The Effect of Pressure on the Hydrogen Bond Structure of Liquid Water

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The results of molecular dynamics simulations of low and high pressure liquid water using a modified central force potential have been analyzed in order to study the effect of pressure on the hydrogen bond structure of water. The properties investigated and discussed include the hydrogen bond angle distribution, the O−O distance distribution between the neighbour molecules, the structure of the first coordination sphere in the high density liquid and the average number of hydrogen bonds.

1. Introduction

Theoretical and experimental studies of the effect of pressure on the structural and kinetic properties of water can be expected to give new insight into our understanding of the structure of this liquid. The experimental investigations include neutron diffraction [1], X-ray diffraction [2], NMR [3−5] and Raman spectroscopic studies [6−8] of water under high pressures (several kilobars). On the theoretical side three molecular dynamics (MD) simulations have been performed at a density of 1.346 g/cm^3 corresponding to that observed at the ice VI − ice VII − liquid triple point ($t = 81.6\,°C$ and $p = 22.0$ kbar). The MD simulations reported by Stillinger and Rahman [9] and Impey, Klein and McDonald [10] used the ST2 [11] and Matsuoka-Clementi-Yoshimine [12] water-water potential, respectively, whereas Jancsó, Bopp and Heinzinger [13] employed a modified version of the central force potential [14] which is capable of describing the effect of pressure on the internal vibrational motions of water. Although the overall agreement between the results of MD simulations and the available experimental data can be considered qualitatively good, there are non-negligible quan-

titative differences between the simulations and experiment in some properties e.g. in the O−O distances [2].

As to the general effect of the increase in pressure on the hydrogen-bonded network of liquid water the following questions have already been addressed in various ways: How many first neighbours are hydrogen bonded [1, 7]? Does the increase in pressure break hydrogen bonds or, on the contrary, increase the number of H-bonds? Does the structure of water become similar to that of a monatomic liquid insofar as its packing characteristics are concerned [1, 9, 10]? Does the association increase with rising pressure [7]?

By analyzing the available MD simulation results, answers to these questions can be obtained and − in spite of the fact that these may not be unequivocal in all cases and may depend on the model potential employed in the simulation − the conclusions are expected to be helpful in the interpretation of experimental results.

The purpose of the present paper is to investigate the effect of pressure on the hydrogen bond structure of liquid water on the basis of MD simulations of liquid water carried out at densities of 0.9718 and 1.346 g/cm^3, and at temperatures of 63 and 77 °C, respectively.

2. Calculation Methods

The MD simulations have been performed by using a modified central force potential [14] and

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details of the simulations as well as the comparison of the results with experimental data have been published elsewhere [13]. The low and high density states represent the liquid water under normal pressure and at about 22 kbar, respectively, and the simulations span 2.5 ps.

For the analysis to be carried out here, and to investigate the changes in the coordination shells of water molecules, we classified them into two groups: the first nearest neighbours (four molecules) and the second nearest neighbours (also four molecules), where the selection criterion is the oxygen-oxygen intermolecular distance. Accordingly, all calculated properties (hydrogen bond angle distribution, O−O distance distribution and hydrogen bond population) will be given separately for the two classes of neighbours. The above choice seems to be a reasonable one, since the coordination number in normal and high pressure water has been found to be about 4 and 7, respectively, if the integration was carried out up to the first minimum of g_{OO} at normal pressure (3.28 Å) [13].

3. Results and Discussion

The distribution of the average of the two "hydrogen bond angles" (the definition of which is shown in Fig. 1) for the two sets of neighbours in the normal pressure (NP) and high pressure (HP) liquids is shown in Figure 2. The differences in the mean values of the H-bond angles for the four nearest neighbours (28.7° and 32.8° in NP and HP water, respectively) as well as in the root-mean-square deviations (see Table 1) suggest that the hydrogen bonds become more distorted in the
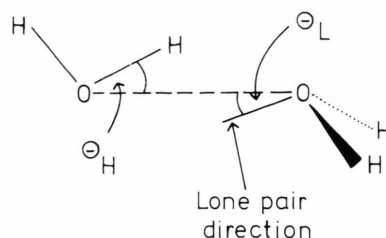

Fig. 1. The definition of the hydrogen bond angles.

compressed liquid. It is interesting to note that the behaviour of the hydrogen bond angles in the hydrogen and lone pair directions (Θ_H and Θ_L) is quite different with respect to the pressure increase: while $\langle \Theta_H \rangle$ increases by 12°, $\langle \Theta_L \rangle$ decreases by 4° (Table 1).

