

## RADIAL DISTRIBUTION FUNCTIONS OF ATOMS AND VOIDS IN LARGE COMPUTER MODELS OF WATER

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The molecular dynamics method is employed to construct models of 5832 water molecules at temperatures from 330 K to 250 K. The radial distributions of atoms and interstitial voids, as well as the corresponding structural factors, have been calculated. The first maximum of the structural factor of voids coincides in its position with the first maximum of the structural factor of oxygen atoms. Thus the first diffraction peak of water located at much smaller angles than for normal liquids (so-called prepeak) is caused by correlations in the arrangement of voids. The tetrahedrality of the hydrogen bond net of water described in different ways becomes more pronounced after overcooling of water.

**Keywords:** liquid and overcooled water, computer models, radial distribution functions, voids.

### INTRODUCTION

Structural and dynamic inhomogeneities in computer models of water were studied in a series of works [1-4] both at ambient temperature and under conditions of overcooling, which simulate loose and dense amorphous phases of water. Inhomogeneities are typically sized ~1 nm and consist of hundreds of molecules. The largest among the models included 729 molecules. Apparently, these models are too small for studying large-scale correlations believed to be an essential structural feature of water. Here we describe a much larger model, consisting of 5832 molecules. We did not examine inhomogeneities in this work; instead, we considered more traditional features of large models, namely, the radial distributions of atoms and voids. Large models have significant advantages: effective averaging of noise at large distances in the radial distribution functions and thus more correct calculation of the structural factor.

The atomic radial distribution function is a well-known and most widespread tool in structural analysis. The radial distribution function of voids, however, has been introduced not long ago in view of the application of the Voronoi–Delaunay methods to analysis of computer models (see monograph [5] for more details). Examination of interatomic (interstitial) voids in disordered systems is interesting in itself as an alternative aspect of atomic structure effectively employed in crystallography [6]. However, when applied to water models, this allows us to solve one more important problem, namely, to explain the unusual form of the curve of their structural factor.

As a matter of fact, on the curve of the structural factor of liquid water and its amorphous phases, the first peak lies at anomalously small values of the wave vector  $q$ . In this respect, water resembles amorphous inorganic glasses such as Si, Ge, SiO<sub>2</sub>, ZnCl<sub>2</sub>, etc. Their curves contain a peak at even smaller  $q$  often referred to as prepeak. For glasses [7, 8] and water [9], the prepeak was associated by Elliott with correlated arrangement of voids in these substances. However, he described

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**TABLE 1.** Parameters of the Models

Temperature, K	250	260	270	290	330
Cube edge, nm	5.847	5.800	5.700	5.614	5.598
Density, g/cm <sup>3</sup>	0.8725	0.8939	0.9418	0.9858	0.9942

this correlation in terms of so-called “chemical ordering,” which has no illustrative structural interpretation. This explanation became convincing only after calculation of radial distributions for voids and the corresponding structural factor for glass [10] and water [11] models. Importantly, a prepeak appears in the structural factor of voids only in the case of correlated arrangement of voids. This was proven [12] by using specially constructed models. In this work, we continue analysis of voids carried out [11] for the water model of 256 molecules. It is demonstrated once again that the prepeak of water is actually caused by correlations in the spatial arrangement of interstitial voids.

