On the Structure Factor for Water at Small Wavenumbers

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Z. Naturforsch. **50,** 18–20 (1995); received November 4, 1994

Dedicated to Professor H. Ohtaki on the occasion of his 60th birthday

The possibility of the existence of a pre-preak in the structure factor of water at 0.6 $Å^{-1}$ is discussed on the basis of the combination of computer simulation and integral equation theory techniques. It indicates spatial correlations in water at distances of the order of 10 Å.

1. Introduction

In experimental as well as in theoretical investigations the structure of liquids is usually described by radial distribution functions (RDF) and structure factors which are uniquely related by Fourier transformations (FT). The structure factors can be measured in diffraction experiments or can be calculated from simulations directly as well as through FT of the RDFs. The experimental RDFs are an indirect measure of the structure obtained from FT only but they are more convenient for the interpretation of liquid structures.

Presently the investigation of liquid structures by diffraction studies concentrates on medium and long distances equivalent to structure factors in the wavenumber region $k < 1.5$ $Å^{-1}$. From numerous neutron- and X-ray diffraction studies of oxide glasses, molten salts with divalent and trivalent metal ions and intermetallic liquid alloys a maximum in this wavenumber region (a so-called pre-peak or first sharp diffraction peak) has been reported. General features of these liquids are three-dimensional bondings which cause stable local coordination. For a detailed discussion the reader is referred to a review paper by Tosi [1]. In water there also exists a preference for local tetrahedral coordination due to hydrogen bonding, but in diffraction studies of pure water such a pre-peak has not been seen so far. In diffraction studies of aqueous electrolyte solutions again a pre-peak has been found, which has been attributed to ion-ion interactions solely (see e.g. [2] and further citations therein).

Because of the limited size of the basic periodic cube in computer simulations of water spatial correlations beyond about 10 Å cannot be seen, and consequently no pre-peak has been found. We recently reported an approach based on the combination of computer simulation and integral equation theory techniques to extend the simulated RDFs to larger distances [3]. This approach has been tested for thermodynamical and static dielectric properties [4]. In this report we used the results of this approach to discuss the link between the shape of the structure factor and the local molecular order in water modelled by the BJH potential functions [5]. The simulation was performed for 200 water molecules at 292 K and a density 0.9718 g/cm^3, leading to a sidelength of the basic periodic cube of 18.17 Å. The simulated RDFs have been extended then till 25.6 Å as it has been described in [3]. The distance of 25.6 Å follows from the procedure of the numerical solution of the Ornstein-Zernike integral equation with 1024 grid points at a spacing of 0.025 Å.

2. Results and Discussions

a) Structure Factor

From the oxygen-oxygen RDF extended in the way described above the structure factor $S_{OO}(k)$ has been calculated according to

$$S_{OO}(k, R) = 1 + \frac{4\pi \varrho_O}{k} \int_0^R (g_{OO}(r) - 1) \sin(kr)\, r\, dr \quad (1)$$

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0932-0784 / 95 / 0100-0018 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

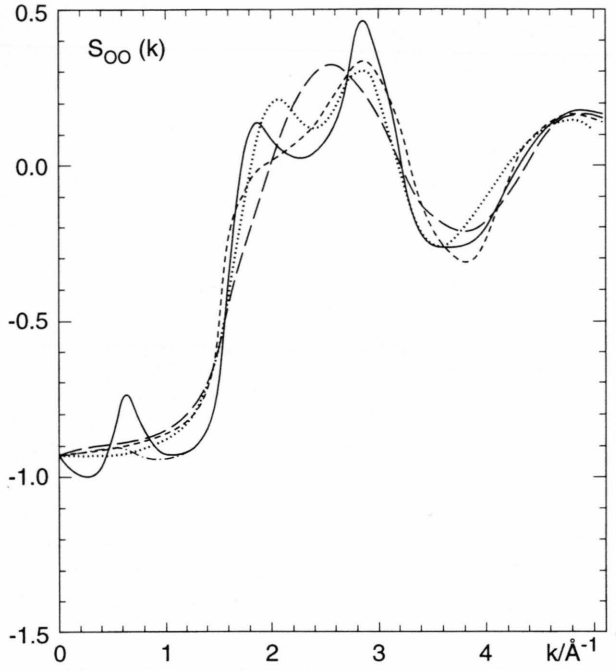

Fig. 1. Oxygen-oxygen structure factor for water at small wavenumbers from experiment (· · · ·) and for various upper limits of the integral in (1): $R = 3.3$ Å (— —), 5.5 Å (– – –), 13 Å (– · –), and 25.5 Å (——). The curves for 13 and 25.6 Å differ only for $k < 1.1$ Å^{-1}.

for various upper limits of the integral. ϱ_O is the average number density of the oxygen atoms. Figure 1 shows these $S_{OO}(k, R)$ for $R = 3.3$, 5.5, 13.0, and 25.6 Å. They have been chosen from the condition that in the limit $k = 0$ $S_{OO}(k, R)$ gives the correct value of the compressibility (see below). The latter value of R is the largest one in the present investigations (see above). The curves are presented with an increment of 0.32 Å^{-1}. This step is rather important for the region of $k < 1.5$ Å^{-1} and follows from the necessity to satisfy the condition that structure factors describing density and charge fluctuations have to be positive [6].

