Physical Chemistry

Structural properties of liquid water

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Monte Carlo simulations of molecular configurations of liquid water in the *NVT*-ensemble at $T = 298$ K using unit cells containing 125 and 1000 molecules were carried out. Comparison of experimental and calculated radial distribution functions suggests the existence of two types of spatial ordering in water. Structural properties of low-energy molecular clusters and associates of closed cycles of H-bonds were determined. The properties of the network of H-bonds can be described by a set of fundamental constants and one free parameter, *viz.*, the probability of bond formation. The existence of long-range correlations in spatial arrangement of both the molecules and the cycles of bonds was established.

Key words: water, structure, computer simulation, network of hydrogen bonds.

A large number of publications are dedicated to the problem of studying the properties and structure of water. Experimental results were reviewed and a critical analysis of existing models has been reported in monographs[1—4] and articles.[5,6] Despite numerous experimental and theoretical studies, water and aqueous solutions have not been adequately investigated as yet. To gain an insight into the essence of the observed phenomena and elucidate the mechanisms of processes occurring in aqueous systems, it is necessary to establish the regularities of structural organization of water on the molecular and supramolecular level.

Only statistical mean values averaged over the ensemble and characterizing the diffusion-averaged *D*-structure of liquids can be determined using experimental methods. To describe the observed properties, numerous phenomenological models of the structure of water have been developed; the composition, structure, and properties of molecular associates are postulated in the framework of these models.[1—4] Regularities of the spatial ordering of molecules are described in terms characterizing the vibration-averaged *V*-structure. However, attempts to reduce a vast variety of instantaneous configurations to an arbitrarily selected limited set of the most significant configurations lead to a situation where the same phenomena are explained by different reasons. As a consequence, none of the phenomenological models can describe all available information on water.

Computer simulation of liquids[7] makes it possible to obtain information on the coordinates of the molecules and interactions between them that characterize the initial instantaneous *I*-structure of liquids. However, the potential of intermolecular interactions, the number of species in the unit cell, and the type of boundary

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conditions can be chosen to a great extent arbitrarily when constructing a computer model. The ergodicity problem remains unsolved in the case of water simulation.[7,8] Nevertheless, in contrast to phenomenological models, computer models are based on first principles (the type of the Hamiltonian of the interaction and the type of the statistical ensemble) and, therefore, are more well-founded theoretically.

Currently, regularities of the mutual arrangement of water molecules at short intermolecular distances are determined fairly well.[9—11] Much more difficult is to establish the structure and properties of the system of H-bonds formed by virtually all molecules using experimental and theoretical methods. To investigate the supramolecular structures whose elements consist of tens of molecules, it is necessary to substantially increase the number of species placed in the unit cell and the length of the Markovian chain.

In our previous studies[8,12—16] dedicated to the investigation of water and aqueous solutions in the framework of the systemic-structural approach, we determined several topological properties of networks of H-bonds and established certain structural regularities that are independent of the type of the potential used and simulation procedure. It was suggested[15] to consider the network of H-bonds in water as a hierarchic system in which three topologically different structures can be conditionally distinguished. Structural transformations of the network of H-bonds in the water—organic nonelectrolyte systems were studied.[16] Nevertheless, the search for long-range correlations in the spatial arrangement of molecules and the elements of the supramolecular structure and the determination of universal regularities of the formation of the network of H-bonds and molecular associates is topical. To solve this problem, it is required to calculate a system consisting of a large number of species in the unit cell.