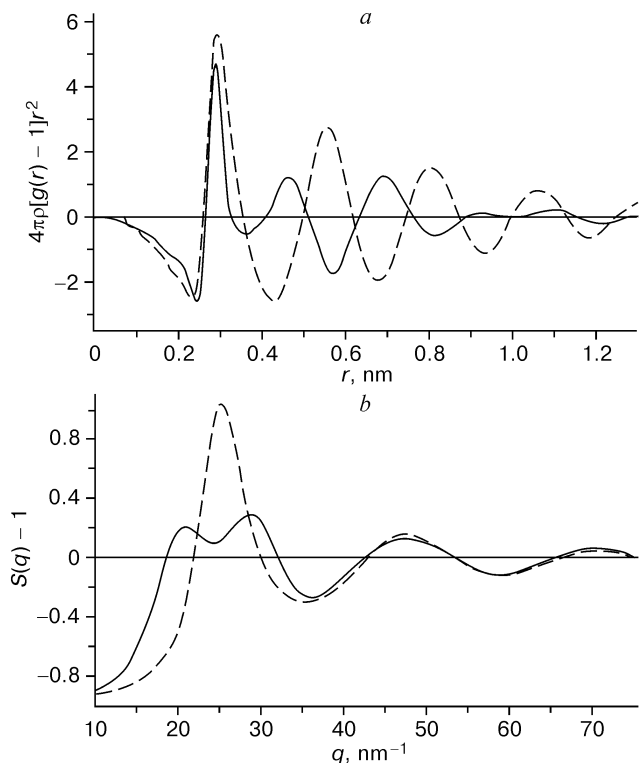
## MODELS

A model of 5832 molecules was created from 27 models of 216 water molecules constructed earlier [13] with the ST2 potential at several values of temperature and density indicated in Table 1 (also giving cell dimensions for large models) by their integration within the same cube. The resulting model was relaxed by the molecular dynamics method at an appropriate temperature. Relaxation led to equilibrium at most temperatures, as suggested by the invariance of radial distributions during calculation. The only exception was 250 K, at which we failed to reach the equilibrium state because the radial distributions continued to change at the end of the relaxation process. Thus the model at 250 K remained incompletely relaxed, which is shown by the shape of the radial distribution functions (see below). However, this model may be used for qualitative discussion.

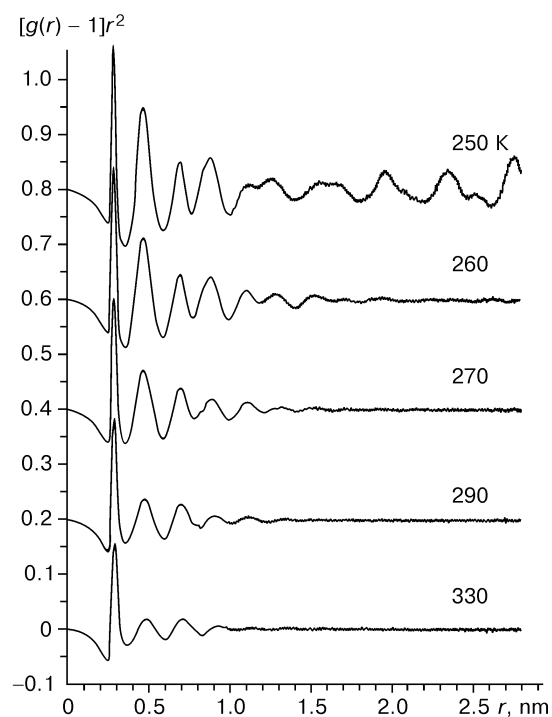
## ATOMIC RADIAL DISTRIBUTION FUNCTION

The pair correlation function  $g(r)$  is the most common structural characteristic of liquids, generally shown in pictures. However, it quickly decays with distance and is therefore convenient for describing only short-range order. To visualize long-range correlations, the *difference* radial distribution function (DRDF)  $G(r) = r^2[g(r) - 1]$  is more convenient; it clearly demonstrates the character of long-range oscillations. This work deals only with distributions of the centers of water molecules assumed to coincide with the centers of oxygen atoms. Therefore,  $g(r)$  is understood here as the pair correlation function  $g_{OO}(r)$  of oxygen atoms. The DRDF of water has some features that distinguish water from simple liquids. Figure 1a shows the behavior of the DRDF obtained in a diffraction experiment for real liquids. For neon as a simple close-packed liquid (atomic size is close to the molecular size of water), regular exponential damping of oscillations occurs, and the second maximum lies at a distance  $R_2$ , which is a nearly doubled distance to the first peak:  $R_2 \approx 2R_1$ . This is typical of all simple liquids and for close packing of solid spheres. The situation is different for water. The second peak is determined by the second neighbors in the tetrahedral net of hydrogen bonds; its position at  $R_2 \approx 1.63R_1$  corresponds to the tetrahedral angle between two H bonds, as pointed out in the classical work of Bernal and Fowler [18]. The third maximum relates to distances in the six-, seven-, and eight-membered rings of hydrogen bonds. Oscillations at distances greater than 9 Å cannot be seen at all at ambient temperature. The absence of correlations at  $r > 9$  Å probably suggests strong fluctuations of torsion angles between H bonds in different rings. Irregular behavior of this kind is difficult to notice on the plot of the  $g(r)$  function.

