HYDROGEN BOND RING STRUCTURES IN LIQUID WATER
A MOLECULAR DYNAMICS SIMULATION STUDY

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1. Introduction

The biological and technical importance of water as well as the prominence of its anomalies promoted a strong interest in the detailed description of its structure on a molecular level. One outstanding feature is the presence of a space-filling random network of hydrogen bonds (hb) [3] which shows a preference for the development of tetrahedral local order. The supercooled region of water is especially interesting because fluctuations and several fluctuation determined thermodynamic properties increase strongly while lowering the temperature. A possible divergence of these properties at $T_s \approx -46°C$ (at ambient pressure) is actually being discussed.

Several models have been proposed to account for this unique and fascinating behavior. We mention here the theories of STANLEY and TEIXEIRA [12], STILLINGER [15] and SPEEDY [10]. These models empasize the significance of certain structural elements which are imbedded in the hb-network and whose occurrence probability increases in a self-amplifying manner if the temperature decreases.

The so-called "polychromatic correlated-site percolation model" of STANLEY and TEIXEIRA [12] uses the idea of a geometric cooperativity: the clustering of fourfold h-bonded water molecules (characterized by reduced local density and enhanced local order) exhibits a percolation threshold at T_s. STILLINGER [15] developed a partition function in terms of two order parameters ψ and θ which describe the concentration of bicyclic octamers (bifurcated hexagonal hb-rings) and other bulky, unstrained polyhedra on the one hand, and the average potential energy of the molecules on the other hand. The corresponding $\psi-\theta$-surface then implies the possibility of a "catastrophe" with diverging fluctuations in the supercooled water regime. The model of SPEEDY [10] also uses the idea of a geometric cooperativity. He argues that pentagonal hb-rings have a natural tendency for "self-replication". Thus bulky low-density patches are generated. In this model the increase of the fluctuations is connected with an approach of a limit of mechanical stability. At this boundary—a spinodal line—the fluctuations grow without limit. This line is supposed to run continuously from the supercooled region through the region of negative pressure ("stretched water") up to the critical point.

The importance of h-bond rings has also been discussed by several other authors. For example, TORCHET *et al.* [16] could only fit their electron diffraction data on smal

water clusters, if the occurrence of distorted rings of three to six molecules was allowed. The unability of the SCEATS–RICE random network model [9] to produce the "anomalous" properties of water suggests again the importance of h-bond ring closures which are ignored in this Cayley-tree based model.

In a current simulation project we study the occurence of the different structural units, proposed in the various models. In earlier studies we concentrated on the distribution of h-bonds and the clustering of fourbonded water molecules [1, 4]. Here we investigate the occurence of hb-ring structures. For this purpose we evaluate two series of water simulations, comprising eight runs each, which penetrate into the supercooled as well as the stretched water region. Polygon-polygon correlations are calculated for hb-rings of size three to eight and interpreted in terms of simple geometrical arrangements. The temperature and density dependence of the distributions is discussed in detail for the most interesting species, i.e. pentagons and hexagons.

2. Details of the MD Simulations

In all simulation runs we use systems of 216 water molecules, which are confined to a cubic box under periodic boundary conditions. The water-water interaction is described by the ST2 pair potential [14]. The direct interaction cutoff ($R = 7.8$ A) is supplemented by a reaction field [13]. The equations of motion are integrated with the Verlet algorithm in Cartesian coordinates, applying constraint forces to keep the molecules rigid [8]. The timestep is $t = 1.22 \cdot 10^{-15}$ s.

