

# COMPUTER SIMULATION STUDY OF THE HYDROGEN-BOND NETWORK IN METASTABLE WATER

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## **Abstract**

We study the changes in the topology of the hydrogen-bond network when penetrating into the metastable region of water. The statistics of four-bonded water molecules as well as of bond-rings are evaluated. We also give some evidence for the existence of numerous clathrate-like holes in liquid water. Finally, we exemplify the influence of hydrogen bonding on the microdynamic properties of water and deduce a simple explanation for the occurrence of hydrophobic hydration.

## **1 INTRODUCTION**

The structure of liquids is usually described by pair correlation functions. But obviously this information is not sufficient to understand the properties of water, as one can deduce from the fact that in the literature various structural models have been proposed and discussed, which all contain in some form higher correlations between the water molecules (see for example Frank 1972, Stillinger 1977). Unfortunately, there are only very limited experimental possibilities for getting structural information which go beyond the pair distribution function. Therefore, we perform molecular dynamics (MD) computer simulations of a waterlike model liquid (Stillinger and Rahman 1974), extracting details which are considered in the structural models.

One of the most prominent features of water molecule interaction is the formation of hydrogen bonds. In the crystalline forms of water this leads to the development of a complete, regular and quasi-infinite network, each water molecule acting as the origin of exactly four hydrogen bonds. On melting, the distribution of existing hydrogen bonds becomes broader with respect to the range of bond angles, lengths and strengths which occur. Some of the occurring arrangements may be characterised as broken and some as branched hydrogen bonds. Moreover the lifetime of individual bonds becomes very short. As a consequence, the network of hydrogen bonds will become irregular and distorted and subject to a constant restructuring, but, as previous computer simulation studies have shown very clearly, at any instant and for any reasonable definition of a hydrogen bond, there will exist an 'infinite' network, spanning the whole system and encompassing many finite, disconnected networks of various sizes. In other

words, the system will be above the bond percolation threshold (Geiger *et al* 1979b).

During the past few years a detailed and quantitative description of the existing network has been achieved using the concept of percolation theory (see for example Stanley *et al* 1984). Nevertheless, to explain the properties of water it is not sufficient to know the topology of the network. Therefore, several authors directed their attention to various structural units which are produced by and embedded in the bond network and which induce a decreased local density and increased local order. These are four-bonded molecules (Stanley and Teixeira 1980), pentagonal bond rings (Speedy 1984), unstrained bulky polyhedra (Stillinger 1980a,b) and clathrate-like cavities (Pauling 1959), all of them structural sections of bulky crystalline forms of water, the simpler units serving as building blocks for the more complex ones. The clustering of such units leads to the formation of extended 'patches'. Thus, the statistical nature and the constant restructuring of the network provide a mechanism to produce the observed fluctuations of density and entropy (Stanley and Teixeira 1980, Geiger and Stanley 1982).

As the careful study of the properties of supercooled water revealed, these fluctuations seem to increase without limit, when approaching a low temperature 'singularity' line in the  $p, T$  diagram (Angell 1983a,b, Lang and Lüdemann 1982). This has been conjectured by Speedy to be a spinodal line, forming the boundary of a connected uniform region of metastable (supercooled, 'stretched' and superheated) water and marking the limit of its mechanical stability (see figure 5 of Speedy 1982). There has also been speculation that the structural explanation for this thermodynamic behaviour may be found in the approach to a percolation threshold for the low density, higher order patches or some other kind of order-disorder phenomenon (Stanley and Teixeira 1980, Stillinger 1980a).

In this paper we study the changes in the hydrogen-bond network when penetrating into the metastability region of water; we look at the statistics of the four-bonded water molecules as well as of bond rings. Furthermore, we give some evidence for the existence of numerous clathrate-like holes in liquid water, and finally we exemplify the influence of hydrogen bonding on the microdynamic properties of water.

## 2 MD SIMULATION OUTLINE

Most of our former hydrogen bond analysis refers to a system of 216 water molecules interacting via an ST2 pair potential (Stillinger and Rahman 1974), density and temperature being  $\rho = 1.0 \text{ g cm}^{-3}$  and  $T = 284 \text{ K}$ . To study the structural changes which occur in the metastable region and to separate the influences of temperature and density, we performed two supplementary series of simulation runs. In the first the density was kept constant at  $\rho = 1.0 \text{ g cm}^{-3}$ , while the temperature was decreased in several steps from 287 to 235 K. Details of the simulation technique and many results have been published and can be found in the paper of Geiger *et al* (1984).

In this paper we now compare these constant- $\rho$  results with those of a new simulation series, where we varied the density from  $\rho = 1.0$  to  $0.7 \text{ g cm}^{-3}$ , keeping the temperature approximately constant at  $T = 273 \text{ K}$ . As in the constant- $\rho$  series, we use a cut-off distance  $r_c = 7.8 \text{ \AA}$  for the direct water-water interaction, combined with a reaction field (Steinhauser 1982). Since we have to cope with increasing fluctuations and increasing relaxation times when penetrating into the

metastable 'stretched water' region and approaching the conjectured spinodal, we apply equilibration runs of increasing duration, extending up to 300 ps at the lowest densities (see figure 1 for characterisation of the runs). During the subsequent 'production' period of 12 to 25 ps every eighth configuration was saved on tape and examined more extensively later. The results discussed in the following always refer to those periods, which are shown hatched in figure 1. This procedure was adapted to our use of lowest-priority computer time on a special configuration of a VAX 780/FPS 164 with very limited mass storage access. The attainment of equilibrium was controlled by monitoring among other quantities the structure factor  $S(Q)$  for the lowest accessible  $Q$  values ( $Q_{\min} = 2\pi/L$ , where  $L$  is the size of the periodic box containing our 216-particle system).

