

Study of the Hydrogen Bond Network in sub- and supercritical Water by Molecular Dynamics Simulations

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Dedicated to Professor Manfred Zeidler on the occasion of his 65th birthday.

For 12 points along the tangent to the saturation curve at the critical point the temperature dependencies of the heights of the first maximum in the O–O RDF, the average number of hydrogen bonds, and the self-diffusion coefficients have been calculated from MD simulations. The curves of these three properties show an inflection near the critical point. To improve the understanding of these changes in going from subcritical to supercritical water the librational spectra and the change in the fractions of water molecules with a given number of hydrogen bonds as a function of temperature have been derived from the simulations, additionally.

Key words: Super Critical Water; Molecular Dynamics.

1. Introduction

The discussion of the hydrogen bond network in supercritical water is still controversial in spite of the numerous publications which have appeared on this subject (see e.g. [1–14]). In most of the publications the existence of hydrogen bonded clusters have been reported for supercritical water [14–22]. Some authors even claim that the number of hydrogen bonds is higher than the percolation threshold [4]. One can say that it is generally accepted that in supercritical water hydrogen bonds are formed, although hydrogen bonded networks do not exist. The transition from hydrogen bonded networks in subcritical water to hydrogen bonded clusters in supercritical water is not completely understood.

The study of the structure and dynamics of hydrogen bond networks in a wide temperature and pressure range might clarify the situation. Experimental investigations of the diffusion coefficient of supercritical water indicate the existence of an inflection point in the curve giving the dependence of the diffusion coefficient on temperature [23, 24]. The use of computer simulations for the study of supercritical phenomena has proven to be very fruitful [25–33], especially for the estimation of dynamical properties of supercritical fluids. In this work we study this phenomenon by the simulation of twelve points along the tangent to the saturation curve in the phase diagram of water.

2. Model and Details of the Simulations

A flexible model for water, based on the BJH intramolecular potential [34], was used in this work. For the intramolecular interactions, the SPC/E [35] model was chosen because it can reproduce many of the experimentally determined dynamical properties. However, some parameters were modified; i.e. the atomic charge on H was chosen to be 0.426, the intramolecular OH distance 0.9572 Å and HOH angle 104.52°. The quality of this model in reproducing the experimental heat capacity, diffusion coefficient and vibrational spectra can be seen from Table 1.

All simulations were performed for the NVT ensemble for a selected set of temperatures and densities that belong to the sub- and supercritical regions, as shown in Figure 1. The basic cube contained 216 water molecules. Periodic boundary conditions, the shifted force potential method for the short-range interactions, and Ewald summation for the long-range electrostatic interactions were employed. Each simulation extended over 200 ps after equilibration with a time step length of 0.25 fs.

3. Results and Discussion

The main goal of this paper is the study of water properties close to the saturation curve and the critical

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Table 1. Potential parameters of the present water model and comparison of simulated properties with literature data.

T, K	584	630	673	680
$d, \text{kg} \cdot \text{m}^{-3}$	714.8	693.4	660	971.8
$C_V, \text{J mol}^{-1} \text{K}^{-1}$	50 (55) [36]	70 (52) [38]	43 (51) [36]	60 (54) [38]
$D \cdot 10^5, \text{cm}^2 \text{s}^{-1}$	18.4 (34.8) [11]	33.3 (37.0) [38]	29.1 (39.4) [11]	17.6 (23) [38]
μ, D	2.48 (2.27) [11]	2.46 (2.03) [38]	2.47 (2.27) [11]	2.48 (2.05) [38]
$V_{\text{SYM.STR.}}, \text{cm}^{-1}$	3437 (3520) [11]	3488 (3500) [38]	3454 (3520) [11]	3449 (3530) [38]
$V_{\text{ASYM.STR.}}, \text{cm}^{-1}$	3619	3619 (3675) [38]	3596	3579 (3630) [38]

Potential parameters of water models

	σ	ϵ	Q	D	U
SPC/E	3.166	78.23	0.4238	2.4	41.3
TIP4P	3.153	78.08	0.5200	2.1	40.9
Present (SPC2/F)	3.166	78.23	0.426	2.1	41.8
expt					41.4

