given these observations, the question as to whether the critical behavior of low-temperature water found in recent MD simulations [7,8] is a property of real water or a property of specific computer models has yet to be fully addressed.

Acknowledgement

We are grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada. We wish to thank Dr. P. Poole for many stimulating discussions.

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