Figure 2 shows the behavior of the model DRDFs for water at different temperatures. Each curve is obtained by averaging over 1075 configurations at a given temperature. The model at  $T = 250$  K is an exception; averaging in it was done over the last 258 configurations. A single configuration is enough to calculate  $g(r)$  for our large models with a low level of noise. However, a single configuration is not enough to trace  $G(r)$  at long distances. In this case, the multiplier  $r^2$  leads to a strong increase in statistical noise at large values of  $r$ . The curve for 330 K demonstrates that there are actually no oscillations



**Fig. 1.** Plots of difference radial distribution functions (a) and structural factor (b) for water (25°C, solid lines [14]) and liquid neon (35 K, dashed line [15]). The scale of  $r$  for neon is decreased by 1.07 to make the positions of the first peak of  $g(r)$  coincide with each other. The pair correlation function  $g(r)$  of the water oxygen atoms was calculated from Narten's experimental data on  $S(q)$  [14] by the procedure described in [16] that eliminates abrupt maxima (see also [17]).



**Fig. 2.** Difference radial distribution function of oxygen atoms for water models at different temperatures.

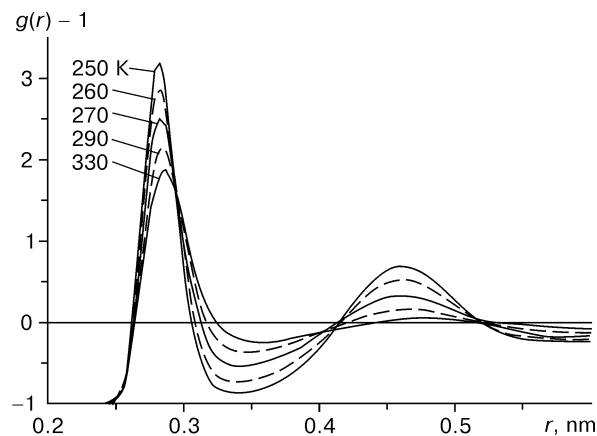
at this temperature in water at long distances. Only three peaks remained, which is in good agreement with the experiment (compare with Fig. 1a): the calculation gave only slightly higher intensity of the first peak, which is the specifics of the ST2 potential.

At elevated temperatures, we can visualize increased height of the second peak of the DRDF and deeper valley between the first and second maxima; the latter can be seen more clearly on the  $g(r)$  function (Fig. 3). A similar picture was also observed at lower densities [19]. This is indicative of enhanced local tetrahedrality in the structure of water. Second, the oscillation amplitude gradually increases, and correlations become notable at increasingly long distances. This evidently means that local tetrahedral order enhances the correlations of torsion angles between hydrogen bonds.

The DRDF for 250 K is inconsistent with the general pattern in Fig. 2. Strengthening of long-range correlations has no physical sense and demonstrates that this model is insufficiently relaxed and retains long-range order. This cannot be seen on the  $g(r)$  function; therefore, the behavior of DRDF at long distances can serve as a quality criterion for computer models.

## RADIAL DISTRIBUTION OF VOIDS

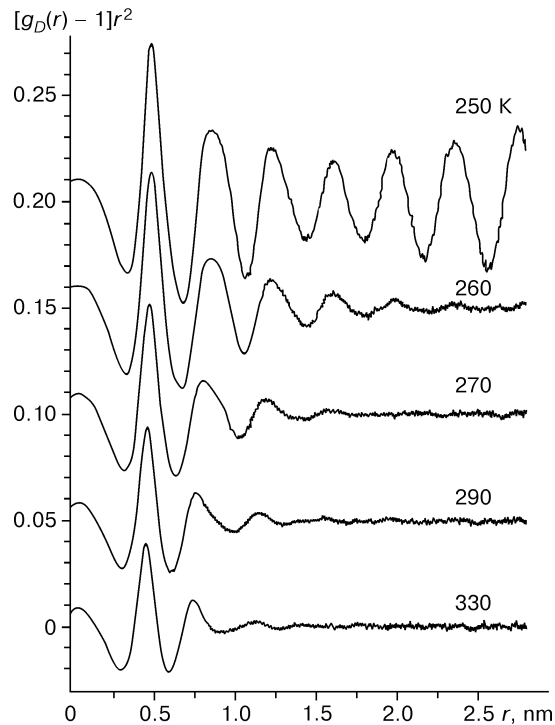
The distribution of distances between atoms is only one aspect of system structure. Additional information about the structure of water may be derived by Voronoi–Delaunay geometrical methods, which were very effective in analysis of computer models for simple liquids [20, 21]. In addition to a set of points  $\{A\}$  that represent the centers of atoms (water



