Wide angle X-ray scattering measurements of supercritical water using synchrotron radiation

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Abstract. Wide angle X-ray scattering measurements of sub- and supercritical water have been carried out using synchrotron radiation at SPring-8 in Japan, to study density dependence of the local structure. X-ray diffraction spectra were measured from 300 K to 1023 K at 40 MPa, and up to 1100 K at 100 MPa, corresponding to the density ρ from 1 g cm⁻³ to 0.10 g cm⁻³. The nearest neighbour distance and the nearest neighbour coordination number depending on the density indicate that water is uniformly expanded from 1 g cm⁻³ to 0.6 g cm⁻³ with destruction of hydrogen bonding. With further volume expansion, the coordination number becomes approximately one at 0.15 g cm⁻³ while the nearest neighbour distance is approximately 3.3 Å. This experimental fact may be a first direct observation of dimeric molecules in the supercritical water.

1. Introduction

While water is a common liquid on the earth, it exhibits unique properties due to hydrogen bonds (HB). To observe HB between water molecules, neutron scattering is a powerful probe though hydrogen atoms should be replaced with deuterium ones. It has been debated if HB in water is preserved or not, in the supercritical region at high temperature and high pressure (the critical constants of water are T_C=647 K, p_C=22.05 MPa and ρ_C=0.32 g cm⁻³) [1, 2]. Recent studies on the supercritical water (SCW) indicate that HB are preserved at high temperature and high pressure while the number of HB decreases with decreasing density ρ as estimated from the chemical shift of nuclear magnetic resonance [3, 4].

It is interesting to study how static and dynamic structures of SCW change with ρ, especially correlation between breaking of HB and the critical density fluctuation. Small angle X-ray scattering (SAXS) measurements using synchrotron radiation were carried out and Ornstein-Zernike behaviour of SAXS spectra was observed near the critical density [5]. As is well known, the dynamics slows down near the critical point. Results of inelastic X-ray scattering (IXS) for SCW [6] show a narrow quasielastic peak suggesting the critical slowing down at ρ_C. However macroscopic dielectric relaxation becomes fast at approximately 0.5 g cm⁻³ near ρ_C [7] and the relaxation time increases with further decreasing ρ. A recent IXS study [9] reports that slow structural relaxation at the ambient condition becomes fast near ρ_C. Meanwhile the previous IXS study [6] reports that fast sound in normal water [8] almost disappears near ρ = 0.8 g cm⁻³.

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Figure 1. (color online) The structure factor \( S(Q) \) (a) and the pair distribution function \( g(r) \) (b) of supercritical water obtained from wide angle X-ray scattering. Solid and broken lines denote the results at 40 MPa and 100 MPa, respectively. Each spectrum is shifted by 1 for clarity. (c) \( g(r) \) (solid line) at 0.3 g cm\(^{-3}\) at 40 MPa and \( g_{OO}(r) \) (open circles) at 0.32 g cm\(^{-3}\) obtained from FPMD [16]. The exact thermodynamic conditions in the experiments are indicated in Fig.2.

but the dynamical sound again becomes approximately twice as fast as the adiabatic sound as \( \rho \) decreases to \( \rho_C \). These curious results motivated us to study short and long range structure of SCW in wide \( \rho \) region by X-ray scattering using synchrotron radiation despite that X-ray scattering cannot observe HB directly. In this article, we report \( \rho \) dependence of the nearest neighbour distance \( r_1 \) and the first nearest coordination number \( N_1 \) of SCW and try to relate them to several properties of SCW, on the basis of exact information on O-O correlation provided by X-ray scattering.

2. Experimental procedure

Wide angle X-ray scattering measurements were carried out at superphoton ring 8-GeV (SPring-8) in Japan. The synchrotron accelerator was operated at a constant current mode of 100 meV during the experiments. The measurements were conducted at the white beam X-ray diffraction beamline (BL28B2) using the energy-dispersive mode. White X-rays were incident on the sample and the scattered X-rays were detected with a pure Ge solid state detector. These beams were collimated with double slits.

The same high-pressure gas apparatus to perform structural studies on supercritical metallic fluids [10, 11, 12] was used in the present studies. The apparatus permits X-ray scattering experiments up to 196 MPa using high-purity grade He gas as a pressure transmitting medium.

High purity water was contained in a sapphire cell and wide angle X-ray diffraction spectra were measured from 300 K to 1023 K at 40 MPa, and up to 1100 K at 100 MPa, corresponding to the density \( \rho \) from 1 g cm\(^{-3}\) to 0.1 g cm\(^{-3}\). The sample thickness of 3 mm, which is much smaller than the optical depth of the X-ray for low density SCW, was chosen to achieve good temperature homogeneity of the sample. After the measurements of the sample, background was measured at the same set-up using the empty cell obtained from evacuating the high pressure vessel to evaporate the water in the cell. The procedure to deduce the structure factor \( S(Q) \) from the observed spectra are described in the literature [10].
3. Results and Discussion