To separate the influences of temperature and density on the h-bond network we performed two distinct series of simulations. In one we keep the density constant at $\varrho = 1.0$ g/cm³ and vary the temperature in eight steps from $T = 287$ K to 235 K. In other we vary density from $\varrho = 1.0$ to 0.7 g/cm³ at roughly constant temperature of $T = 275$ K. Thus in the first series we are penetrating into the metastable supercooled region of water, in the second into the metastable "stretched" water region.
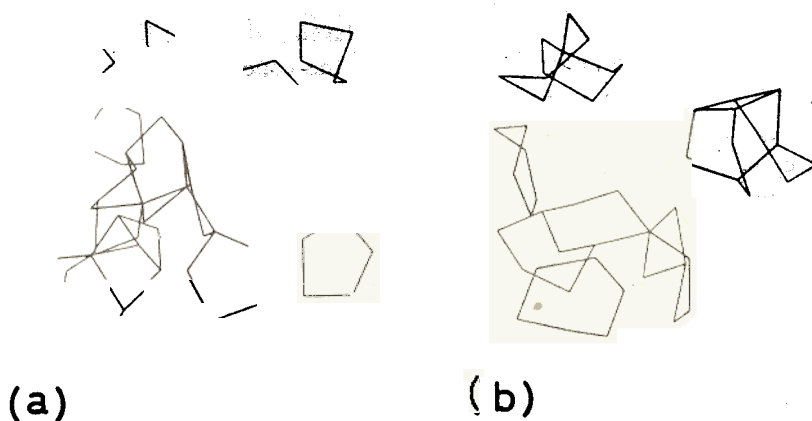

$$(a) \qquad\qquad (b)$$

FIG. 1. Snapshot of random distribution of pentagonal (a) and hexagonal (b) hb-rings in liquid water
$T = 282$ K, $\varrho = 1.0$ g/cm³, $V_{HB} = -3.03$ kcal/mole.

Since relaxation times increase strongly in the metastable region, we apply very long equilibration runs: up to 300 ps in the stretched water region. A more detailed description of the simulation runs is given in [4, 5]. The computations were performed on a VAX 11/780 with an attached array processor FPS 164.

To detect non short-circuited hydrogen bond-rings, we utilize the pattern recognition routine of RAHMAN and STILLINGER [7]. This program identifies polygons of various size that occur in the hydrogen-bond network. Figure 1 illustrates the distribution of pentagons and hexagons in a randomly selected configuration.

3. Occurence Probability and Distribution of Polygons

In accord with our previous h-bond network analysis the following definition of h-bond is used: Two water molecules i and j are considered to be bonded, if their interaction energy V_{ij} lies below a negative cutoff value V_{HB} and their mutual oxygen-oxygen separation is less than 3.5A. As before we do not choose just one threshold value V_{HB}, but do all analysis calculations for a whole series of V_{HB} values, taking into account that h-bonds of various strengths are present. Thus the problems are circumvented that would be implied by the use of only one (arbitrary) bond definition.

Having identified a (non short-circuited) h-bond ring, its position is defined as the center of mass of the assembly of water molecules forming the polygon. Next, radial pair distribution functions $g_{\alpha\beta}(R)$ are determined, where $4\pi R^2 \varrho_\beta g_{\alpha\beta}(R)dR$ gives the number of polygons one finds on the average within a center of mass distance R and $R+dR$ from a reference polygon α (ϱ_β is the average number density of polygons β).

Figure 2 shows pentagon-pentagon correlation functions g_{55} R for different V_{HB}-values: at $T = 282$ K and water density $\varrho = 1.0$ g/cm³. Three very marked peaks are observed. The third at $R = 3.2$ A is the most interesting one and has already been discussed by SPEEDY and MEZEI [11]. It corresponds to a clathrate-like arrangement as indicated in Fig. 2. The aggregation of pentagons in such a bulky ordered form has been made responsible for the occuring density and entropy fluctuations in supercooled water [10]. The peak structure becomes more pronounced if we eliminate weak h-bonds by varying V_{HB} from −2.1 to −3.9 kcal/mole. The same behavior is shown for example by the pair distribution function of the four-bonded water molecules [6]. Note that with decreasing V_{HB} (increasing strictness of the h-bond definition) fewer pentagons are found, therefore the pair distribution function becomes very noisy.