**Fig. 3.** Pair correlation function of water oxygen atoms at different temperatures.

oxygen atoms in our case) in a system, these methods consider an alternative set of points  $\{D\}$  that are nodes on the Voronoi net. The net is composed of edges from the whole tessellation of Voronoi polyhedra constructed for atoms of the system (for points of set  $\{A\}$ ) [5]. The sites of this net (vertices of the Voronoi polyhedra) are the centers of interstitial empty spheres that can be inscribed between the nearest four atoms. These four atoms define the vertices of a tetrahedron called a Delaunay simplex [5]. Thus  $\{D\}$  is a set of the centers of Delaunay simplices. The structural sense of points from set  $\{D\}$  is describing empty interatomic space. The latter is explicitly defined by the arrangement of atoms so that both sets,  $\{A\}$  and  $\{D\}$ , are complementary representatives of system's structure.

For set  $\{D\}$ , it is possible to construct a pair correlation function similar to the  $g(r)$  function for set  $\{A\}$ ; it is designated as  $g_D(r)$ . The corresponding difference radial distribution function is  $G_D(r) = [g_D(r) - 1]r^2$ . The functions  $G_D(r)$  for our models are shown in Fig. 4. Fifty configurations is enough for averaging here because the number of Delaunay simplices



**Fig. 4.** Difference radial distribution function of the centers of interstitial voids in the water models at different temperatures.

(more than 40,000) in each configuration is much larger than the number of molecules. When interpreting the functions  $G_D(r)$ , one should keep in mind the fundamental difference between sets  $\{A\}$  and  $\{D\}$ . While the distance between each pair of points in  $\{A\}$  remains always finite because of repulsion between adjacent atoms, the points in  $\{D\}$  may be randomly close. This leads to a maximum at zero for  $g_D(r)$  and at about 0.1 nm for  $G_D(r)$ . This kind of maximum is associated with overlapped interstitial spheres and is typical not only for water, but also for other noncrystalline systems like Lennard-Jones liquids and glasses [6, 12].

The fundamental maximum of the function  $G_D(r)$  lies at 0.45 nm at  $T=330$  K and gradually shifts to 0.5 nm as the temperature decreases to 250 K. It probably corresponds to the distance between the centers of the nearest ring voids between water molecules. For Ih ice, this distance coincides with the distance between the second molecules in H bonds, i.e., with the position of the second peak  $R_2$  on  $g(r)$ . However, the temperature dependence of the position of  $R_2$  is the inverse of that of the fundamental maximum of  $G_D(r)$  (compare Figs. 2 and 4). This means that network topology of overcooled water differs from that of ice.

Figure 4 demonstrates that there are clear correlations in the arrangement of voids, which become more distinct at reduced temperatures. These correlations are obviously significant elements in the structure of the hydrogen bond net of water. Here again one can see amplification of oscillations at 250 K at long distances, which is an indication to incomplete relaxation of this model.