According to the expectations, the second four nearest neighbours in the NP water can hardly be considered as hydrogen bonded on the basis of any geometric definition of hydrogen bonding. The Θ distribution for the second four water molecules nearest to a central molecule, i.e. neighbours five to eight, has a mean value of 50° in the HP water which means that these molecules in spite of their being much closer to the central molecule than the corresponding second neighbours in the NP water (vide infra) are in general in an unfavourable position to form hydrogen bonds. On the other hand, the fraction of the molecules with H-bond angles less than 30° is larger for the fifth to eight closest neighbours in HP water than for the four second neighbours in NP water (see Figure 2).

We now turn our attention to the question of the coordination number in the HP liquid. The integration up to the first minimum in g_{OO} gives 4.2 and

Table 1. Mean values of hydrogen bond angle and O−O distance distributions.

	NP 1−4[a]	HP 1−4	NP 5−8	HP 5−8
$\langle \Theta_H \rangle$[b]	23.5° (19.1°)[c]	35.5° (23.2°)	55.4° (20.8°)	50.1° (23.4°)
$\langle \Theta_L \rangle$	34.0° (20.8°)	30.0° (22.2°)	55.5° (24.1°)	49.9° (22.5°)
$\langle \Theta \rangle$[d]	28.7° (20.6°)	32.8° (22.7°)	55.4° (22.5°)	50.0° (22.9°)
$\langle R_{CN} \rangle$[e]	2.92 (0.19)	2.81 (0.13)	3.71 (0.35)	3.18 (0.20)
$\langle R_{NN} \rangle$[e]	4.30 (0.80)	3.90 (0.85)		

[a] NP = normal pressure, HP = high pressure water. 1−4 and 5−8 denote the molecules in the first and second group of neighbours (see text).
[b] The definition of the hydrogen bond angles is shown in Figure 1.
[c] The numbers in parentheses are the root-mean-square deviations.
[d] No distinction has been made between Θ_H and Θ_L.
[e] The figures are given in Å. The meaning of R_{CN} and R_{NN} is given in the text.
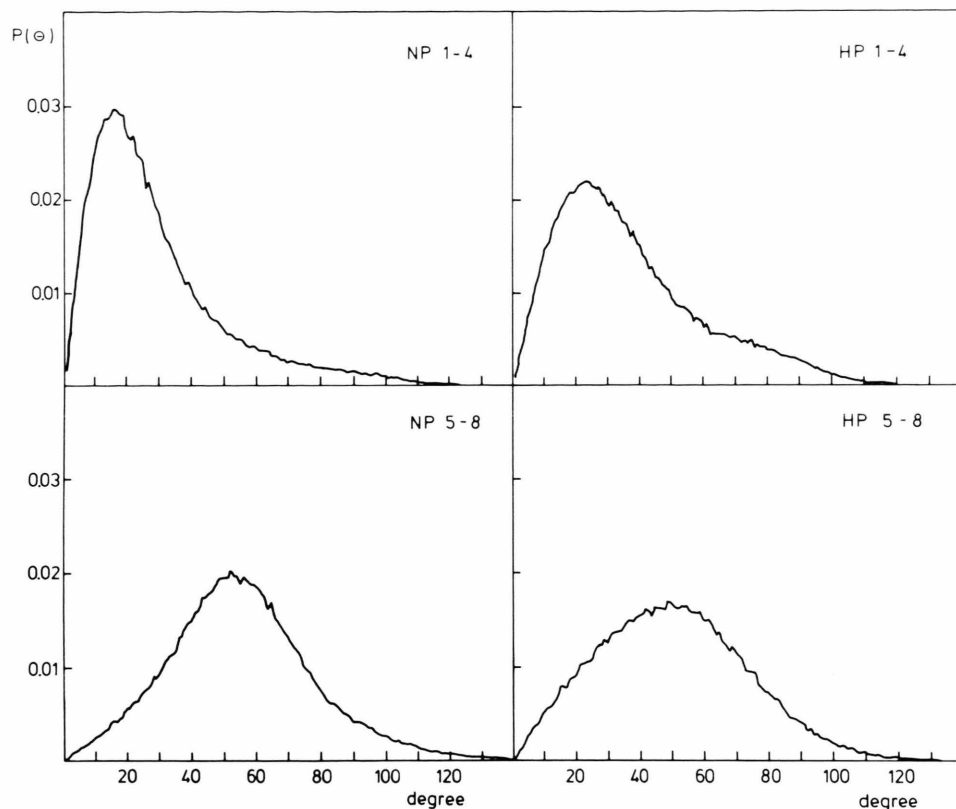
Fig. 2. The distribution of hydrogen bond angles $P(\Theta)$ – the average of Θ_H and Θ_L – for the first (1–4) and second (5–8) group of nearest neighbours in normal pressure (NP) and high pressure (HP) water.