The first two peaks in $g_{55}(R)$ can be understood easier when we discuss the systematic behavior of $g_{pp}(R)$, the distribution functions of bond rings of size p. Figure 3 shows $g_{pp}(R)$ for ring sizes $p = 3$ to 8 at $T = 282$ K and $\varrho = 1.0$ g/cm³. Obviously, $g_{pp}(R)$ contains p-2 marked peaks (for example 3 peaks for the pentagon distribution). This can be explained as follows: the first peak of $g_{pp}(R)$ represents arrangements of two bifurcated polygons with p-2 common h-bonds, the second corresponds to bifurcated polygons with p-2 common h-bonds, the second corresponds to bifurcated polygons with p-3 common h-bonds etc. ... In the following Figs. 4 to 6 these geometric arrangements are drawn close to the corresponding peak. These figures give the distribution of pentagons $g_{55}(R)$

and hexagons $g_{66}(R)$ and the corresponding cross-correlation function $g_{56}(R)$ for the supercooled and the stretched water series, using a fixed h-bond definition with $V_{HB} = -3.0$ kcal/mole.
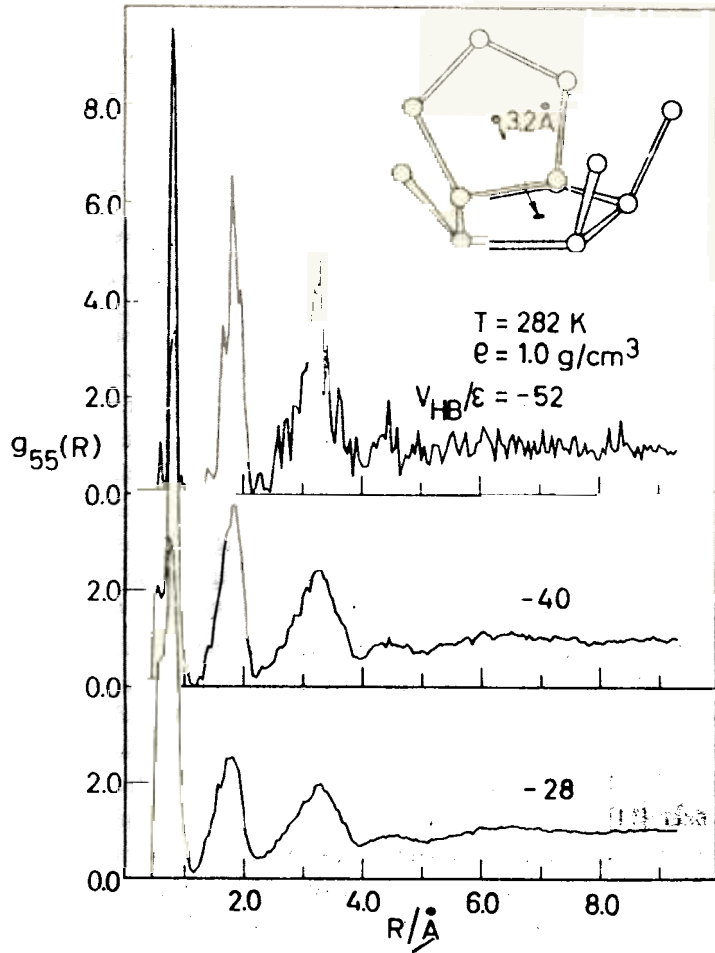

FIG. 2. The pentagon-pentagon radial distribution function $g_{55}(R)$ for different V_{HB}-values at $T = 282$ K and $\varrho = 1.0$ g/cm³, $\varepsilon = 0.07575$ kcal/mole.

As Fig. 4a reveals, on temperature decrease from $T = 287$ K to 235 K the first two peaks of $g_{55}(R)$ are reduced. This means that the occuring ring aggregations shift from the compact forms to the more open clathrate-like structures.

Additionally, at the low temperatures, $g_{55}(R)$ becomes structured in the region of 4 to 7 A indicating correlations between not directly connected rings.