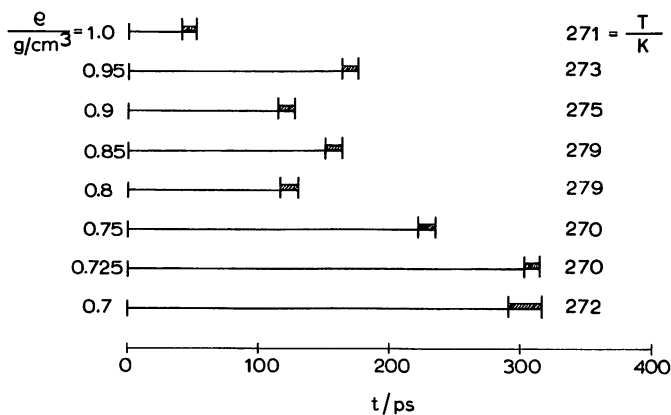


Figure 1. Schematic representation of simulation runs: length of equilibrium periods and periods of analysis (hatched), density and average temperature.

### 3 HYDROGEN-BOND DEFINITION

Since the hydrogen-bond interaction between two water molecules is described by a continuous function of mutual separation and orientation without any saddle points, there is no natural and unambiguous choice for a dividing line between 'broken' and 'intact' hydrogen bonds. As in the previous studies we use the following criterion: two molecules  $i$  and  $j$  are considered to be hydrogen bonded whenever their interaction energy  $V_{ij}$  lies below a negative cut-off value  $V_{\text{HB}}$  and their mutual oxygen-oxygen separation is less than 3.5 Å.

Scanning the continuum of interactions by varying  $V_{\text{HB}}$  and observing the changes so caused in the pattern of the bond network, delivers a detailed picture of the molecular connectivity. This procedure not only adjusts the usual notion of broken and intact hydrogen bonds to the reality of the continuum of interactions, but furnishes a basis for the application of percolation theory: for each choice of  $V_{\text{HB}}$  an average number of hydrogen bonds per water molecule  $\langle n_{\text{HB}} \rangle$  is obtained, from which one can derive a parameter  $p = \langle n_{\text{HB}} \rangle / 4$ ;  $p$  can be identified with the fraction of intact bonds, the fundamental independent variable in bond percolation theory.

Varying  $V_{\text{HB}}$  from the most negative values close to the absolute minimum of the

ST2 pair potential ( $-6.8 \text{ kcal mol}^{-1}$ ) up to values near zero, requires that we start with an extremely strict definition of a hydrogen bond and become more and more permissive. Accordingly the number of observed hydrogen bonds per molecule  $\langle n_{\text{HB}} \rangle$  will vary from near zero to values close to four and  $p$  from 0 to 1 correspondingly (Blumberg *et al* 1984, Geiger *et al* 1984). In the following we discuss various properties as they appear as a function of the number of hydrogen bonds, thus using  $\langle n_{\text{HB}} \rangle$  and  $p$  as independent variables. But it should be kept in mind that this variation is always obtained by varying  $V_{\text{HB}}$ . Hence, these curves indicate the changes in the appearance of the network, when looking for hydrogen bonds of various strengths.

#### 4 LOCAL ARRANGEMENT OF HYDROGEN-BONDED MOLECULES

As it has been proposed by Stanley and Teixeira (1980) and shown subsequently for 'computer water', the fraction  $f_j$  of water molecules with exactly  $j$  intact hydrogen bonds can be described by a simple binomial distribution

$$f_{j,\text{ST}}(p) = \binom{4}{j} p^j (1-p)^{4-j}$$

over a large range of  $p = \langle n_{\text{HB}} \rangle / 4$ . Only for  $j > 2$  and values of  $\langle n_{\text{HB}} \rangle$  above 3.0 can noticeable deviations be seen (Blumberg *et al* 1984, Geiger *et al* 1984). These discrepancies at large  $\langle n_{\text{HB}} \rangle$  can be attributed to deviations from the strict local tetrahedrality of the network: if weaker bonds are also considered, bifurcated hydrogen bonds and molecules with five bonds may occur.

Figure 2 shows for  $j = 3$  and 4 and for several densities  $\rho$  the deviations  $\Delta f_j$  of our MD results  $f_{j,\text{MD}}$  from the binomial distribution  $f_{j,\text{ST}}$ . Starting from  $\rho = 1.0 \text{ g cm}^{-3}$  the binomial distribution becomes more and more valid with decreasing density. At  $\rho = 0.75 \text{ g cm}^{-3}$  the deviations are less than 0.01 over the whole range of  $\langle n_{\text{HB}} \rangle$  values up to  $\langle n_{\text{HB}} \rangle \approx 3.8$ . This indicates that there are fewer and fewer molecules with five bonding possibilities; the network becomes locally more tetrahedral with decreasing density.