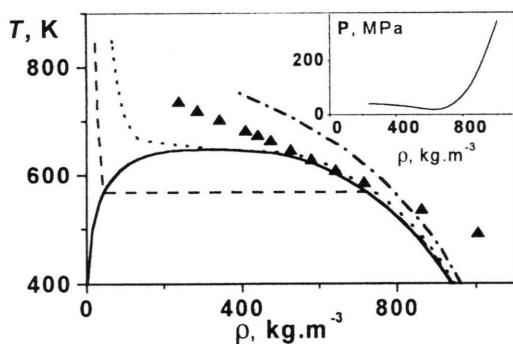


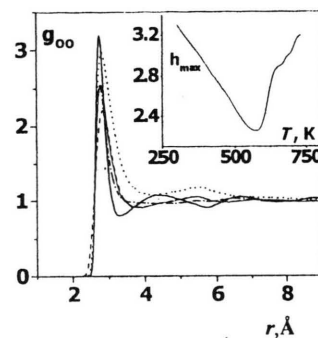
Fig. 1. Temperature versus density for 12 states of water (triangles) in comparison with the saturation curve and the isobaric lines: 8 MPa (dashed), 30 MPa (dotted) and 90 MPa (dash-dotted). Insert: Pressure versus density for the same density range.

point in order to follow the decrease of the hydrogen bond network and its influence on the diffusion coefficients. For this purpose the structure and diffusion coefficients for twelve points along the line in the phase diagram which tangents the saturation curve near the critical point (see in Fig. 1) have been calculated, six states each for the sub- and the supercritical regions. The pressures along this line are shown in the insert of Figure 1. The minimum of this pressure curve corresponds to the tangent point. Obviously, the gradient of the pressure versus density diagram is much higher for

subcritical than for supercritical conditions. This is easy to understand because the densities in the supercritical region are quite low and one can expect more gas like structure.

3.1. Structure

The O–O Radial Distribution Functions (RDFs) for four selected temperatures are shown in Fig. 2 together with the heights of the first peaks. It can be seen from the figure that the second peaks in the RDFs disappear, indicating a uniform distribution beyond the first shell, for temperatures above 490 K.

Fig. 2. Selected O–O radial distribution functions: 300 K (full line), 490 K (dash-dotted), 540 K (dashed), 734 K (dotted). Insert: Height of the first peak in $g_{\text{OO}}(r)$ as a function of T .

The changes of the heights of the first peaks of the RDFs with temperature are more complicated. In the range 400–580 K the height of the first peak decreases when the temperature increases. This behavior is quite similar to the one reported in [11, 32, 33, 37] and obviously means a decreasing water structuredness. In the range 580–740 K, the height of the first peak increases. Yoshii *et al.* [37] have reported the same behavior for densities lower than $0.27 \text{ g} \cdot \text{cm}^{-3}$ and $T = 600 \text{ K}$, while Kalinichev and Bass [32] found that even for low densities, and temperatures higher than 800 K, the first peak decreases. Therefore, this behavior can be understood as a low density effect, by taking into account that at low density cluster formation can start during destruction of hydrogen bond networks. The dependence of the height of the first peak on temperature exhibits a point of inflection near the critical point. To the best of our knowledge such a finding has so far not been reported in the literature. It might be connected with the high structural fluctuation near the critical point.

