

Voids in the H-bonded network of water and their manifestation in the structure factor

David R. Barker, Mark Wilson, and Paul A. Madden

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

Nikolai N. Medvedev

Russian Academy of Science, Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

Alfons Geiger

University of Dortmund, D-44221 Dortmund, Germany

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The main peak of the oxygen-oxygen structure factor $S_{OO}(Q)$ of liquid water shows an unusual doublet structure. The low- Q feature of the doublet shifts appreciably with pressure, between limits which correspond to the position of the first peak in the low- and high-density forms of amorphous ice. This pressure dependence has been cited as evidence of polyamorphism in water. It is shown that this feature is analogous to the ‘‘prepeak,’’ or ‘‘first-sharp-diffraction peak’’ which is well known in network-forming ionic liquids, like SiO_2 , and that its position is determined by the nearest-neighbor separation of *voids* in the spatial distribution of oxygen atoms.

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There has been much interest of late in the suggestion that water may exhibit polyamorphism, and that there exists a second critical temperature associated with the separation of water into two distinct amorphous phases [1–5]. The location of the critical point has been estimated by a number of means to be in the vicinity of $T_c \sim 220$ K and $P_c \sim 500$ bar, which is in the deeply supercooled region where equilibration of the fluid is not possible. Nevertheless, a number of observable phenomena within the equilibrated liquid (in experiment and computer simulation) indicate the presence of the critical point. Furthermore, thermodynamic measurements on the high- and low-density amorphous phases of water (HDA and LDA, respectively) are consistent with a line of first-order transitions separating these two phases, and terminating at the critical point [3]. Angell and co-workers [6–8] stressed that polyamorphism should be observed in other tetrahedrally coordinated fluids besides water, such as SiO_2 and GeO_2 .

The most direct evidence pertaining to the microstructure of the two distinct liquid phases comes from neutron and x-ray diffraction experiments on liquid water at a range of pressures and temperatures undertaken by Bellissent-Funel and co-workers [9,10], Okhulkov, Demianets, and Gorbaty [11] and Bizid *et al.* [12], respectively. Bellissent-Funel and co-workers [4,5] discussed the neutron data in light of the postulated polyamorphism. They showed that for pressures below P_c the position of the principal peak of the molecular structure factor (which has a mixed inter and intramolecular character) shifts gradually toward lower Q , and extrapolates at low temperatures to the position of the first diffraction peak observed in the low density (LDA) form of amorphous water ($\sim 1.69 \text{ \AA}^{-1}$) [10]. At pressures well above P_c , the position of the first peak is relatively temperature independent, and extrapolates toward that of the structure factor of HDA ice. The implication is that the micro-structure of liquid water for pressures below P_c resembles that of the LDA form, and for pressures above P_c that of the HDA.

The x-ray diffraction data also appear compatible with this viewpoint [11]. Since the x-ray scattering is dominated by oxygen atom scattering, the x-ray structure factor closely resembles the (purely intermolecular) oxygen-oxygen partial structure factor [$S_{OO}(Q)$], and is more simply interpreted than the neutron data. In water under ambient conditions, $S_{OO}(Q)$ shows an unusual double peak structure (see Fig. 2) in the vicinity of the normal principal peak ($\sim 2 \text{ \AA}^{-1}$). The x-ray structure factors of LDA and HDA also show doublet structures [12], though with different separations. The high- Q peak of the doublet appears at roughly the same position ($\sim 3 \text{ \AA}^{-1}$) in the liquid at all state-points and in the LDA and HDA amorphous states. However, as the pressure is raised in the liquid the intensity of the low- Q peak increases, and its maximum shifts to higher Q , toward the position of the first peak in HDA. In LDA ice, the low- Q peak appears at $\sim 1.69 \text{ \AA}^{-1}$. The low- Q peak of the x-ray structure factor [and of $S_{OO}(Q)$] therefore parallels the behavior of neutron scattering.