At  $\rho = 0.70 \text{ g cm}^{-3}$  a sudden change occurs, indicated by strong deviations appearing again. We explain this by a decomposition of the system at this low density and negative pressure state.

The strong density-dependence of  $\Delta f_j(p)$  is contrasted by the temperature dependence at constant density. Although  $p$  increases with decreasing temperature for fixed  $V_{\text{HB}}$ , in that case the  $\Delta f_j(p)$  curves for different temperatures almost fall on top of each other (see figure 3 of Geiger *et al* 1984).

As we will see more clearly later on, on lowering the density the topology of the hydrogen-bond network seems to gradually approach the topology of low-density amorphous ice (note our comment on this at the end of § 7). On achieving close agreement (near  $\rho = 0.75 \text{ g cm}^{-3}$ ), the mechanical stability of the 'stretched water' seems to be lost and the system disrupts. Here it is quite interesting to remember that Speedy predicted a density of  $\rho = 0.81 \text{ g cm}^{-3}$  at the conjectured limit of stability of 'stretched water' (Speedy 1982). The similarity of these densities is even closer, if one recalls that the ST2 model tends to produce slightly too low densities of the bulky ice forms (Morse and Rice 1982).

Another recommendation for the gradual approach to the low-density ice structure is given in figures 3 and 4. Figure 3 reveals an extremely unusual

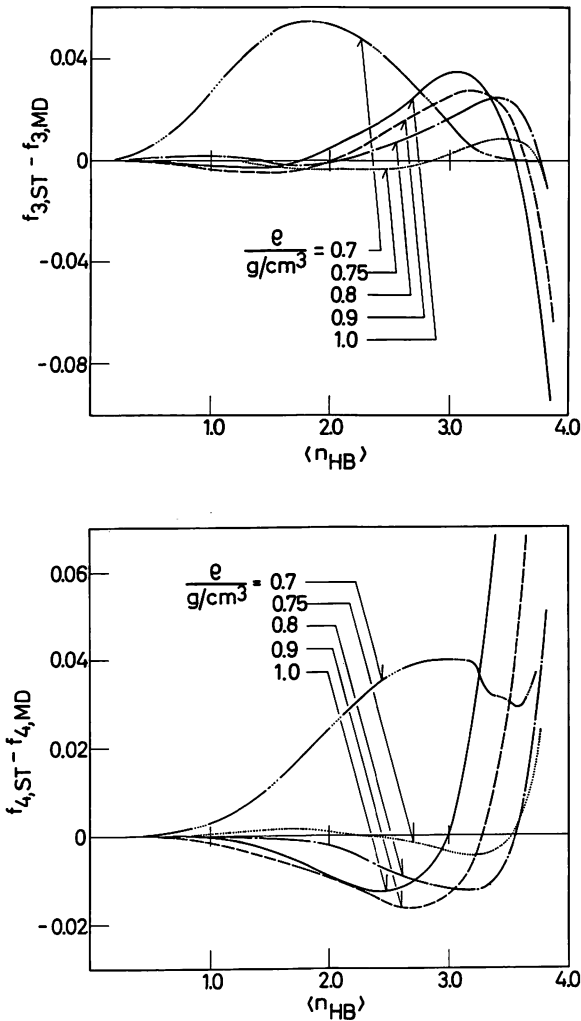


Figure 2. Fraction  $f_j$  of water molecules having exactly  $j$  intact hydrogen bonds (for  $j = 3$  and  $4$ ); deviations of MD results from binomial distribution (ST).

behaviour of the oxygen–oxygen pair correlation function  $g_{OO}(r)$ . The oscillations of  $g_{OO}(r)$  become more pronounced and in particular the height of the first peak increases with decreasing density. This is totally opposite to the behaviour that one expects from simple liquids but demonstrates the development of a more ordered structure with decreasing density. Also, the slight shift of the second peak to larger distances indicates the formation of more linear hydrogen bonds.

Integrating over the first peak of  $g_{OO}(r)$  up to the first minimum yields the number of nearest neighbours  $n(r)$ . This quantity is shown in figure 4 and indicates again, in accord with our previous interpretation, a clear tendency towards a tetrahedral, icelike surrounding when lowering the density.

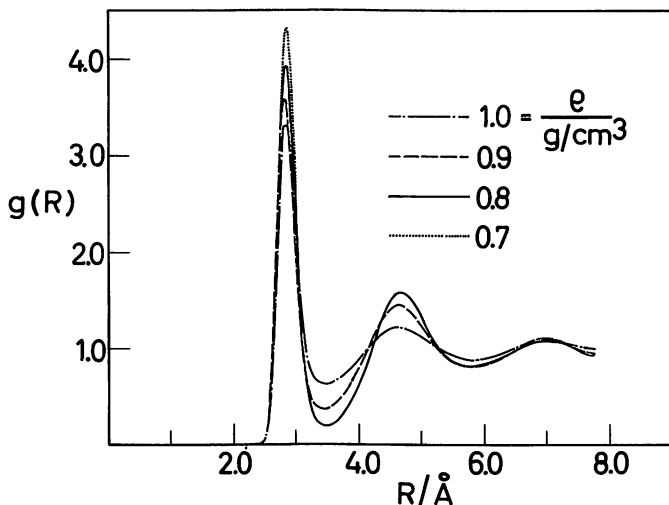


Figure 3. Density dependence of oxygen-oxygen pair correlation function  $g_{oo}(r)$ . For  $\rho = 0.7 \text{ g cm}^{-3}$  only the peak values deviate from the curve for  $\rho = 0.8 \text{ g cm}^{-3}$ .

