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Abstract

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ON THE STRUCTURE OF WATER

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The most reliable and direct information on the structure of liquids can be obtained from the study of the scattering of X-rays by liquids, reconstructing from the angular dependence of the scattering intensity the radial function of atomic distribution $g(r)$. Until recently, the study of the function $g(r)$ was carried out mainly in the direction of estimating the mean coordination numbers of atoms in a liquid and comparing the results of such an estimate with the corresponding crystalline structures. In the work of the authors ([1]) it was shown that knowledge of the function $g(r)$ also makes it possible to obtain an estimate of the fluctuations of the mean coordination numbers of atoms in a liquid, and the corresponding estimates were given for liquid argon at various temperatures. From our point of view, fluctuations of coordination numbers are no less important a characteristic of the structure of a liquid than the coordination numbers themselves, since they can serve as a direct measure of the deviation of the local structure of a given liquid from the structure of the corresponding crystal.

Of particular interest is the question of the structure of water. With the aid of the equations obtained in ([1]), we calculated the fluctuations of the first two coordination numbers of oxygen atoms in water, as well as the correlation between the fluctuations of both coordination numbers. For the calculations we used the experimentally obtained radial distribution functions for water at different temperatures from ([2]). The results of the calculations for the first coordination number are given in Table 1.

Table 1

$t, ^\circ$C	r_1, Å	$\bar{z}_1$	$\sqrt{\overline{(\Delta z_1)^2}}$	$\sqrt{\overline{(\Delta z_1)^2}}/\bar{z}_1$
1.5	3.3	4.5	1.5	0.33
13.0	3.3	4.4	1.5	0.35
30.0	3.3	4.6	1.5	0.33
62.0	3.45	5.0	1.4	0.28
83.0	3.5	5.0	1.3	0.26

The numbers in the first column of the table indicate the temperature to which the corresponding functions $g(r)$ from $(^2)$ refer; the second gives the position of the first minimum of the function $4\pi r^2 g(r)$; the third gives the mean value of the first coordination number, equal to the area under the graph of the function $(4\pi r^2/v)g(r)$ from $r = 0$ to $r = r_1$. In the last two columns are given the results of calculations of the absolute and relative values of the root-mean-square fluctuation of the first coordination number. The error of calculation is approximately 0.1 for the data in the third and fourth columns of the table.

Table 2 gives the results of analogous calculations for the peak of $4\pi r^2 g(r)$ that exists at low temperatures and is weakly expressed in the region $r \sim 3.6$ Å, arising from atoms dislocated and introduced into the voids of the water structure $(^{3,4})$. The coordination number $\bar{z}_2$ is defined as the area under the curve $(4\pi r^2/v)g(r)$ from $r = r_1$ to $r = r_2$, where r_2 is the position of the second minimum of the function $(4\pi r^2/v)g(r)$. In the last column of the table

the values of the quantity

$$\delta = \overline{\Delta z_1 \cdot \Delta z_r} \Big/ \sqrt{\overline{(\Delta z_1)^2} \cdot \overline{(\Delta z_r)^2}},$$

which is a measure of the correlation of the fluctuations of the first and second coordination numbers.

As is seen from the tables, the level of fluctuations of both coordination numbers is approximately the same and very large in magnitude. The large negative value of δ indicates a fine structure of the order fluctuations in water.

On the experimental curves $4\pi r^2 g(r)$ from $^{(2)}$ one can also distinguish a “normal” second coordination sphere in the region approximately between $r = 3.9$ Å and $r = 5.7$ Å, corresponding well to the coordination of water molecules in ice. Unfortunately, the data in $^{(2)}$ are insufficient for a rigorous calculation of the particle fluctuations in this coordination sphere. The approximate estimate we made of $\overline{(\Delta z)^2}$ turns out to be no less than 30% of $\bar{z}$ itself at all temperatures at which the “normal” second coordination sphere can be distinguished.

Table 2

t, °C	r_2, Å	$\bar{z}_2$	$\sqrt{\overline{(\Delta z_2)^2}}$	$\sqrt{\overline{(\Delta z_2)^2}}/\bar{z}_2$	δ
1.5	3.9	3.0	1.5	0.51	–0.52
13.0	3.8	2.5	1.4	0.56	–0.56

The stable existence of an approximately tetrahedral coordination in water at all temperatures naturally led to the conclusion that water has a comparatively high degree of “quasicrystallinity” (on a small scale). However, the extremely high level of fluctuations of the coordination numbers contradicts this. The level of fluctuations here is of the same, or even of a greater, order than in liquid argon (1). It should also be taken into account that the number of peaks that can be distinguished in the function $g(r)$, which determines the size of the region of nearest ordering in a liquid, is 2–3 for water and does not differ from the number of peaks of $g(r)$ for all known simple liquids (5). Therefore water is "quasicrystalline" to no greater extent than other simple liquids. This is entirely consistent with the comparatively small value of the coefficient of internal viscosity of water.

The results we have obtained agree well with O. Ya. Samoilov' s ideas on the influence of temperature on the structure of water and on the great role of translational motion of water molecules in explaining its structure and its physical and physicochemical properties (3,4). Fluctuations of the first coordination number may serve as a direct measure of the intensity of translations of liquid molecules from their mean equilibrium positions to new equilibrium positions as a result of thermal motion. As is seen from Table 1, the fraction of translationally displaced molecules in water is quite appreciable. The anomalous temperature dependence of $\sqrt{\overline{(\Delta z)^2}}$ (the decrease of $\sqrt{\overline{(\Delta z)^2}}$ with increasing t) in water fully corresponds to the tendency of its structure, as the temperature is raised, to approach the structure common to all simple liquids (3,4), in which the level of relative fluctuations is somewhat smaller than in water.

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Note: Figure translations are in progress. See original paper for figures.

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