It has been suggested that the low- Q peak of the doublet in the x-ray structure factor of water should be regarded as a ‘‘prepeak’’ or ‘‘first-sharp diffraction peak’’ [13], analogous to the low- Q peaks which appear in network-forming ionic liquids, like ZnCl_2 or SiO_2 . It appears at a considerably lower Q than would be expected from the nearest O—O separation (R_{OO}); in simple liquids, the principal peak of the structure factor is found close to $2\pi/R_{OO}$. Furthermore, unlike R_{OO} , its position is sensitive to temperature and pressure. Since the low- Q peak is not simply related to any particular feature of the real-space partial *pair* distribution functions, its temperature and pressure dependence are not readily interpreted as changes in the real-space structure. Elliott and co-workers [14] argued that the most profitable way to think about the origin of the length scale associated with the position of a prepeak is as an *intervoid* correlation length. They already showed that the position of the low- Q peak in the HDA form can be understood as the void-void separation

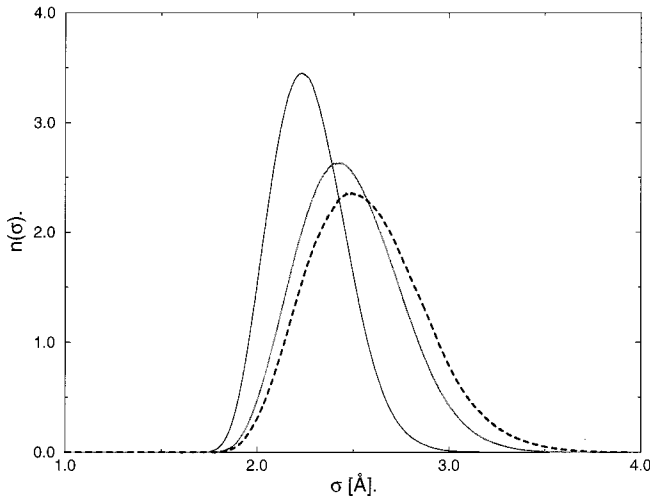


FIG. 1. Circumsphere radii distribution for the SPC-E H₂O model at 300 K and densities of 0.94 (dashed line, LDL), 1.00 (light, AL) and 1.17 g cm⁻³ (solid line, HDL).

in a continuous random network model of a tetrahedral glass [15]. A suitable way to define the position of voids which can be applied to the liquid phase is to associate them with the positions of the Delaunay simplices (DS's) obtained from a Voronoi analysis [16,17] of an instantaneous configuration in a computer simulation. In a topologically disordered structure the vertices (DS's) of the Voronoi polyhedra define the center of a group of four atoms. We have shown how such an analysis can be applied to understand the origin of the prepeak observed in liquid ZnCl₂ [18] and related tetrahedrally coordinated ionic liquids [19].

The purpose of the present paper is to show that the void-void correlations are a useful way to understand the prepeak position in $S_{OO}(Q)$ in the liquid and amorphous phases of water. We hope, thereby, to substantiate the link between the origin of the prepeak in water and in the tetrahedrally-coordinated ionic liquids, like SiO₂, and also to suggest it as an underlying signature of polyamorphism in both types of liquid.

The assignment of voids in the molecular environment is based upon a Voronoi analysis [16,17]. In the present work the analysis is performed on the oxygen atom positions only. In an idealized water structure, each oxygen is connected to four others by "bonds" occupied by H atoms. In the tetrahedrally coordinated ionic liquids (SiO₂), the cation (Si⁴⁺) is analogously surrounded by four others with the "bond" occupied by oxide anions.

Such an analysis has been carried out on the atomic positions found in simulations of liquid water using various in-

TABLE I. Circumsphere distributions and FWHM's.