Calculation procedure

Simulation of liquid water was carried out by the Monte Carlo method using a standard Metropolis sampling algorithm in the NVT-ensemble for $N = 125$ and 1000 at a density of 0.997 g cm^{-3} and $T = 298.15$ K. Original software was used. Specific details of the calculation procedure of aqueous systems associated with the slow convergence of the results obtained to average values and non-ergodicity of simulation were discussed previously.[7,8]

Usually, the error of the determination of structural characteristics is reduced by choosing a "proper" initial configuration and lengthening the Markovian chain. To obtain a randomly ordered initial configuration, a system consisting of 125 H_2O molecules placed in a cubic cell was "strongly heated."[8] Periodic boundary conditions and spherical cut-off of the SPC/E potential were used in calculations of the energy of intermolecular interaction. After decreasing the temperature to 298 K a fraction of the Markovian chain of length $15 \cdot 10^6$ configurations was used for the system to relax to the equilibrium state, which was monitored by tracing behavior of the average interaction energy and correlation functions. The subsequent 20 million events were used to select 3200 configurations for the determination of structural characteristics. The system containing 1000 H_2O molecules in the unit cell was formed by placing eight cells into one of the configurations obtained at the preceding step. Thus, the imposition of periodic boundary conditions on the new cell and the use of the same potential function did not change the internal energy of the system. The new procedure suggested made it possible to considerably reduce the time required for simulating a large molecular system. After excluding a nonequilibrium fraction of length $15 \cdot 10^6$ events, due to the loss of periodicity in the arrangement of the molecules inside the new unit cell, 800 molecular configurations selected on a chain fraction of length $30 \cdot 10^6$ events were analyzed.

Clusters in the molecular configurations were identified using the algorithm reported previously.[17] Taking into account the ambiguity of the determination of an H-bond in liquid water, the energy threshold criterion was used. The molecules i and j were considered to be bonded if the energy of their pair interaction (E_{ij}) was not higher than the threshold value (E_{HB}). The probability of bond formation (p) was calculated by the formula $p = 2N_{\mathrm{HB}}/(4N)$, where N_{HB} is the number of H-bonds in the unit cell. Varying the E_{HB} value made it possible to determine the properties of clusters over a wide range of changes in the argument p with an increment of 0.05.

All possible types of cycles[18—20] with three to eight vertices were revealed when constructing and investigating the properties of the networks of H-bonds. In contrast to our previous studies,[12—15] the cycles formed by closing the chains of bonds because of periodic boundary conditions were ignored in this work. This affected the number of cycles with eight vertices in the simulation of the systems containing 125 molecules.

Results and Discussion

Analysis of the behavior of the atom-atom radial distribution functions (RDF) is a common procedure for the determination of the regularities of mutual spatial arrangement of atoms in liquids. Currently, the most characteristic features of these functions have been established[6,9—11,21—25] despite experimental errors and ambiguity of the procedure for processing the data on the neutron and X-ray scattering by molecules of liquid water. The experimental RDF ($g(r)$) of oxygen atoms and those calculated from the results of our computer simulation are plotted in Fig. 1.

Ambiguity of determination of the height of the first peak of the experimental RDF is revealed at short intermolecular distances. The problem of the behavior of the $g(r)$ functions at r ranging from 0.35 to 0.37 nm had been a moot question for long.[23—25] The shape of an experimentally observed function can be reproduced using computer simulation by fitting the parameters of the potential of interparticle interactions.

The influence of specific details of the calculation procedure and processing of primary information can be considerably reduced by tracing changes in the $g(r)$ function occurring as external conditions (temperature or pressure) are varied. In the studies of temperature dependence of the RDF in the range including the supercooled state of water, the isochoric temperature