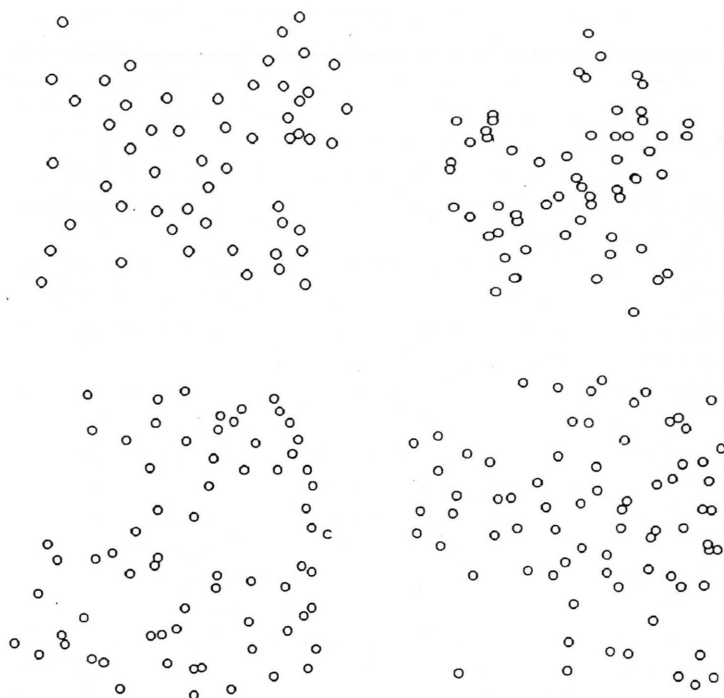


Fig. 3. Snapshots of the projections of all oxygen atoms in a 9 Å layer for $T = 671$ K, depicted for the same layer with an elapsed time of 50 ps between each projection.

The high correlation of the nearest neighbors at supercritical conditions is illustrated in Fig. 3, where the projections of all oxygen atoms in a 9 Å layer (about one third of the sidelength of the basic cube) are shown for $T = 650$ K. They are depicted for the same layer for four different times with 50 ps elapsed between each projection. It is evident from the figure that clusters are formed and empty spaces exist. The cluster formation during the destruction of the hydrogen bond network could explain the increase of the height of the first peak in the O–O RDF. This qualitative picture has, of course, to be quantified by the calculations of the numbers of hydrogen bonds.

Two criteria for the existence of a hydrogen bond have been extensively discussed in literature: a geometrical and an energetical one [11, 32, 37]. While Kalinichev and Bass [32] were the first who have found that the geometrical criterion overestimates the number of hydrogen bonds under supercritical conditions, Marti [11] has noted that there is no reliable threshold for the energetical criterion. Kalinichev and Bass [32] have introduced a hybrid OH distance-energy criterion, but still the threshold problem remains. Anyway, the threshold should depend on temperature as the energy barrier should be higher than the kinetic energy of the mole-

cules: $U_{\text{low}} = 3$ kT. Malenkov *et al.* [40] discussed a dynamical criterion which seems to be more reliable, but for high temperature and pressure there is no reliable definition for the life-time of a hydrogen bond.

The average number of hydrogen bonds as calculated from the coordination numbers of the O–H RDFs and from the hybrid distance-energy criterion with an energy threshold 3 kT are shown in Figure 4. The latter definition leads to higher numbers than the first one for

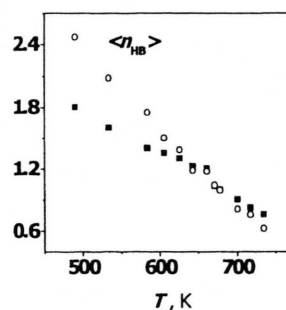


Fig. 4. Average number of hydrogen bonds per molecule as a function of temperature, calculated from an energy criterion (circles) and from the running integration numbers over the O–H RDFs.

temperature less than 650 K. For higher temperatures both criteria give very similar values for the average number of hydrogen bonds. Beyond the critical point both criteria lead to a number of hydrogen bonds which is lower than the percolation threshold, demonstrating that there exists no hydrogen bond network for temperatures above the critical point as expected from Figure 3. The result reported in [25], where $\langle n_{\text{HB}} \rangle = 1.4$ for $T = 573$ K, is very close to our one, while Marti [11] found $\langle n_{\text{HB}} \rangle = 2.4$ for $T = 573$ K and $\rho = 720 \text{ kg} \cdot \text{m}^{-3}$ which is higher than for ambient conditions and seems to be too high. The hydrogen bond numbers as a functions of temperature show for both criteria an inflection point near the critical point (see Fig. 4). This finding can be explained by a breaking of the hydrogen bond network at this temperature (Figs. 2 and 4). The number of hydrogen bonds at high temperature is significantly less than one per molecule, but the probability of hydrogen bond formation is even for the highest temperature near 0.7 and, therefore, small clusters can be formed. This result corresponds to that found by Kalinichev and Bass [32], where such clustering has been reported for similar conditions.