T (K)	σ_{\max} (Å)			FWHM		
	HDI	AL	LDL	HDL	AL	LDI
190	2.25	2.47	2.62	0.47	0.62	0.70
240	2.23	2.45	2.55	0.48	0.61	0.70
290	2.24	2.42	2.49	0.46	0.64	0.74

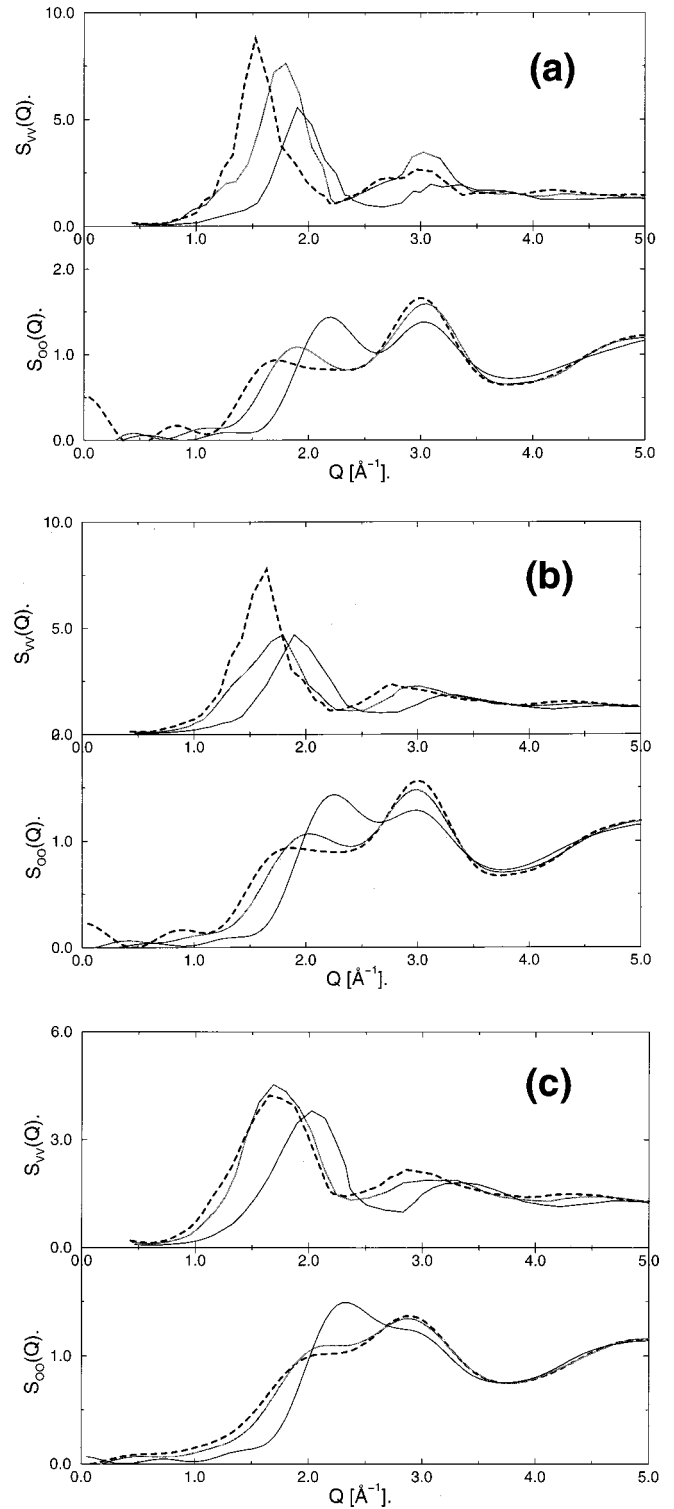


FIG. 2. O-O (lower panel) and void-void (upper) structure factors for the three densities (dashed line 0.94 g cm⁻³; light, 1.00 g cm⁻³; solid line, 1.17 g cm⁻³), and three temperatures studied: (a) 190 K, (b) 240 K, and (c) 300 K.

teraction models-SPC-E¹ [20], Watanabe-Klein [21], TIP4P² [22], and Rahman-Stillinger [23]—with Ewald methods used

¹Extended simple point charge model.