12.2 for the total number of first neighbour molecules in NP and HP water, respectively [13]. However, as was mentioned before, if in both cases the integration is carried out to the same O–O distance, e.g. to the first minimum in the g_{OO} for normal pressure water (3.28 Å), which seems to be a reasonable choice for comparison, then a value of seven is obtained for HP water in good agreement with other estimates [1].

In Fig. 3 the distribution of O–O distances between the central molecule and the neighbour molecules (R_{CN}) is shown for both densities studied. It is seen that in the case of the first nearest neighbours the width of the peak (which represents in fact the contribution from the first four neighbours to the peak in the g_{OO} function) decreases and the mean O–O distance ($\langle R_{CN} \rangle$) shifts only by about 0.1 Å to a smaller distance (see Table 1) with increasing pressure in good accord with the shift of the first maximum of g_{OO} (0.05 Å) [13].

We must emphasize that the present results are in contrast to the much larger rate of contraction of the O–O first neighbour distances (0.01 Å/kbar) obtained from recent X-ray diffraction experiments [2] which would result in a shift of 0.22 Å for the HP water.

In our opinion the apparently large difference between this experimental finding and those obtained from MD simulations [9, 10, 13] can be accounted for by the uncertainty inherent in the fitting procedure employed to derive the shifts of the peak positions in the experimental radial distribution function.

The distribution function of R_{CN} distances for the second neighbours in the LP water has a mean value of 3.7 Å and it is significantly wider than that for the HP water (see Figure 3). In the compressed water the value of $\langle R_{CN} \rangle$ for the second group of molecules consisting of neighbours five to eight is about 3.2 Å which seems to indicate that the eight
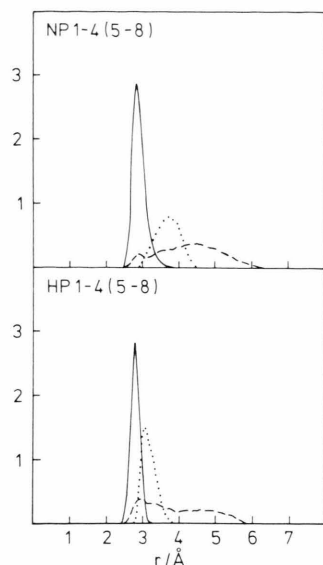
Fig. 3. The distribution of O−O distances: between the central molecule and neighbour molecules (1−4: full lines; 5−8: dotted lines); and between the molecules in the first group of nearest neighbours (dashed lines).

first neighbours cannot be considered as equivalent and the molecules transferred into the neighbourhood of the central molecule due to the increase in pressure form a "subshell" within the first coordination sphere.

The formation of a subshell can also be demonstrated by a three-dimensional drawing which illustrates the density distribution of the nearest neighbour molecules around a central molecule [15]. For this purpose a molecule-fixed coordinate system has been defined in such a way that the plane of the central molecule coincides with the yz plane of the coordinate system, the center of mass is positioned at the origin and the oxygen atom in the positive z direction (insertion in Figure 4). In the figure the projections of the oxygen atom positions onto the xy plane of the coordinate system are shown separately for all nearest neighbours, the first four and the second four neighbours. (The four peaks in the drawings represent the oxygen positions of the nearest four neighbours.) It can be clearly observed that there is a decrease in the preference for the occupation of tetrahedral positions in the HP water. The neighbours five to eight in HP water are seen to be closer to the central molecule than the second neighbours in the NP water, but they do not show

any preference for occupying tetrahedral positions. Accordingly, it seems reasonable to conclude that the first coordination sphere of high pressure water consists of neighbours of two different types. Similar conclusions have been drawn from the results of other two MD simulations [9, 10] in which an interpenetration of the subsections of the random hydrogen bond network has been proposed.

The distributions of distances between molecules in the first group of nearest neighbours (R_{NN}) are also shown in Fig. 3 (dashed lines) and the corresponding mean values ($\langle R_{NN} \rangle$) are listed in Table 1. The shift of 0.4 Å brought about by the pressure rise suggests a more compact arrangement of the molecules within the coordination sphere. This is in harmony with the changes observed in the hydrogen bond angle distributions discussed at the beginning of this section and supports the view according to which when liquid water is compressed the volume reduction is due largely to the O−O−O angle deformation and not to the decrease in the O−O distance [16, 17].