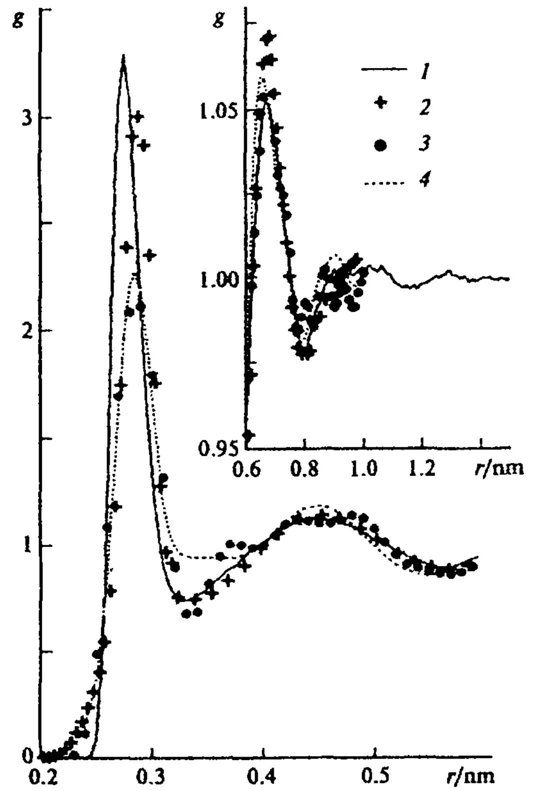

Fig. 1. Calculated (*1*) and experimental (*2*,[21] *3*,[22] *4* [23]) radial distribution functions ($g(r)$) of the oxygen atoms of water molecules. For clarity, here and in Figs. 2 and 3 the intervals of the plots along the ordinate axis are enlarged.

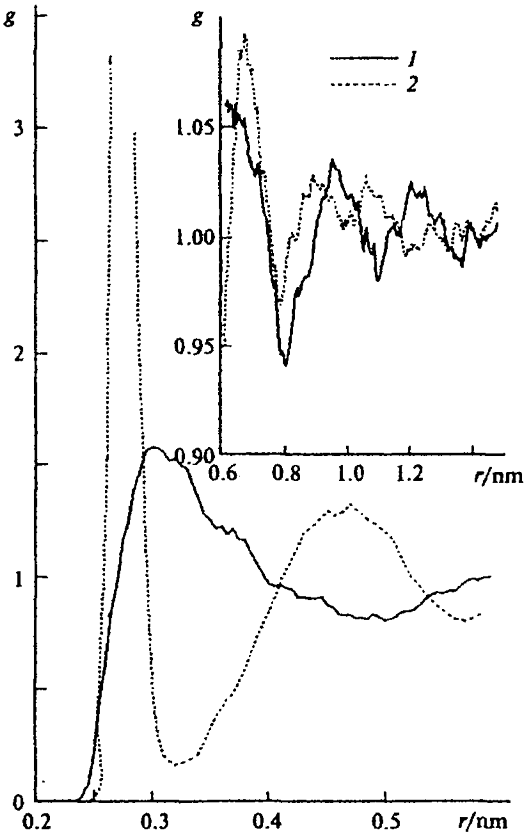

Fig. 2. Radial distribution functions ($g(r)$) of oxygen atoms of water molecules with high (*1*) and low (*2*) potential energy.

differential functions $\Delta g(r,\Delta T)$ were introduced[6,22] as the difference between the $g(r)$ values corresponding to the same densities of water at different temperatures. The $\Delta g(r,\Delta T)/\Delta T$ ratio was shown to remain constant in the temperature range from −11 to 40 °C.

Other authors substantially extended the temperature (25—500 °C) and pressure (to 2000 bar) range.[23—25] They approximated the first $g(r)$ peak by the sum of three Gaussians. The analysis of the behavior of the functions showed that two types of molecular coordination can be distinguished for water. The first of them is characterized by a tetrahedral environment and narrow distribution of intermolecular distances with the centers at 0.28 and 0.45 nm, whereas a broader distribution of distances between the nearest water molecules with the center at ~0.32 nm is characteristic of the second type. It was concluded that the molecules coordinated according to each of the coordination types are spatially separated.