²Transferable intermolecular with four points.

to treat the long-ranged interactions. Although there are differences in detail of the liquid structure obtained with these models, the properties of the voids in relation to S_{OO} is very similar in all of them, and we will only describe results obtained with the SPC-E model below. The calculations were performed at temperatures of 300, 240, and 190 K, and at densities of 0.94 low-density liquid (LDL), 1.17 high-density liquid (HDL), and 1.0 amorphous liquid (AL) g cm^{-3} , which correspond to the densities of the LDA and HDA forms and of light water under ambient conditions, respectively [4]. 256 molecules were included in the simulation cell. The initial coordinates for each run were taken from a previous run at a higher temperature. As well as the temperatures for which data are presented, runs were also done at intermediate temperatures. Run lengths ranged from 20 ps at the highest temperature to 0.5 ns at the lowest. Even such long runs are insufficient to fully equilibrate the liquid at the lowest temperature.

About each DS a circumsphere can be constructed which passes through the four surrounding atoms such that no other atom center lies within. The distribution of circumsphere radii is, therefore, a measure of the empty (void) space in the system, and so yields information not readily accessible from a consideration of the atom positions alone. Figure 1 shows the distribution of circumsphere radii for LDL, ambient density, and HDL water at 300 K. The differences between the three systems are clear. The lowest density (LDL) form considered here has both the broadest distribution [the full width at half maximum (FWHM) is 0.70 Å] and largest maximum position (2.62 Å) reflecting the more open nature of the hydrogen-bonding network with respect to both the AL and HDL densities. The characteristics of these distributions for different temperatures are given in Table I. As the temperature is raised both the position and FWHM of the circumsphere distribution converge for the LDD and AL systems, while the HDL form remains distinct.

The relative positions of the voids may be characterized by calculating a void-void structure factor [18,19]

$$S_{VV}(Q) = \left\langle \frac{1}{N_V} \sum_{i,j=1}^{N_V} \exp(i\mathbf{Q} \cdot \mathbf{R}^{ij}) \right\rangle, \quad (0.1)$$

where N_V is the total number of voids identified in a given configuration, with \mathbf{R}^{ij} the vector joining the centres of a pair of voids, and the average is over configurations. Figure 2

shows S_{VV} along with the corresponding O—O structure factors for the three densities at three temperatures. The evolution of the simulated S_{OO} with density and temperature parallels that seen experimentally. The position of the high- Q component of the doublet is insensitive to temperature and pressure, and its position is in good agreement with the corresponding x-ray peak in water and the HDA and LDA forms. The position of the low- Q component is, on the other hand, very sensitive to density. At the lowest temperature, its position in the LDL and HDL simulations is very close to where it is observed in the LDA and HDA forms, respectively. In the HDL simulations, the position (and amplitude) of the low- Q component is insensitive to temperature, whereas in the LDL and AL simulations its position shifts progressively toward lower Q as the temperature is lowered.

Comparison with the upper panels of the figures shows that the position of the *principal* peak of S_{VV} corresponds quite closely with that of the low- Q component of S_{OO} at all temperatures and densities. In each case, it lies slightly to low Q of the S_{OO} feature. This situation is similar to that found in SiO_2 [19], but not ZnCl_2 [18], where the prepeak and the principal peak of S_{VV} are at very similar positions. This finding strongly suggests that the length scale associated with the low- Q feature in S_{OO} may be identified as an intervoid separation. Although the density dependence of these lengths parallel each other, as has been pointed out, the intensities of the features of S_{OO} and S_{VV} do not. There are several factors which may contribute to this. The voids affect S_{OO} through their influence on the spatial distribution of oxygen atoms; consequently, there is some effective “form factor” for the distribution of atoms around the voids which will influence the relationship between S_{OO} and S_{VV} . Second, there is not a one-to-one relationship between voids (the Delauney simplices) and physical “cavities” in the spatial arrangement of oxygen atoms. A given cavity may contain several voids (depending on cavity size), and this may affect the shape of S_{VV} relative to what would be expected for an atomic fluid.

In summary, we have confirmed the close relationship between the low- Q component of major peak in $S_{OO}(Q)$ in water and the prepeak observed in tetrahedral-network ionic fluids, like SiO_2 and ZnCl_2 . The position of these features reflects an intervoid correlation length arising from the detailed three-dimensional arrangement of the atomic network.

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