The same features appear in a much more pronounced way when studying the density dependence (Fig. 4b). This corresponds to our earlier experience that density has a much stronger influence on the h-bond network structure than temperature [5]. The first peak of $g_{55}(R)$ disappears totally at $\varrho = 0.8$ g/cm³, reappearing at 0.7 g/cm³. We observed a similar behavior with respect to many thermodynamic, structural and microdynamic
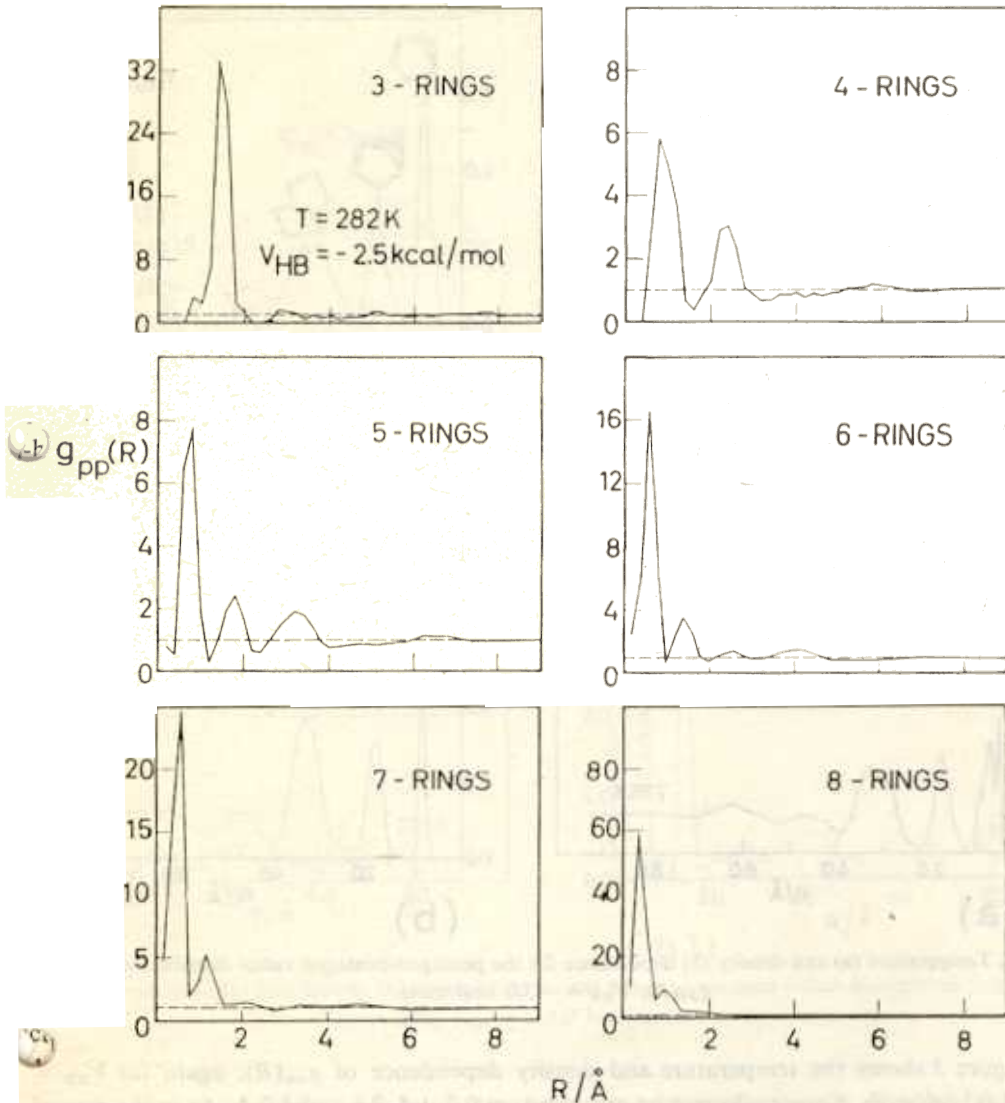
FIG. 3. Polygon-polygon radial distribution functions $g_{pp}(R)$ for hb-rings of size three to eight for $T = 282$ K $\varrho = 1.0$ g/cm^3 and $V_{HB} = -2.5$ kcal/mole.