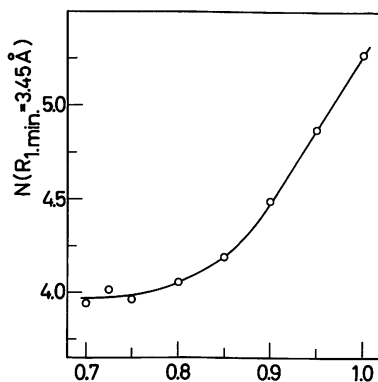


Figure 4. Number of nearest neighbours obtained by integrating over the first peak of  $g_{oo}(r)$ . The bottom axis shows density  $\rho \text{ (g cm}^{-3}\text{)}$ .

## 5 SIZE DISTRIBUTION $W_s^c(\rho)$ OF CLUSTERS OF FOUR-BONDED MOLECULES

To get a more detailed and quantitative description of the hydrogen-bond network, we calculated, in our previous studies, distribution functions giving the weight fraction  $W_M^N(\rho)$  of water molecules, which belong to 'bond-nets' of  $M$  molecules. Likewise we determined the corresponding weight fraction  $W_s^c(\rho)$  of molecules, belonging to 'clusters' of  $s$  connected water molecules, which all have exactly four intact hydrogen bonds. It was quite striking to see the degree of quantitative agreement between the MD results and the predictions of percolation theory. Nevertheless, a closer inspection of  $W_s^c(\rho)$  revealed a small but systematic difference (Blumberg *et al* 1984).

It had been speculated that these deviations indicate an increased tendency for aggregation of the four-bonded molecules, which goes beyond the correlations built into the percolation model. Another reason could just be the deviation from the assumed lattice topology in the percolation model.

We expected to get a hint as to the correct explanation from the temperature and density dependence. Our constant-density simulation series showed no change with temperature of the difference between the MD results and the Stanley–Teixeira percolation model (ST). Within the accuracy of the MD result the  $\Delta W_s^c(p)$  curves fell on top of each other (Geiger *et al* 1984). In contrast to this, when varying the density at roughly constant temperature strong changes can be observed (figure 5). With decreasing density, the differences  $\Delta W_s^c(p)$  decrease and are close to zero near  $\rho \approx 0.75 \text{ g cm}^{-3}$ . On further decrease of the density, at  $\rho = 0.70 \text{ g cm}^{-3}$ , the deviations again increase, but now in the opposite direction.

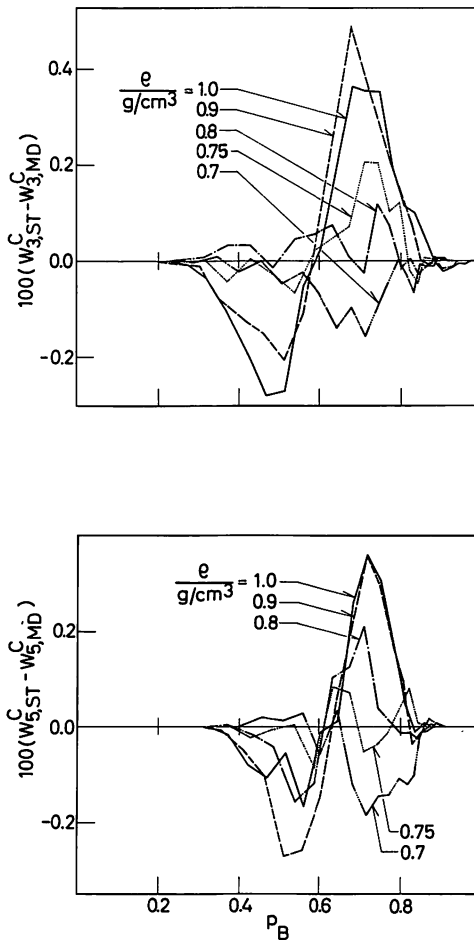


Figure 5. Size distribution of clusters of four-bonded molecules  $W_s^c(p)$ : deviation of MD results from percolation theory (ST) for clusters of size  $s = 3$  and 5.

This behaviour parallels that of  $\Delta f_j(p)$  and also the explanation can be given along the same lines. Whereas the pure temperature influence does not change the topology of the network, decreasing the density leads to a more tetrahedral, more icelike network topology. The maximum agreement is again reached at  $\rho \approx 0.75 \text{ g cm}^{-3}$ .

The following has to be emphasised: when we talk of an approach to icelike structure, we do this in the sense of close agreement with percolation calculations, which have been obtained by underlying the topology of an ice Ih lattice. The use of cubic ice does not change the percolation results so much that detectable differences occur. The same would probably be true even for some kind of amorphous ice, which contains for example also five- and seven-membered bond rings. On the other hand, as was shown earlier, the differences between lattice percolation and Flory theory (which neglects bond cycles) are already quite large for  $W_s^c$  with  $s = 5$  (Stanley *et al* 1983), and the deviations of the Flory model from the MD results would increase with decreasing density.

In §7 we show that bond rings other than hexagons are present in appreciable numbers, even in the density region where maximum agreement with lattice percolation is obtained.