Two subsets of molecules, *H* and *L*, with high ($E >$ -75 kJ mol^{-1}) and low ($E < -117$ kJ mol^{-1}) potential energy, respectively, were distinguished in molecular configurations calculated using computer simulation and the $g(r)$ functions were calculated for both cases. The choice of numerical values of the criterion for such a division is rather conditional and was determined by two requirements. First, the possibility of revealing structural peculiarities of the functions at long intermolecular distances against the background of sharply increased statistical noise caused by decreasing the number of species in the subsets should be retained. Second, the two energetically and structurally differing states of molecules have to be distinguished in the most "pure" form. At the above criteria values the fraction of the high-energy molecules was 8.5% and that of the low-energy molecules was 6.7%.

As follows from the behavior of the dependences shown in Fig. 2, the spatial arrangement of the molecules with high potential energy has no specific features observed on the RDF plots of liquid H_2O and corresponds to the distribution of atoms in simple liquids. In fact, the positions of maxima of the $g^H(r)$ functions (at 0.31, 0.63, 0.95, and 1.25 nm) are approximately multiple to the diameter of the water molecule. On the contrary, the $g^L(r)$ function for molecules with low potential energy oscillates much more pronouncedly and has maxima at $r \approx 0.275$, 0.45, 0.68, 0.91, and 1.1 nm, which correspond to intermolecular distances in linear chains of tetrahedrally coordinated molecules. The $g(r)$ curve for the species with intermediate values of the

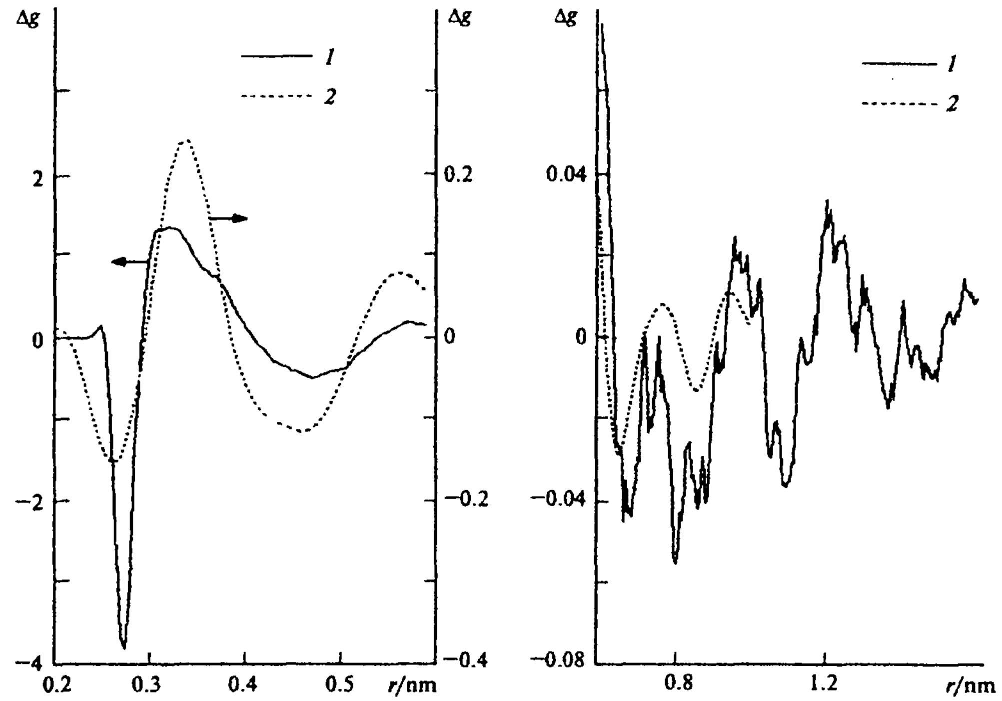

Fig. 3. Experimental isochoric differential function $\Delta g(r,51)$[22] (*1*) and function $\Delta g(r)$ (*2*) defined by Eq. (1).

potential energy does not differ from the curve calculated with consideration of all molecules.

The experimental isochoric differential function[22] $\Delta g(r,51)$ and the $\Delta g(r)$ function defined by the equation

$$\Delta g(r) = g^L(r) - g^H(r) \qquad (1)$$

are shown in Fig. 3.