An interesting question − connected with many particle correlations − is how often the four water molecules near a central one occupy simultaneously tetrahedral positions. In order to obtain this information from the MD simulation solid angles in the tetrahedral directions are defined. This makes it then possible to decide whether the oxygen atom of a given water molecule lies in a tetrahedral direction or not. The selection of these angles involves, of course, some arbitrariness, nevertheless a value of about 20° for the half of the aperture angle of the cones in the tetrahedral directions seems to be a reasonable choice since results obtained with different hydrogen bond definitions have led to the conclusion that the average hydrogen bond is bent about 20° [18, 19]. In Fig. 5 we show the results obtained for the probability of finding a given number of tetrahedral directions occupied simultaneously by water molecules for both NP and HP water. At normal density the fraction of water molecules with a complete tetrahedral environment is about 5% while the corresponding value for ST2 water is 10% [15]. It is clear from the figure that the compression of liquid water is accompanied by a significant increase in the probabilities of finding only one neighbour or no neighbour at all in the tetrahedral directions. The mean value of the simultaneously occupied tetrahedral directions of a
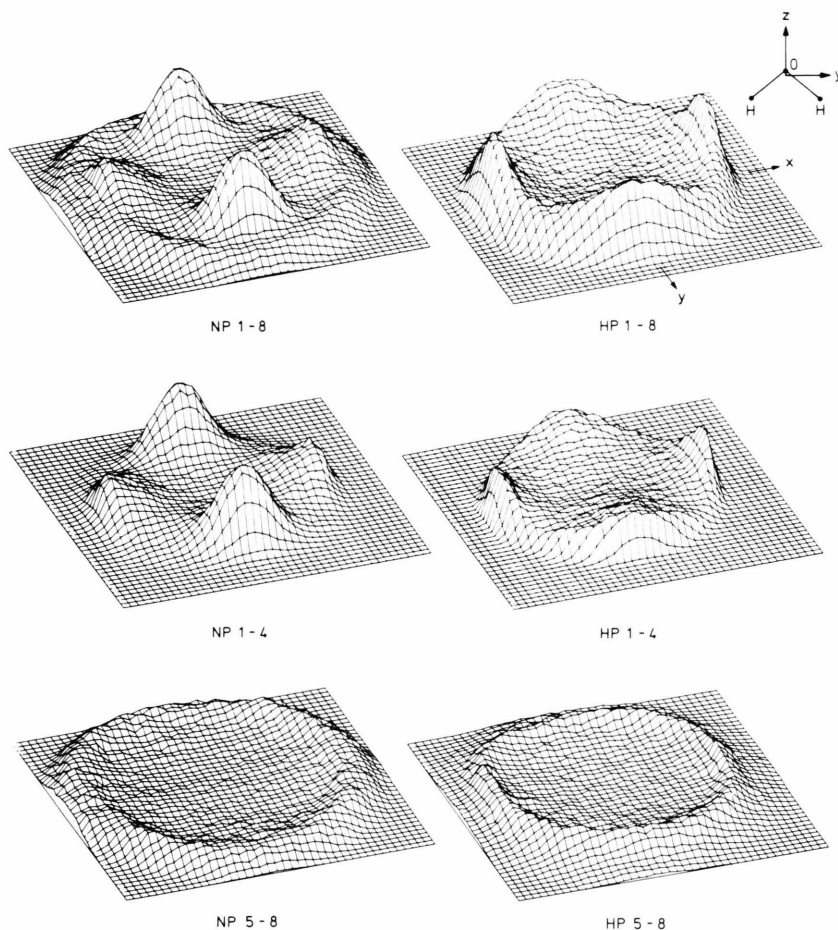
Fig. 4. Three-dimensional drawings of the projections of the oxygen atom position distributions of the nearest neighbour molecules around a central water molecule onto the xy plane of a coordinate system as shown in the insertion calculated from the MD simulations of NP and HP water.
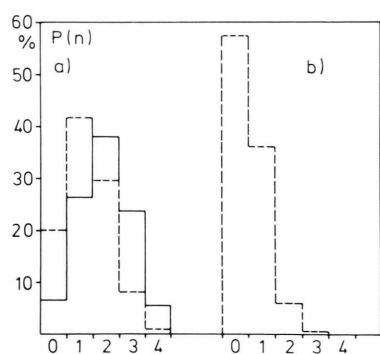

Fig. 5. The probability of finding a given number of tetrahedral directions occupied simultaneously by water molecules, calculated for the first four (a) and for the second four (b) neighbours. NP water: full line; HP water: dashed line. (The distribution for the second neighbours in NP water is not shown because they are outside of the range where H-bond forming can be expected.)

water molecule is 1.95 for NP water which means that in average only two of the four tetrahedral positions are simultaneously occupied by water molecules. For the HP water values of 1.3 and 0.5 have been found for the molecules in the first and second subshell, respectively.