properties: an extremum is passed in this density region, which has been interpreted by us to be due to an onset of network disruption and whose position corresponds to the density at the spinodal line in the stretched water region [10]. Also, the structuredness of $g_{55}(R)$ at larger distances becomes very pronounced at low ϱ. There is a well resolved peak at 4.7 A and a broader one between 6 and 7 A. Configurations which correspond to these peaks have been discussed by SPEEDY and MEZEI (Figs. 8c resp. 8a/b of ref. [11], but these authors could not find these peaks at the density of 1.0 g/cm^3, in agreement with our calculations.
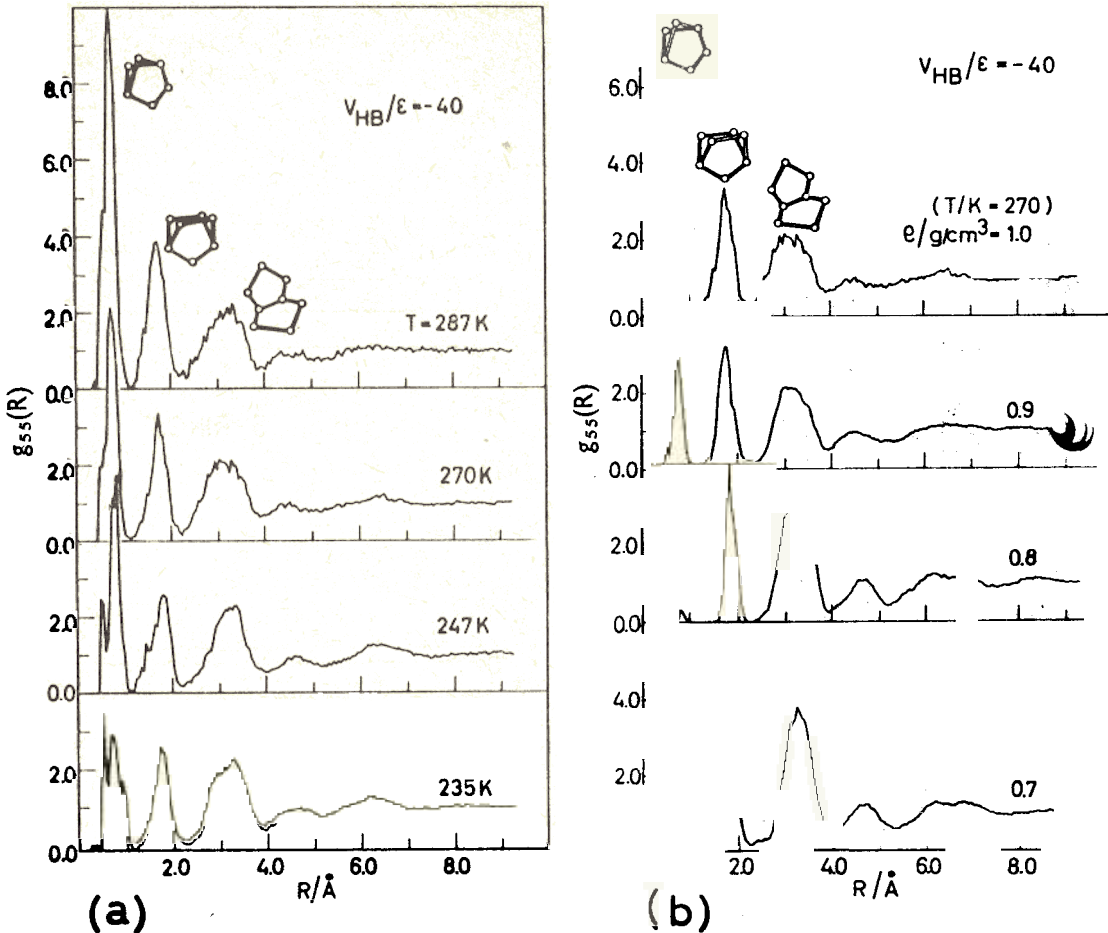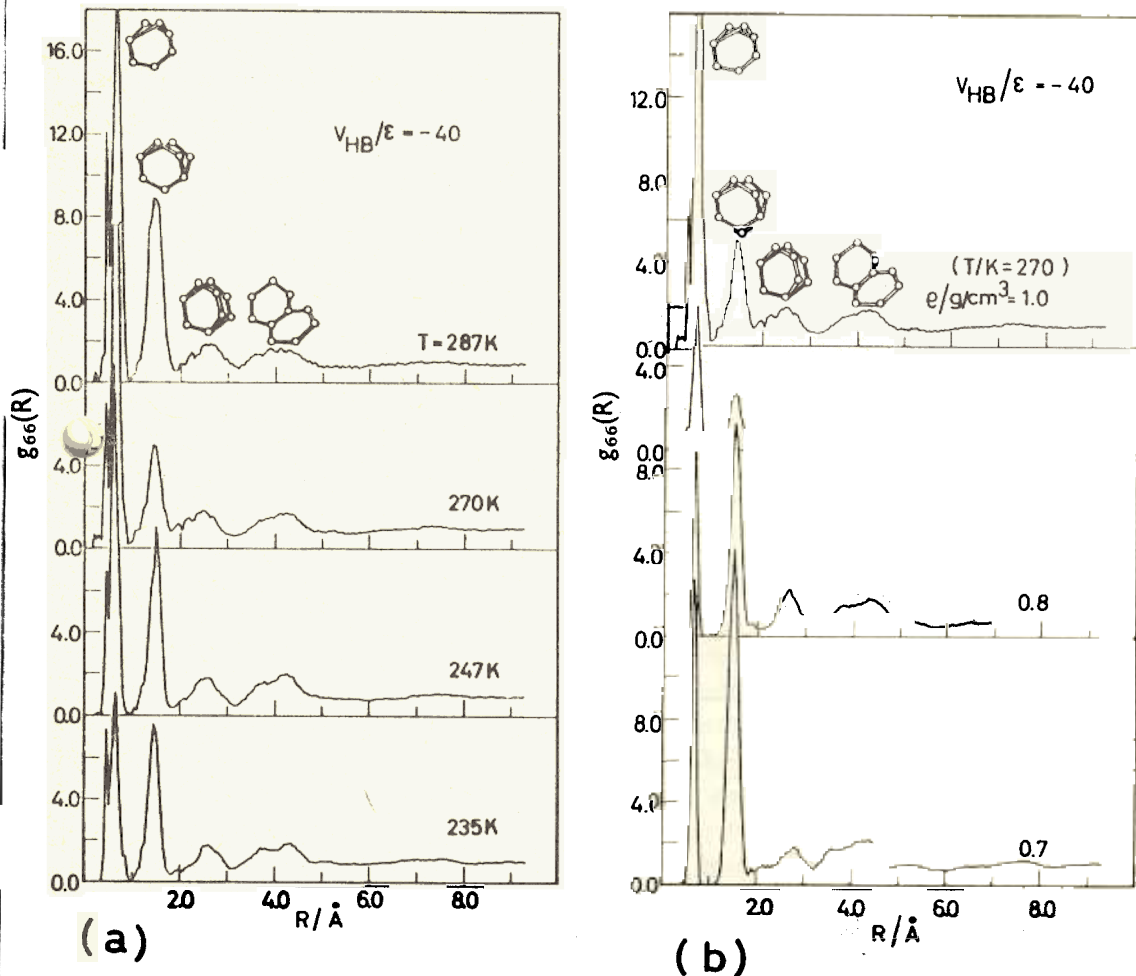
FIG. 4. Temperature (a) and density (b) dependence for the pentagon-pentagon radial distribution function $g_{55}(R)$, $V_{HB} = -3.0$ kcal/mole.