## STRUCTURAL FACTOR FOR VOIDS

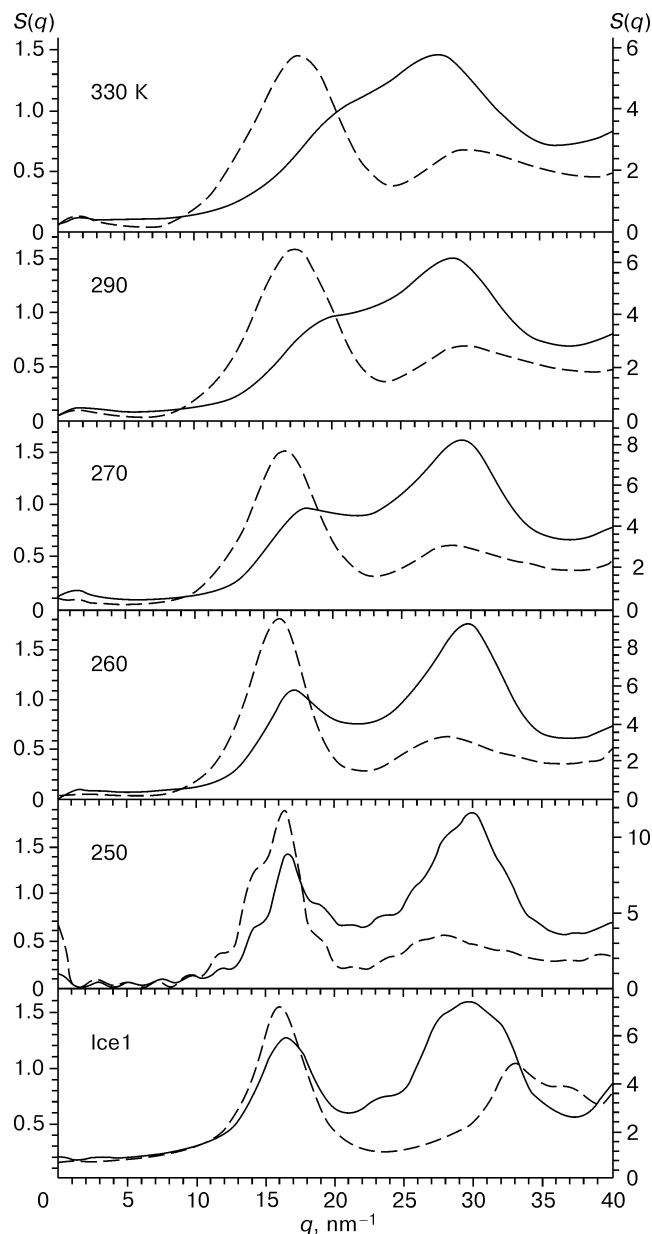
The experimental structural factor  $S(q)$  of water is characterized by the doublet structure of the first peak not inherent in simple liquids, where it is unimodal (Fig. 1b). The first maximum of this doublet lies at anomalously low values of the wave vector ( $Q_1 = 20 \text{ nm}^{-1}$ ), so it is often referred to as prepeak by analogy with a similar peak in glasses. Computer models adequately reproduce this feature of water, although the intensity ratio for the doublet does not agree with the experimental ratio at ambient temperature, and the prepeak is found at lower values of the wave vector ( $16\text{-}18 \text{ nm}^{-1}$ ) than in experiment. Analysis of literature data indicates that the doublet structure is extremely sensitive to the type of model potential. Since the ST2 potential is far from being perfect, it is no wonder that it fails to adequately describe details of the structural factor.

Figure 5 shows the temperature evolution of the fundamental peak of the structural factor calculated as Fourier integral of RDF for our models:

$$S(q) - 1 = \frac{4\pi\rho}{q} \int_0^{\infty} r[g(r) - 1] \sin(qr) dr. \quad (1)$$

One can see that at reduced temperatures the doublet becomes increasingly resolved due to the narrowing of components. As mentioned above, the prepeak on the curve of the structural factor of covalent glasses and water was correlated with the arrangement of voids. We can now verify this assumption.

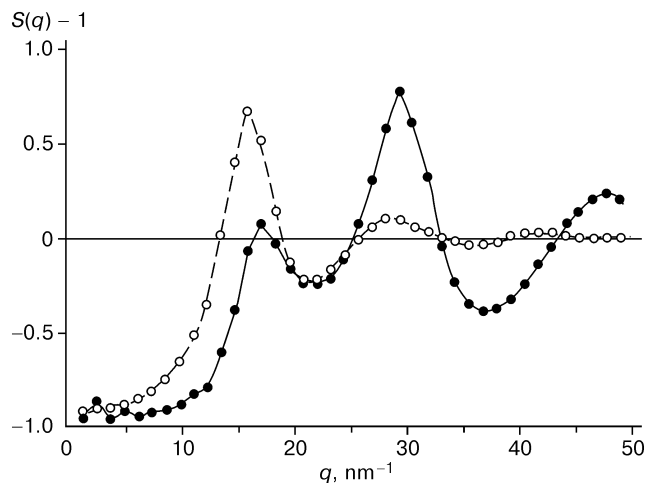
The “structural factor of voids”  $S_D(q)$ , or to be more exact, the structural factor for set of points  $\{D\}$  may be calculated by substituting  $g_D(r)$  for  $g(r)$  in formula (1). The resulting functions are shown in Fig. 5 (dashed lines) together with the structural factor for water that reflects diffraction on oxygen atoms. We can see that the curve of the structural factor for voids shows a pronounced first peak, whose position at low temperatures coincides with the position of the prepeak of the structural factor of water and thermally excited ice. This coincidence becomes still more obvious if prior to calculation of the structural factor for voids the first maximum is excluded from  $g_D(r)$  at distances from 0 to 0.3 nm. Then the structural factor  $S_D(q)$  for voids, as well as the structural factor  $S(q)$  for atoms, oscillates around unity (Fig. 6). At elevated temperatures, comparison of  $S(q)$  and  $S_D(q)$  is difficult because of the displacement of the doublet components of  $S(q)$  caused by overlapping of these components. However, Fig. 5 unambiguously demonstrates that the prepeak bears direct relationship to the spatial arrangement of voids.