Despite different physical natures of the phenomena described by these functions, a good correlation is observed for positions of their extrema (appreciable deviation in the values of differential effects at $r < 0.6$ nm is due to the conditional division of the molecules into two subsets). This indicates the possibility of interpreting experimental results using the concepts of two types of spatial coordination of molecules in liquid water. Rising temperature of the liquid shifts the dynamic equilibrium toward increasing the fraction of molecules with higher energies and less pronounced tetrahedral ordering.[23–25] Thus, two structural types of coordination of water molecules can be distinguished and it can be said that water has a microheterogeneous structure. There exist spatially localized elongated regions of bound tetrahedrally ordered low-energy molecules in a less structured medium. This conclusion corresponds to the concepts[1–4] that serve as grounds for the interpretation of many experimentally observed properties of water and is an explanation for the RDF dependence on temperature and pressure.

To determine the composition and geometric parameters of the substructure formed by the molecules with low potential energies, it is necessary to obtain information on clusters, *i.e.*, groups of molecules united by strong H-bonds. To this end, the methods developed in polymer physics,[26–28] *viz.*, the classical self-consistent field theory and percolation theory, can be used. Previously,[29] a phenomenological percolation theory was proposed, according to which the properties of water are determined by the relationship between the probability (p) of the formation of an H-bond and the value of the percolation threshold (p_c). In this case, the structural characteristics of molecular associates are described by universal scaling dependences. A particular role in the theory is assigned to the molecules that form four H-bonds; mutual association of molecules belonging to this type leads to the formation of inhomogeneities in the network of bonds, *viz.*, regions ("patches") characterized by lower local density and entropy.[29–32]

The results of computer simulation[30–32] and the experimentally observed[5] abnormal scaling behavior of the dependence of the neutron vibrational density of states on the energy indicate that the properties of the network of bonds of water can be described using mathematical tools of percolation theory. However, the results of experiments[5] on small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) revealed no structural inhomogeneity and long-range correlations in the mutual arrangement of water molecules. The authors of this study believe[5] that the absence of manifestation of microheterogeneity can be explained by small differences in the properties of regions with different types of molecular coordination or, which is more probable, dynamic spatial correlation of the molecules in clusters.

Previously,[30] the percolation parameters of the system of H-bonds of liquid water were calculated by the molecular dynamics method at 284 K for 216 H_2O molecules using the ST2 potential of intermolecular interaction. To elucidate the effect of specific details of the calculation procedure used in the computer experiment on the parameter values, it is necessary to compare the results of calculations obtained using different models of water. It is logical to assume that the increase in the number of species and configurations over which the averaging is performed should increase the reliability of the determination of percolation parameters.

According to theoretical concepts, in the vicinity of the percolation threshold, the weight fraction of clusters of size s (the number of species in these clusters is s) (W_s), the average number of molecules in a finite cluster (S), the fraction of molecules belonging to an infinite cluster (P_∞), and the radius of gyration of the finite clusters (R_s) obey the scaling relations[26—30]:

$$S(\varepsilon) = a\varepsilon^{-\gamma},\ P_\infty(\varepsilon) = b\varepsilon^{\beta},$$
$$W_s(s) = cs^{-(\tau-1)},\ R_s(s) = ds^{\nu/(\gamma+\beta)}. \qquad (2)$$

Here $p = 2N_{HB}/(4N)$ is the probability of the bond formation; $\varepsilon = |(p - p_c)|/p_c$, where p_c is the p value at which the infinite cluster is formed (destroyed); $S = \Sigma sW_s/\Sigma W_s$ (summation is performed over finite clusters); $R_s^2 = [\sum_{i=1}^{s}(\mathbf{r}_i - <\mathbf{r}>)^2]/s$, where $\mathbf{r}_i$ is the position vector of ith molecule in a cluster and $<\mathbf{r}> = (\sum_{i=1}^{s}\mathbf{r}_i)/s$ is the position vector of the geometric center of a cluster of size s; β, γ, τ, and ν are critical exponents; and a, b, c, and d are constants.