## 6 AVERAGE HYDROGEN-BOND NUMBER $\langle n_{\text{HB}} \rangle$ AND AVERAGE CLUSTER SIZE $S_c$

In figure 6(a) the average number of hydrogen bonds  $\langle n_{\text{HB}} \rangle$  is shown as a function of density at constant temperature  $T \approx 273 \text{ K}$  for a series of definition values  $V_{\text{HB}}$ . Lowering the density results in an increased formation of hydrogen bonds, as if the temperature were decreased. Between  $\rho = 0.8$  and  $0.75 \text{ g cm}^{-3}$   $\langle n_{\text{HB}} \rangle$  passes a maximum. This indicates an onset of rupture of the network at densities below  $0.8 \text{ g cm}^{-3}$ .

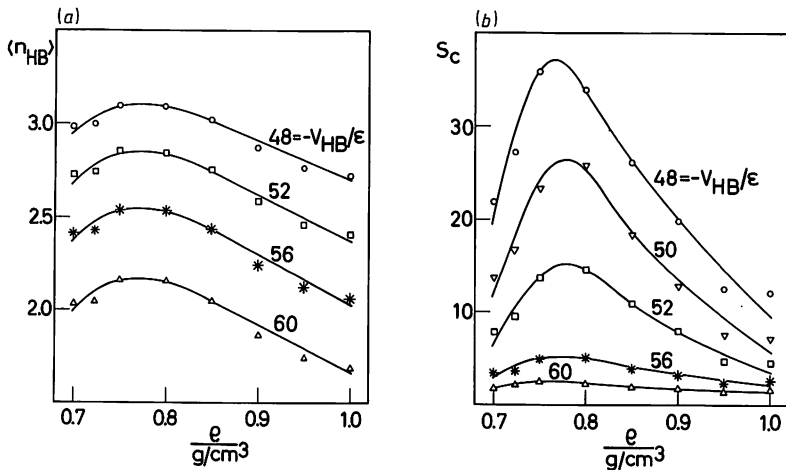


Figure 6. Density dependence of (a) average number of hydrogen-bonds  $\langle n_{\text{HB}} \rangle$  and (b) average cluster size  $S_c$  for different values of  $V_{\text{HB}}$  ( $\epsilon = 0.07575 \text{ kcal mol}^{-1}$ ).



From the existence of a nearly temperature-invariant point in the pair-energy distribution Stillinger and Rahman (1974) suggested a value close to  $-4 \text{ kcal mol}^{-1}$  as a realistic choice for  $V_{\text{HB}}$ . Therefore it is interesting to note that for  $V_{\text{HB}} = -48\varepsilon = -3.64 \text{ kcal mol}^{-1}$  the maximum value of  $\langle n_{\text{HB}} \rangle$  comes close to the percolation threshold value of 3.18 (Blumberg *et al* 1984). This suggests the possibility for unification of two major views about the nature of the singularity line limiting the metastable water region: the existence of a percolation threshold for low-density, high-local-order patches on one hand (Stanley and Teixeira 1980) and the decomposition of the system when reaching a spinodal line on the other hand (Speedy 1982).

Variation of  $V_{\text{HB}}$  results only in a parallel shift of the  $\langle n_{\text{HB}} \rangle$  curves (figure 6(a)). In contrast to this the density dependence of the average cluster size (summing only over non-spanning aggregates)

$$S_c = \Sigma' s W_s^c / \Sigma' W_s^c$$

becomes much more accelerated (figure 6(b)) when approaching the percolation threshold. Here again the maximum between 0.8 and 0.75  $\text{g cm}^{-3}$  and the following decrease can be interpreted as indicating network rupture.

## 7 HYDROGEN-BOND RINGS

The knowledge of the probability of occurrence of bond rings and its dependence on temperature and density is of special interest for the following reasons: Speedy (1984) suggested that the presence and the aggregation behaviour of bulky pentagons may be responsible for the observed density fluctuations and entropy fluctuations in water; and low density ice, into which supercooled water nucleates very easily, is composed of hexagons, without any pentagonal hydrogen bond rings.

Using the method of Rahman and Stillinger (1973), we determine the number of hydrogen bond rings for different definition values  $V_{\text{HB}}$ . Figure 7 shows the number of pentagons  $N_5$  and hexagons  $N_6$  per water molecule, as a function of temperature  $T$  at constant density  $\rho = 1.0 \text{ g cm}^{-3}$  (figure 7(a)) and as a function of density at roughly constant temperature  $T \approx 273 \text{ K}$  (figure 7(b)). The results for two different  $V_{\text{HB}}$  are shown.

In figure 7(a) we also draw a curve, predicted by Speedy (1984) for the temperature dependence of pentagons at constant pressure  $p = 1 \text{ atm}$  (see also Speedy and Mezei 1985). One observes close agreement with our results for  $V_{\text{HB}} = -52\varepsilon = -3.94 \text{ kcal mol}^{-1}$ , a definition value in accord with the considerations of Stillinger and Rahman (1974). The stronger increase of Speedy's prediction is due to the fact that this curve also includes density changes. For both  $V_{\text{HB}}$ ,  $N_5$  and  $N_6$  show a marked parallel in the temperature dependence.