Figure 1(a) shows $S(Q)$ of SCW at 40 MPa and 100 MPa. $S(Q)$ at the ambient condition exhibits oscillations up to 12 Å$^{-1}$ and the oscillations are damping with decreasing $\rho$. The profile of $S(Q)$ at 100 MPa exhibits noisy oscillations because the subtraction of the empty cell background did not work well compared to the data at 40 MPa. Overall consistency between 40 MPa and 100 MPa is reasonably good for $S(Q)$ at $\rho > 0.4$ g cm$^{-3}$, while at $\rho \leq 0.4$ g cm$^{-3}$ the large second peak at 100 MPa must be affected by a Laue peak from the sapphire cell. The pair distribution function $g(r)$ obtained from Fourier transform of $S(Q)$ is shown in Fig.1(b). Because X-rays are strongly scattered from oxygen atoms, the present $g(r)$ mainly represents the O-O correlations. The second peak at approximately 4.5 Å in $g(r)$ at 1.0 g cm$^{-3}$, which is considered as an evidence of a HB network, disappears with volume expansion as previously reported [13].

We define the first peak position of $g(r)$, as $r_1$. Figure 2 shows $\rho$ dependence of $N_1$ and $r_1$ together with X-ray scattering results previously reported by Yamanaka et al. [13] and Gorbaty and Kalinichev [14]. $N_1$ of the present data was obtained from twice that integrating the radial distribution function $4\pi m_0 r^2 g(r)$ in the range from the minimum distance to $r_1$, where $n_0$ denotes the number density. The errors of $\pm 0.05$ Å and $\pm 0.3$ are estimated for $r_1$ and $N_1$, respectively, from the results at $\rho \geq 0.3$ g cm$^{-3}$. At $\rho < 0.3$ g cm$^{-3}$, scattered plots of the symbols indicate the errors of $r_1$ and $N_1$ much larger. As shown in the figure, $r_1$ at 40 MPa is approximately 2.9 Å at the ambient condition. With decreasing $\rho$ to 0.6 g cm$^{-3}$, $r_1$ increases to 3.0 Å and remains to be approximately constant to 0.4 g cm$^{-3}$. The $\rho$ dependence of $r_1$ is consistent with the previous results [13, 14] while the results of Yamanaka et al. are apparently shorter than the present $r_1$ because we plot shorter distance of their two Gaussian peaks located at approximately 2.9 Å and 3.5 Å which were used to reproduce $g(r)$ that they obtained.

The present $r_1$ at 100 MPa reaches 3.0 Å from 2.9 Å at $\rho$ larger than the one at 40 MPa. This result hints that the increase of $r_1$ from 2.9 Å to 3.0 Å is caused by thermal effects. $N_1$ gradually decreases from approximately 4 at 1 g cm$^{-3}$ with decreasing $\rho$. It is noteworthy that in the $\rho$ region where $r_1$ increases from 2.9 to 3 Å, $N_1$ is approximately constant. Meanwhile the number of HB in the corresponding $\rho$ range decreases with decreasing $\rho$ as indicated by broken line [3, 4] in Fig.2. The coordination number of the Gaussian peak located at 2.9 Å reported [13] looks consistent with the number of HB. These evidences suggest a uniform expansion of high temperature water at $1 \geq \rho \geq 0.6$ g cm$^{-3}$ due to destabilization of a HB network. The reason why fast sound in normal water almost disappears near $\rho = 0.8$ g cm$^{-3}$ must be related to the disruption of a HB network as discussed in [6].

With further decreasing $\rho$, $r_1$ increases again and $r_1$ and $N_1$, respectively, become approximately 3.3 Å and 1 at 0.15 g cm$^{-3}$ at 40 MPa as seen in Fig.2. These results may be a first direct observation of a dimeric water molecule in the supercritical region at $\rho$ less than $\rho_C$. The long range fluctuation must not contribute largely to the short range structure because from SAXS spectra at 40 MPa we obtain $S(0) = 4$ and the correlation length $\xi = 6$ Å near $\rho_C$ using the Ornstein-Zernike equation [15], which are much smaller than the ones reported as the critical opalescence [5].

Finally we compare the present $g(r)$ with the O-O partial pair distribution function $g_{OO}(r)$ obtained from a first-principles molecular dynamics simulation (FPMD) by Boero et al. [16] as shown in Fig. 1(c). Their results show that SCW is constituted from monomers, dimers and trimers in a gaseous state and $g_{OO}(r)$ actually shows a broad maximum. However the present $g(r)$ exhibits a distinct first maximum and $N_1$ is approximately two near $\rho_C$. These experimental results suggest a chain-like HB network near $\rho_C$ in real SCW. We speculate that such HB network in a low density SCW is strongly correlated with the dynamical sound approximately twice as fast as the adiabatic sound near $\rho_C$. 


**Figure 2.** (color online) The coordination number $N_1$ and the nearest neighbour distance $r_1$ deduced from $g(r)$. The exact thermodynamic conditions at which $g(r)$ is obtained are listed in the right table. Closed circles and open triangles denote the present results.

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