Figure 5 shows the temperature and density dependence of $g_{66}(R)$, again for $V_{HB} = -3.0$ kcal/mole. Four peaks can be perceived: at 0.7, 1.5, 2.6 and 4.0 A. As in the case of $g_{55}(R)$, temperature reduction causes a diminution of the first peak and the corresponding density dependence shows a minimum near 0.85 g/cm³. The second peak of $g_{66}(R)$, which can be attributed to the bicyclic octamers of STILLINGER [15] shows a strikingly increasing dominance at low densities.

In Fig. 6 the density dependence of the cross-correlation function $g_{56}(R)$ is shown. Two pronounced maxima are situated at 2.2 and 3.7 A. The first one is positioned between the second peak of $g_{55}(R)$ at 1.7 A and the third peak of $g_{66}(R)$ at 2.6 A, and is probably due to pentagon-hexagon pairs with two common h-bonds. The peak at 3.7 A in $g_{56}(R)$ lies between the third peak of $g_{55}(R)$ and the fourth one of $g_{66}(R)$ at 3.2 A and 4.0 A, respectively. Therefore a pentagon-hexagon pair with one common bond seems to be the corresponding configuration.

. 5. Temperature (a) and density (b) dependence for the hexagon-hexagon radial distribution function $g_{66}(R)$, $V_{HB} = -3.0$ kcal/mole.

Pentagon-hexagon pairs with more than two common bonds are not detected because the hexagon is then excluded as a short-circuited polygon by the pattern recognition routine [7]. The density dependence is very small, but qualitatively the same as for $g_{55}(R)$ and $g_{66}(R)$. The temperature dependence (not shown) of $g_{56}(R)$ is practically vanishing. We also calculated other correlations as $g_{45}(R)$, $g_{57}(R)$ etc., and find a similar behavior as in the case of $g_{56}(R)$.

In Fig. 7 the occurrence probabilities of the pentagonal and hexagonal h-bond rings per water molecule N_5/N and N_6/N are shown as a function of temperature and density for two different definition values V_{HB}. The temperature dependence predicted by SPEEDY [10] is also drawn in Fig. 7a for comparison. There is very good agreement with our results for $V_{HB} = -3.9$ kcal/mole and h-bond definition close to the -4.0 kcal/mole, suggested by STILLINGER and RAHMAN [14] to be the most reasonable choice. The stronger

increase of Speedy's curve at low temperatures is also in accord with our simulations: He considered water at constant pressure of $p = 1$ atm. As one can see from the density dependence (Fig. 7b) the expansion of water at low temperatures results in an additional increase of N_5.
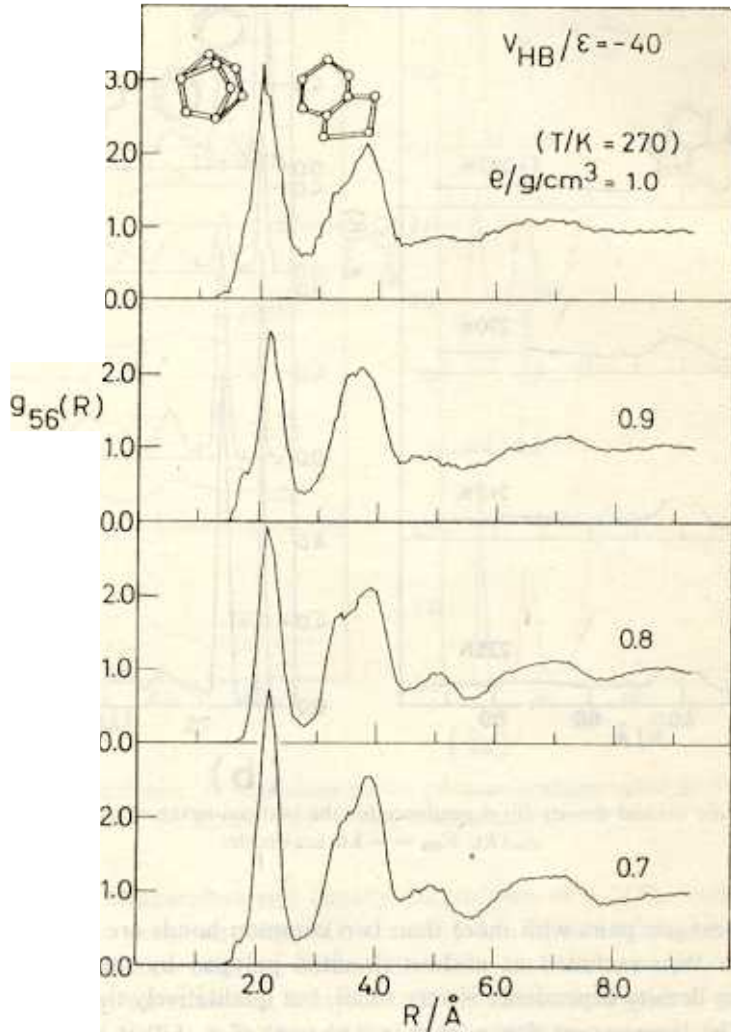

FIG. 6. Density dependence for the cross-correlation function of pentagons and hexagons g_{56} R, $V_{HB} =$ = -3.0 kcal/mole.