The density dependence of  $N_5$  and  $N_6$  is comparable with that of  $\langle n_{\text{HB}} \rangle$ . Lowering the density leads to an increased number of pentagons and hexagons. This indicates that the average structure of metastable water does not really approach an ice lattice structure, because then pentagons should vanish. At most one may say that the number of hexagons seems to increase slightly faster than that of pentagons. Hence, speaking of an approach to the structure of amorphous ice seems to be more appropriate. This is a result which conforms with recent neutron diffraction experiments of Dore (p.89).

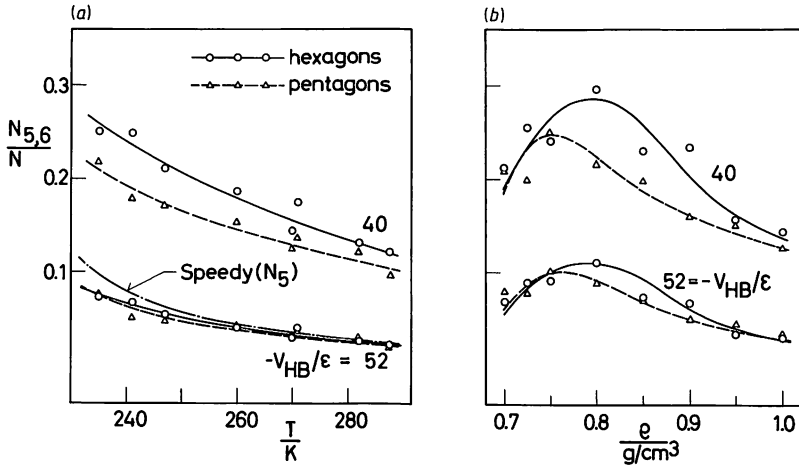


Figure 7. Average number of hydrogen bond rings per water molecule as a function of (a) temperature and (b) density for two different values of  $V_{HB}$ .

## 8 'HYDROPHOBIC CAVITIES'

To come finally to an even more complex structural unit, we mention here the first results of a recent study on cavities in water (Schnitker *et al* 1985). This study refers only to one state, ST2 water at  $T = 283$  K and  $\rho = 1.0$   $\text{g cm}^{-3}$ .

To obtain information about the distribution of cavities, we apply the following procedure. Using a random number generator, we statistically choose points in the periodic box containing the 216 water molecules. Then we check whether there is any oxygen atom closer than some fixed distance  $d_c$ . If we do find such an oxygen atom we reject this point, otherwise we keep it. In this way we trace out the void space. We did this for several values of  $d_c$ . Figure 8 shows one representative configuration: the cubic box of the 216 molecules with the points for  $d_c = 3.0$  Å. Now we bunch all those points into one group, which can be reached from some other member of the group within a distance of  $d_c$ . In this way we construct a small number of distant 'cavities'. (Of course, this procedure is only possible below the percolation threshold of the cavities, which is situated somewhere near 2.6 Å.) Next, we choose a 'centre' of the cavity by searching the one point within the group which has the greatest distance to its nearest oxygen.

In figure 9 we show the distribution of orientations of the water OH bonds with respect to this centre at position  $r_c$  (for a choice of  $d_c = 2.75$  Å):

$$\cos \theta = \hat{\mu}_{OH} \hat{\mu}_{Oc}$$

with

$$\hat{\mu}_{OH} = (r_O - r_H) / |r_O - r_H|$$

and

$$\hat{\mu}_{Oc} = (r_O - r_c) / |r_O - r_c|.$$

If we number the water molecules according to their distance from the cavity centre  $|r_O - r_c|$ , figure 9 represents the average over the three nearest neighbours. When using molecules 4 to 8 and 9 to 16 the distributions become less pronounced, but qualitatively they show exactly the same behaviour.

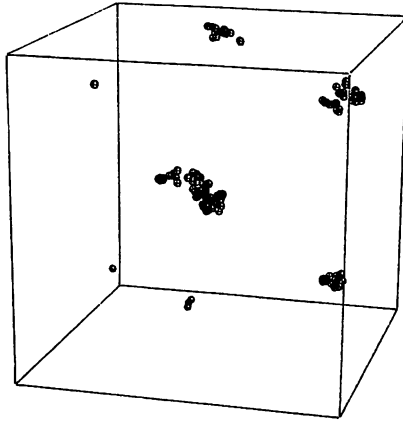


Figure 8. Distribution of cavities. Each point has a distance  $d_c$  of at least 3 Å to the next oxygen.

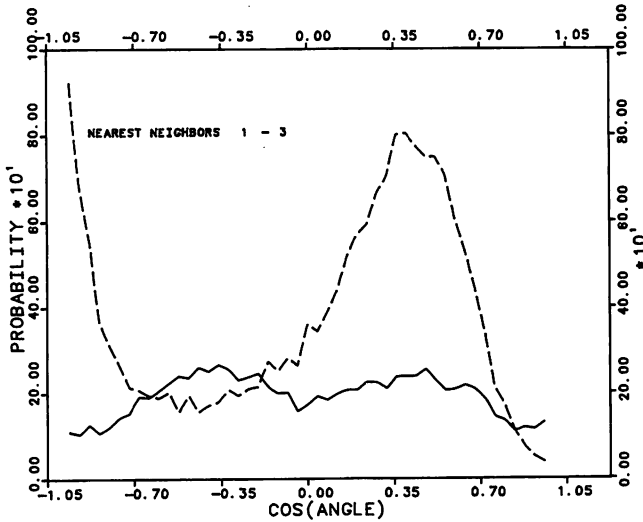


Figure 9. Distribution of orientations of the water OH covalent bond with respect to the centre of the cavities (three nearest water molecules).