If the molecules whose oxygen atoms are situated in tetrahedral direction are considered as hydrogen bonded [20] then we may conclude that the average number of H bonds decreases with rising pressure and that the second group of neighbour molecules in HP water are not hydrogen bonded (see also Figure 4).

It has been suggested in connection with the interpretation of neutron scattering data on high pressure water that the orientational correlations are
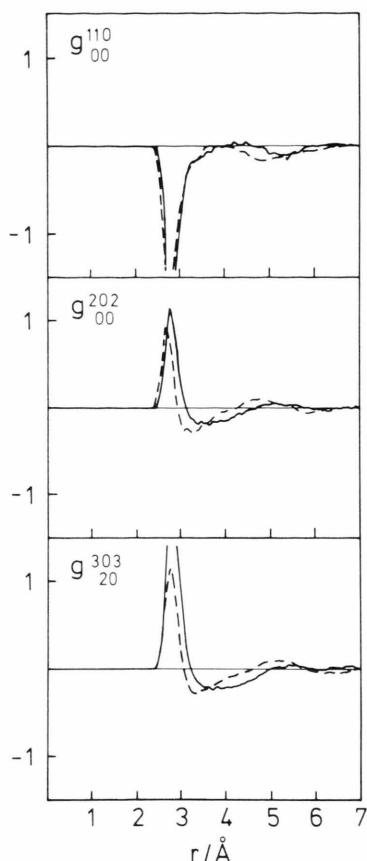
Fig. 6. Some of the expansion coefficients ($g_{\mu\nu}^{mnl}$) of the generalized molecular correlation function for NP (full line) and HP (dashed line) water.

clearly discernible. At large interparticle distances corresponding to the second shell of water molecules an increase in orientational correlations is generally observed. In contrast to this a decrease of such correlation is apparent in the region of the first neighbour shell.

4. Conclusions

The hydrogen bond angle distributions computed from MD simulation results on a modified central force water show a significant distortion of H-bond angles with rising pressure.

The first neighbour molecules in the high pressure water can be considered as forming two "subshells" on the basis of the O–O distance distribution in the first coordination sphere. The molecules that have been transferred into the neighbourhood of a central molecule due to the pressure increase do not show a preference for occupying tetrahedral positions and this together with their H-bond angle distribution can be taken as an evidence that they are not hydrogen bonded.

The probability of finding simultaneously less than two molecules in tetrahedral directions increases and at the same time the tetrahedral character of the first neighbour shell is weakened with rising pressure. The average number of hydrogen bonded molecules decreases from 1.9 to 1.3. It is interesting to note that inspite of the weakening of the H-bond structure in the neighbourhood of the molecules the orientational correlation seems to have been increased by pressure at further O–O distances.

The present results together with those of other MD simulations [9, 10] using the ST2 and MCY potentials do not support the much larger rate of contraction of the nearest neighbour O–O separation with increasing pressure as it has been inferred from X-ray diffraction experiments carried out on light and heavy water to pressures of 6 kbar [2].

increased by pressure [1]. In order to check the effect of pressure on the orientational correlations we calculated – on the basis of MD simulation data – several expansion coefficients ($g_{\mu\nu}^{mnl}(r)$) of the generalized molecular correlation function ($G(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \hat{\mathbf{r}}_{12})$) with $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$ representing the sets of Euler angles of the molecules 1 and 2 in a space fixed coordinate system and $\hat{\mathbf{r}}_{12}$ the spherical angles of the direction vector [21]. In Fig. 6 the three leading invariant expansion coefficients are shown for NP and HP water. The g_{00}^{110}, g_{00}^{202} and g_{20}^{303} coefficients represent the dipole-dipole, quadrupole-center and octupole-center orientational correlations, respectively. Although the differences between the coefficients for LP and HP water are not dramatical, changes in their r dependences are

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