The first curve ($R = 3.3$ Å, first minima of the oxygen-oxygen RDF) describes the situation where a first neighbour shells exists and beyond that a uniform distribution of oxygen atoms. A single peak results at $k_1 = 2.57$ Å^{-1}. Using the relation $d_i k_i = 7.725$ a value of $d_1 = 2.98$ Å is obtained, which approximately reflects the average nearest neighbour distance in water. This curve is very close to the structure factor of liquid water at 200 °C measured by Narten and Levy [7]. This result is not unexpected as with increasing temperature the longer range structure in water decreases. The second curve, calculated for $R = 5.5$ Å (second minimum of the oxygen-oxygen RDF), describes the structure factor when a uniform distribution of the oxygen atoms is assumed only beyond the second nearest neighbours. A splitting of the first peak starts for this cut-off distance while the behaviour at large k does not change. Extending the upper limit of R to 13 Å leads to a complete splitting of the first peak in good agreement with the experimental result. A pre-peak does not appear. The curve resulting from a cut-off distance $R = 25.6$ Å differs from that for $R = 13$ Å only for k-values smaller than 1 Å^{-1}. In this range the structure factor has a minimum at $k = 0.31$ Å^{-1} and a maximum at $k = 0.62$ Å^{-1}.

A minimum of the structure factor for water at about 0.4 Å^{-1} has been found from small angle scattering studies and discussed e.g. in [8, 9]. But diffraction studies have not shown the maximum at about 0.6 Å^{-1} which is obviously connected with medium range correlations in water of the order of 10 Å. Also as a result of computer simulations this maximum has not been reported. The explanation might be that in all these water simulations the sidelength of the basic box is about 20 Å, which means that spatial correlations only up to about 10 Å can be seen. Although the box size in our simulation is similar, the extension of the $g_{OO}(r)$ according to the procedure proposed in [3] allows to see such correlations.

Support for the existence of density fluctuations at a spacing of about 10–30 Å comes from MD simulations, theory and experiment. Rahman and Stillinger calculated from their simulation of ST2 water the sound velocity and related it to a maximum in the structure factor at about 0.6 Å^{-1} [10]. Different from the RDF, where only half of the sidelength of the basic cube can be used to calculate the spatial correlation, in their calculation of the sound velocity the full sidelength of 20 Å becomes effective. From a theoretical extension of the experimental RDF, Fisher and Adamovich [11] found indications of density fluctuations with a wavelength of about 30 Å (see also Ben-Naim [12]). Finally, inelastic neutron scattering experiments by Teixeira et al. [13] indicated density fluctuations in a similar distance range.

The question remains why this pre-peak has not been found in diffraction studies so far. It is not very probable that it is an artifact introduced by the BJH model as this water model proved its usefulness in various simulations of water and electrolyte solutions

[4, 14]. But it cannot be excluded that the hydrogen bond strength in the BJH model might be exaggerated and the pre-peak is in reality less pronounced than demonstrated in Figure 1. A more careful investigation of this k-range by diffraction studies – similar to the ones reported in [9] – might resolve the apparent discrepancy. An experimental investigation at lower temperatures might also be helpful.

b) Compressibility

While (1) is only exact for $R \to \infty$, which cannot be realized because of the limited knowledge of $g_{OO}(r)$ for large r, an exact thermodynamic relation exists for the limits $k = 0$ and $R = \infty$, for which $S_{OO}(k, R) \to \varrho\, k_B T \varkappa_T$, where ϱ is the density and $\varkappa_T$ the isothermal compressibility. In Fig. 2 $S_{OO}(k = 0, R)$ is depicted as a function of R.

For small R the compressibility fluctuates about the experimental value for room temperature. The correct values for $\varkappa_T$ result if R is chosen for such distances where $g_{OO}(r)$ has its first two minima ($R = 3.3$ and 5.5 Å). Beyond 5.5 Å $S_{OO}(k = 0, R)$ remains negative except for distances of 13 and 25.6 Å where again the correct value of $\varkappa_T$ is found. These distances have been chosen for the calculation of the structure factors (Figure 1). It is not clear how $S_{OO}(k = 0, R)$ behaves beyond 25.6 Å. The extension of the $g_{OO}(r)$ to larger distances needs increasing computational effort connected with a significant decrease in accuracy.

As the derivative of $S_{OO}(k = 0, R)$ is proportional to $r^2(g_{OO}(r) - 1)$, the distances where $g_{OO}(r) = 1$ appear in Fig. 2 as maxima or minima and the distance-correlations are much more pronounced here then in $g_{OO}(r)$ itself because of the multiplication by r^2. Thus, Fig. 2 indicates the existence of spatial correlations in water at distances of the order of 10 Å, in agreement with the pre-peak in the structure factor.

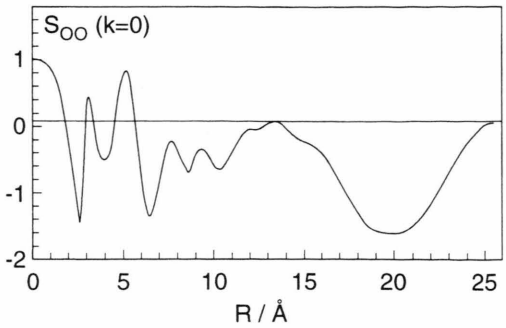

Fig. 2. Isothermal compressibility as a function of the upper limit of the integral in (1). The horizontal line marks the experimental value for water at room temperature.

Acknowledgements

Helpful discussions with J. Dore and G. Pálinkás and financial support by Deutsche Forschungsgemeinschaft and the National Academy of Sciences of Ukraine is gratefully acknowledged. In addition M.H. acknowledges support from the ISF Grant No. U1 J000.

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