3.2 Self-diffusion Coefficients

The self-diffusion coefficient of water is very sensitive to changes of temperature and pressure and is related directly to the persistence of hydrogen bonds. In this study, the self-diffusion coefficients have been calculated from the simulation by employing the Green-Kubo relation and are compared in Fig. 5 with the experimental data of Hausser *et al.* [41] and those calculated ac-

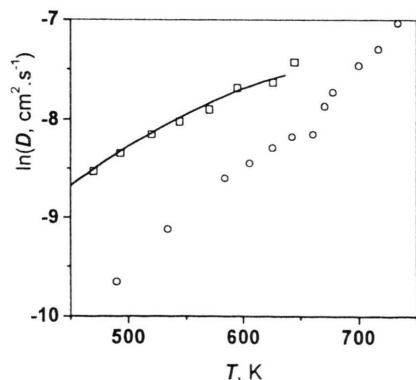


Fig. 5. Self-Diffusion coefficient versus temperature, present work (circles), experimental data of Hausser [41] (squares), as calculated from the Lamanna equation [42] (solid line).

cording to the equation proposed by Lamanna [42]. The experimental data have been measured at different pressures than ours, namely along the 30 MPa saturation curve (see Fig. 1). The pressure effect can, at least partly, explain the differences between simulation and experiment, which become smaller with increasing temperature parallel to the decrease in the pressure difference.

The simulated temperature dependence of the self-diffusion coefficient shows near the critical point an inflection, similar to those found above for two structural properties.

Therefore, it is to be expected that also the effect here is related to the change in the number of hydrogen bonds near the critical point (see Fig. 4) as discussed extensively by Marcus [24].

In order to investigate this question in more detail we have calculated from the simulation the number of 0-, 1-, 2-, 3- and 4-bonded water molecules as a function of temperature. The results are presented in Figure 6. It can be seen that the decrease of the 3- and 4-bonded and the increase of the 0-bonded water molecules with temperature is monotonous while the fraction of the 1-bonded molecules has a broad maximum at 600–700 K and that of the 2-bonded ones is constant up to 600 K and decreases strongly at higher temperatures. Different from the self-diffusion coefficient and the average number of hydrogen bonds (Figs. 4 and 5), inflection points of the temperature dependencies of the various fractions of the hydrogen bonded molecules are indicated but not clearly established in the limits of accuracy. But there

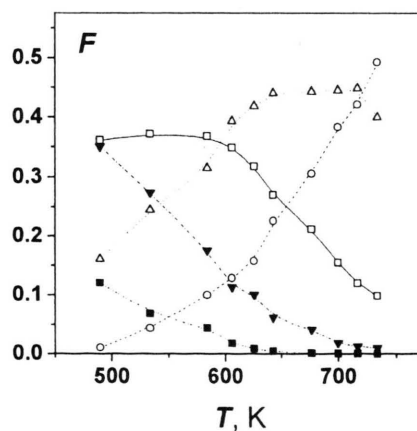


Fig. 6. Fractions of n -bonded water molecules as functions of temperature. Circles, open triangles, open squares, solid triangles, and solid squares refer to $n = 0, 1, 2, 3, 4$, respectively.

exists instead a change in slope near the critical point, most strongly expressed for the 2-bonded molecules.

3.3 Librational Motions

Additional information on the structure of hydrogen bonded clusters can be obtained from the change of the librational spectra with temperature as shown in Figure 7. It can be seen that, although the spectra of the librations shift to lower frequencies with increasing temperature, which corresponds to a decrease and weakening of the hydrogen bonds (see Figs. 4 and 6), the rotational motions around all three principal axes remain hindered up to the critical temperature. Skaf *et al.* [2]

have reported that the rotations around all axes become free, starting from $T = 1500$ K and $\rho = 0.05$ g/cm³.