It is striking to realise that the same shape of the distribution functions has been observed when studying the orientation of water molecules in the hydration shell of hydrophobic solutes (Geiger *et al* 1979a). Then the structure of the hydration shell was characterised as 'clathrate-like', because the hydration shell molecules are oriented in such a way that one of the four tetrahedral bond directions points radially outward and the remaining three bond directions straddle the dissolved particle.

Figure 10 gives another indication of the fact that the cavity wall structure is comparable to the hydrophobic hydration shell. The correlation functions between cavity centres and oxygen  $g_{cO}(r)$  and hydrogens  $g_{cH}(r)$  peak within a distance of less than  $0.2 \text{ \AA}$ , indicating the straddling orientation of the OH bonds. A hump near  $3.8 \text{ \AA}$  is caused by the hydrogens pointing radially outward.

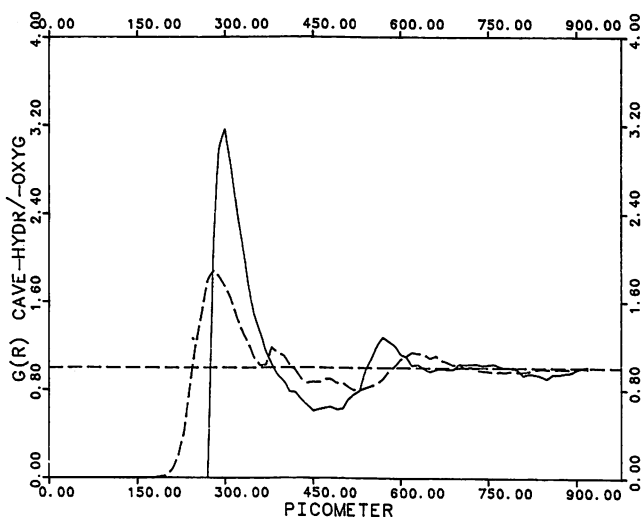


Figure 10. Pair correlation functions cavity centre-oxygen (full curve) and cavity centre-hydrogen (broken curve).

These cavities with 'hydrophobic' or clathrate-like shell structure are quite numerous. For  $d_c = 2.75 \text{ \AA}$  we observe 17 cavities per configuration. Using  $d_c = 3.0 \text{ \AA}$  we still find on the average 5.7 cavities per 216 water molecules, one cavity of a diameter (oxygen to oxygen)  $d \geq 6 \text{ \AA}$  per 38 water molecules.

In figure 11 the cavity centre-cavity centre distribution function  $g_{cc}(r)$  is given (for  $d_c = 2.75 \text{ \AA}$ ). And here again we observe a striking parallel to earlier studies concerning hydrophobic interaction. Simulating a neon pair dissolved in water, the system settled in a 'solvent-separated' pair formation, the neons having an average distance of about  $6.0 \text{ \AA}$  (Geiger *et al* 1979a). The structure of  $g_{cc}(r)$  indicates a similar arrangement (without dissolved particles), the separation of two adjacent cavities by a shared water layer corresponding to two adjacent cavities in a clathrate crystal.

The results reported in this section can be summarised as follows.

(a) In pure water we find a tendency for the formation of clathrate-like cavities, as was postulated some time ago by Pauling (1959).

(b) Due to thermal motion such cavities fluctuate and collapse quickly. The presence of nonpolar solute particles stabilises these structures, leading to the phenomenon of hydrophobic hydration as well as solvent-separated hydrophobic interaction.

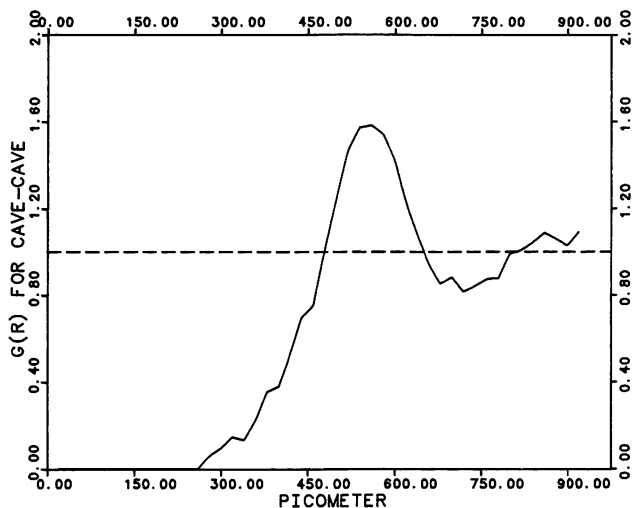


Figure 11. Cavity centre-cavity centre pair distribution function  $g_{cc}(r)$  for cavities of size  $d_c = 2.75 \text{ \AA}$ .

## 9 SELF-DIFFUSION

To give an idea of how the observed structural changes influence the dynamic properties of metastable water, we present here the mean-squared displacements  $\langle \Delta r^2(t) \rangle$  of the water molecules as a function of decreasing density (figure 12(a)) and the self-diffusion coefficients obtained from the slope of these curves (figure 12(b)).