The density dependence of N_5 and N_6 shows again an extremum close to 0.8 g/cm^3. With decreasing density the hexagons seem to increase slightly faster than the pentagons initially.
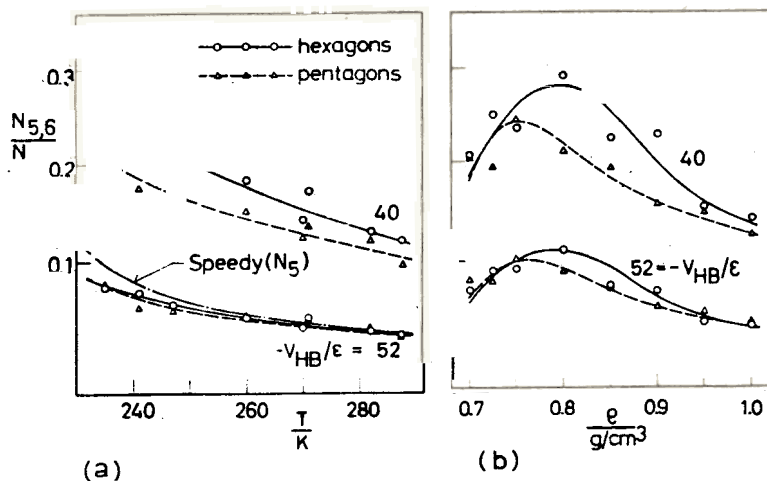
FIG. 7. Occurrence probability of pentagonal and hexagonal hb-rings, temperature (a), density (b) dependence.

4. Conclusions

The results of this study of the aggregation of hydrogen-bond rings do not particularly favor any of the proposed structural models, which concentrate on just one kind of bond rings and aggregation structures. The occurrence probability of pentagons is in good agreement with Speedy's predictions and clathrate-like arrangements of pentagons can also be found; but these structures are by no means dominant. In fact'hexagons show a comparable growth behavior and the increase of the second peak in $g_{66}(R)$ shows an increasing number of bicyclic octamers. Those had been favored in Stillinger's model. The nearly parallel increase of N_5 with N_6 also discords the possibility of an approach to hexagonal or cubic ice structures. Then pentagons should disappear.

Perhaps, the best description of the observed structural changes in the metastable water region is an approach to the structure of amorphous ice, where h-bond rings of all types are expected. The agreement with recent neutron scattering results on amorphous ice [2] with the corresponding distribution functions from our simulations [6] supports this characterization.

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Streszczenie

STRUKTURY PIERŚCIENIOWE W CIEKŁEJ WODZIE WYWOŁANE WIĄZANIAMI
WODOROWYMI
BADANIA SYMULACYJNE DYNAMIKI MOLEKULARNEJ

Dla zbadania modeli strukturalnych wody ciekłej zanalizowano zależność gęstości i temperatury struktur pierścieniowych w obszarach przechłodzonych i poddanych ujemnym ciśnieniem („rozciągana woda"); badania oparto na symulacjach molekularno-dynamicznych (MD).

Резюме

КОЛЬЦЕВЫЕ СТРУКТУРЫ В ЖИДКОЙ ВОДЕ ВЫЗВАННЫЕ ВОДОРОДНЫМИ СВЯЗЯМИ
ИМИТАЦИОННЫЕ ИССЛЕДОВАНИЯ МОЛЕКУЛЯРНОЙ ДИНАМИКИ

Для исследования структурных моделей жидкой воды проанализирована зависимость плотности и температуры кольцевых структур в переохлажденных областях и подвергнутых отрицательным давлениям („растягиваемая вода"); исследования опираются на молекулярно-динамические (МД) имитации.

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