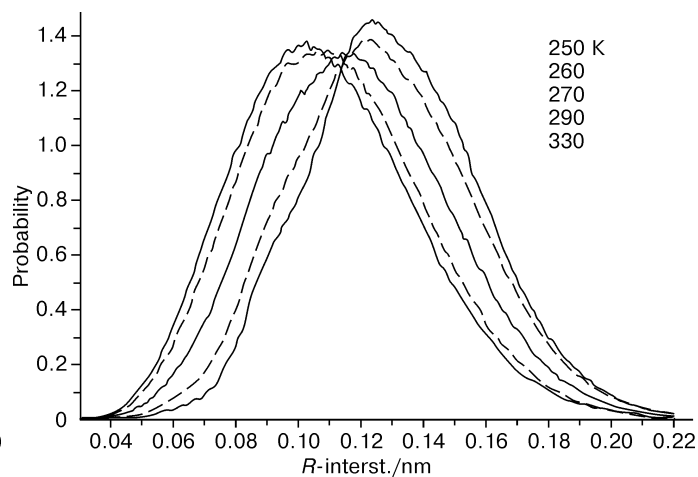
**Fig. 5.** Plots of the structural factor of oxygen atoms (solid lines, scale shown on the left) and the centers of interstitial voids (dashed lines, scale shown on the right) for water models and Ih ice. For ice, Gaussian broadening of lines is given for comparison.

The voids certainly do not scatter electromagnetic waves, but should obviously contribute to the diffraction pattern. Imagine two “complementary” systems: continuum with empty voids distributed in it and empty space with some matter filling the same voids. Since diffraction patterns depend only on contrast between the densities of the substance in the two types of region, they must be identical in the two systems. Distinctions can only be observed in the phase ratios of scattered waves, which do not show themselves in intensity and hence in the structural factor. (In optics, this is called Babinet’s principle [22].) In atomic structures, this pattern will be complicated by modulation effects because of diffraction due to interatomic distances, but will be preserved as a whole.

Thus correlated arrangement of empty voids of approximately identical size must yield a diffraction pattern similar



**Fig. 6.** Plot of the structural factor for the model of water at 260 K. Solid line — oxygen atoms, dotted line — centers of interstitial voids except very close centers ( $r < 0.3$  nm).



**Fig. 7.** Distribution of the radii of the interstitial spheres. The radius of the water molecule is taken to be 0.14 nm.

to that from correlated arrangement of atoms. As already mentioned above for Fig. 4, the distribution of empty space is characterized by pronounced correlations of voids lying at an average distance of about 0.5 nm, which is longer than the distance 0.29 nm between the nearest molecules of water. This implies that the first diffraction maximum of voids must be located at wave numbers smaller than those for the diffraction maximum of atoms. This is exactly the pattern presented in Fig. 5.

Thus it is proven that the prepeak on the curve of the structural factor of water is caused by the regular arrangement of voids. From Fig. 5 we can see that this regularity is preserved at all temperatures studied, and only slightly decreases at elevated temperatures.

## CONCLUSIONS

This paper demonstrates that regular arrangement of voids is no less inherent in tetrahedral nets of hydrogen bonds than is regular arrangement of water molecules.

Voids in water have only recently started to be investigated, and their properties are yet poorly known. In addition to the radial distribution of the centers of intermolecular voids, we also give here the distributions of the radii of interstitial spheres. The plots are shown in Fig. 7. At decreased temperatures, the distribution is markedly displaced toward large radii: the position of the maximum changes by 20% when the temperature changes from 330 K to 260 K. The distribution of the interstitial radii turned out to be more temperature-sensitive than the radial distribution  $G_D(r)$ , whose fundamental peak is displaced by only 10%. It is interesting that the fraction of voids with an interstitial radius larger than the radius of the water molecule (taken to be 0.14 nm) is great enough at all temperatures. These large voids remain empty in the structure, although they can accommodate additional water molecules. This demonstrates that the net of hydrogen bonds in water is really loose (sometimes called “open”). The “openness” of the net increases at reduced temperatures, which is indicative of the enhanced tetrahedrality of the net.

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