It can be read also from Fig. 7 that the rotations around the x -axis become almost free above the critical temperature. With one exception the rotations around all axes are connected with the breaking of a hydrogen bond. Only in the case of a water dimer the water molecule which accepts the bond can rotate around its x -axis with a constant hydrogen bond angle without breaking it. This result is in accordance with the distribution of the number of hydrogen bonds as depicted in Figure 6. Almost 80% of all water molecules exist either as monomers or dimers at 670 K. It should be noted here that at 670 K the hydrogen bond angle deviates from linearity by up to 30° with a hydrogen bond energy of 18 kJ/mol compared with 22 kJ/mol at 490 K. The existence of 2- and even 3-bonded molecules at 700 K does not exclude contributions to the librational spectra from cooperative motions of the whole cluster. These results agree well with those reported in [4, 11, 37].

4. Summary and Conclusions

Several structural and dynamical properties of water have been calculated by Molecular Dynamics simulations for 12 points along the tangent to the saturation curve at the critical temperature (Fig. 1). The height of the first maximum in the O–O RDF, the average number of hydrogen bonds, and the self-diffusion coefficient as a function of temperature show an inflection near the critical point. Changes in the librational spectra and in the fractions of 0-, 1-, 2-, 3-, and 4-bonded water molecules supplement the information collected for the other properties. Snapshots of the projections of the oxygen atom positions indicate clustering of the water molecules near the critical point.

The competition between the structure breaking effect of the temperature increase and the structure making tendency of the decrease in density is a possible explanation for the inflection points discussed above. This competition leads to a transition from a hydrogen bonded network to hydrogen bonded clusters. This transition near the critical temperature can be inferred from the strong changes in the slopes of the fractions of n -bonded water molecules in the temperature range 600–700 K (Fig. 6). The occurrence of even a few percent of 3-bonded water molecules together with the projections presented in Fig. 3 strongly indicates the existence of clusters even at 670 K. This transition is obviously not smooth. The formation

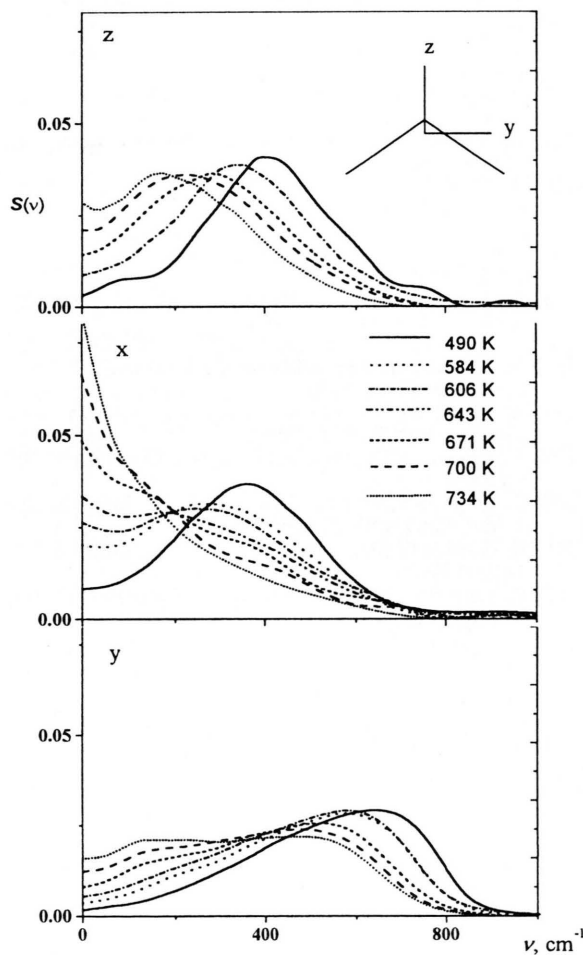


Fig. 7. The librations of the water molecules around the three principal axes as defined in the insertion.

of clusters with a strong tetrahedral arrangement of the water molecules near the critical temperature leads to an increase of the height of the first peak in the O–O RDFs (Fig. 2), to a constant average number of hydrogen bonds (Fig. 4), and a constant self-diffusion coefficient (Fig. 5) for a short temperature range. This conclusion is further supported by a maximum of the heat capacity at 650 K in good agreement with experimental data [36].

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