Although the temperature is kept roughly constant for all the systems, the diffusional motion decreases drastically with density. This observation offers the possibility of understanding the mechanisms governing the single particle motion, which can probably be best understood along the lines suggested by Naberukhin (1984): it is the switching of hydrogen bonds rather than the rupture that has to be considered.

When a molecule is displaced, its hydrogen bonds with some neighbours become weaker, and those with other neighbours simultaneously become stronger, so that for example none of the hydrogens is at any moment outside the influence of hydrogen-bond forces, as can be deduced from intramolecular OH oscillator frequencies measured by IR spectra. This switching is possible if the system contains a certain number of bifurcated moderately strong hydrogen bonds.

As we discussed before, decreasing the density means lowering the number of neighbours and approaching a perfect tetrahedral local order. The number of bonding possibilities and in particular the number of bifurcated bonds is then reduced, leading to the observed decreased mobility.

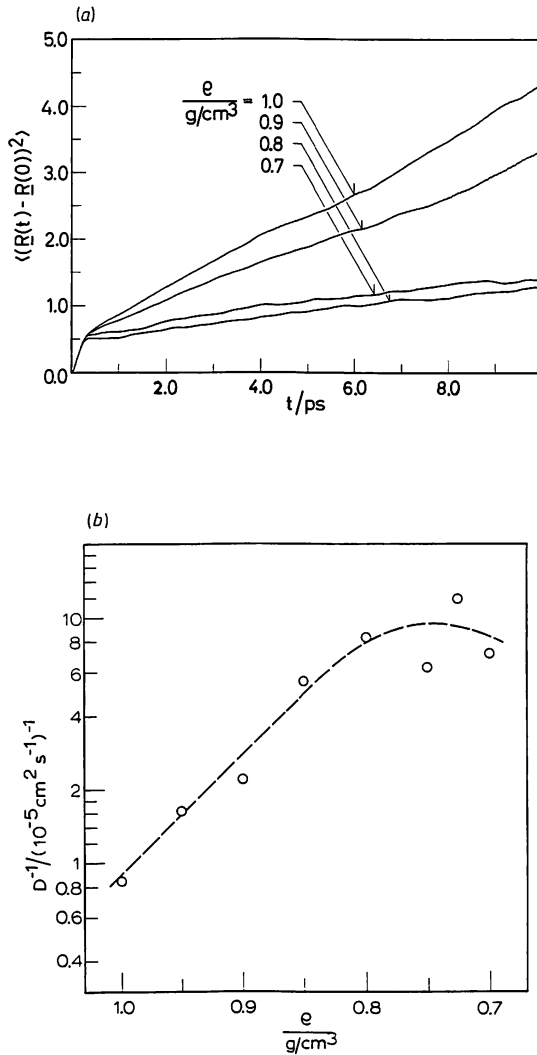


Figure 12. Density dependence of (a) mean squared displacement  $\langle \Delta r^2(t) \rangle$  of water oxygens and (b) self-diffusion coefficient  $D$ , obtained from the slope of  $\langle \Delta r^2(t) \rangle$ .

## 10 SUMMARY AND CONCLUSIONS

We have demonstrated that density has a major influence on the topology of the hydrogen-bond network. With decreasing density the local order becomes more tetrahedral: the number of neighbours decreases to four and local arrangements corresponding to more than four hydrogen bonds disappear. Moreover, the agreement between the network statistics of the liquid and the results of the percolation theory, which are based on the topology of hexagonal ice, becomes

very close. This does not mean that the real crystalline ice topology is obtained, as one can see from the fact that bond rings of sizes other than six are still present in appreciable numbers. Therefore, these structural changes are perhaps best described by an approach to amorphous ice, in agreement with the recent neutron scattering results of Dore (p.89).

A reversal in the tendencies of network structure changes is observed below a density of  $\rho = 0.8 \text{ g cm}^{-3}$ . This can be explained as a manifestation of network rupture. In this context, it is interesting to note that the density of  $0.8 \text{ g cm}^{-3}$  is in agreement with the density extrapolated by Speedy for the conjectured spinodal line which limits the region of metastability (Speedy 1982).

In contrast to the density dependence, the temperature dependence of the network structure is very small. The influence of temperature should presumably best be described by thermal excitation within the topological framework determined by the density.

Studying the influence of the changes in the hydrogen-bond network on the microdynamic properties helps us to understand the mechanisms governing molecular motions. The strong decrease in mobility with increasing tetrahedral local order underlines the importance of a 'switching motion' between close bonding possibilities, which appear at some instances as bifurcated hydrogen bonds. A direct measure for the frequency of such arrangements which support the mobility is also the probability of occurrence of five-bonded water molecules.

Finally, these observations lead to a very simple explanation for the occurrence of hydrophobic hydration: the presence of a nonpolar solute produces a decrease in local water density. The water molecules adopt an orientation, which is already prevalent in pure water as cavity structure and which allows the formation of four hydrogen bonds; but there is no space for a fifth bonding possibility. When the 'catalytic' action of this fifth bond is missing the mobility of the water molecules is reduced, leading also to an increased local order. Both effects had been observed in former MD simulations (Geiger *et al* 1979a), in accord with experimental findings.

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