The results of approximation[30] of the cluster properties using relationships (2) made it possible to conclude that the values of free parameters coincide with those of percolation parameters determined for the diamond-like lattice, *viz.*, $\gamma = 1.73$, $\beta = 0.42$, $\nu = 0.75$, $\tau = 2.2$, and $p_c = 0.388$. Calculations in the framework of the classical theory are performed without considering the effects of excluded volume and the possibility of the formation of closed cycles of bonds. The values of parameters obtained[26,27] differ from those obtained using percolation theory, *viz.*, $\gamma = 1$, $\beta = 1$, $\nu = 0.5$, $\tau = 2.25$, and $p_c = 0.333$.

Clusters were identified in molecular configurations calculated by the Monte Carlo method and dependences of their characteristics on the probability of bond formation p were determined. The p values were varied by varying the energy threshold bond criterion value. The obtained dependences of the cluster properties were approximated by functions (2). Problems that arise when fitting the optimum parameters by nonlinear regression methods should be pointed out.[33] Expressions (2) for S and P_∞ contain three fitting parameters each. In the case of trivial behavior of the dependences the system of equations of the least squares method becomes ill-conditioned, which leads to a situation where appreciably different solutions are characterized by virtually the same approximation error. In the region near the gelation threshold, characterized by the largest changes in the function amplitudes, the small size of the unit cell introduces considerable errors, thus preventing reliable determination of the fitting parameters.

Table 1. Results of approximation of dependences of the average number of molecules in finite clusters (S) and the fraction of molecules in infinite clusters (P_∞) on the parameter $\varepsilon = |(p - p_c)|/p_c$ using relationships (2)

Conditions of simulation	Approximation procedure	a	p_c	γ	s
		Approximation of S			
$N = 1000$, $p < 0.3$, 39 points	I	1	0.441	−1.68	0.02
	II	0.993	0.448	−1.73	0.02
	III	1.230	0.362	−1	0.10
	IV	0.649	0.388	−1.73	0.52
$N = 125$, $p < 0.25$, 47 points	I	1	0.686	−2.82	0.01
	II	1.05	0.487	−1.73	0.03
	III	1.14	0.360	−1	0.07
	IV	0.74	0.388	−1.73	0.33
Conditions of simulation	Approximation procedure	b	p_c	β	σ
		Approximation of P_∞			
$N = 1000$, $0.42 < p < 0.55$ 27 points	I	1.317	0.409	0.425	0.02
	II	1.311	0.410	0.42	0.02
	III	1.314	0.330	1	0.04
	IV	1.143	0.388	0.42	0.05
$N = 125$, $0.42 < p < 0.51$ 18 points	I	1.473	0.393	0.472	0.007
	II	1.420	0.400	0.42	0.007
	III	1.398	0.318	1	0.013
	IV	1.262	0.388	0.42	0.04

Note: σ is the standard deviation. Approximation procedures: I, fitting of three parameters; II and III, calculations with fixed percolation and classical exponent, respectively; and IV, calculations with two fixed percolation parameters.

The results of approximation of the $S(\varepsilon)$ and $P_\infty(\varepsilon)$ dependences using relationships (2) are listed in Table 1. Based on the values of the standard deviations, one can argue that percolation theory describes the cluster properties better than the classical theory. However, in some instances the optimum values of three parameters fitted simultaneously do not necessarily correspond to the theoretical values (see Table 1, the first procedure for determination of S at $N = 125$). As was shown by calculations, varying the number of points used strongly affects the parameter values. The estimated p_c value lies in the range 0.4 to 0.5, which is larger than that obtained previously (0.388).[30] Calculations performed for

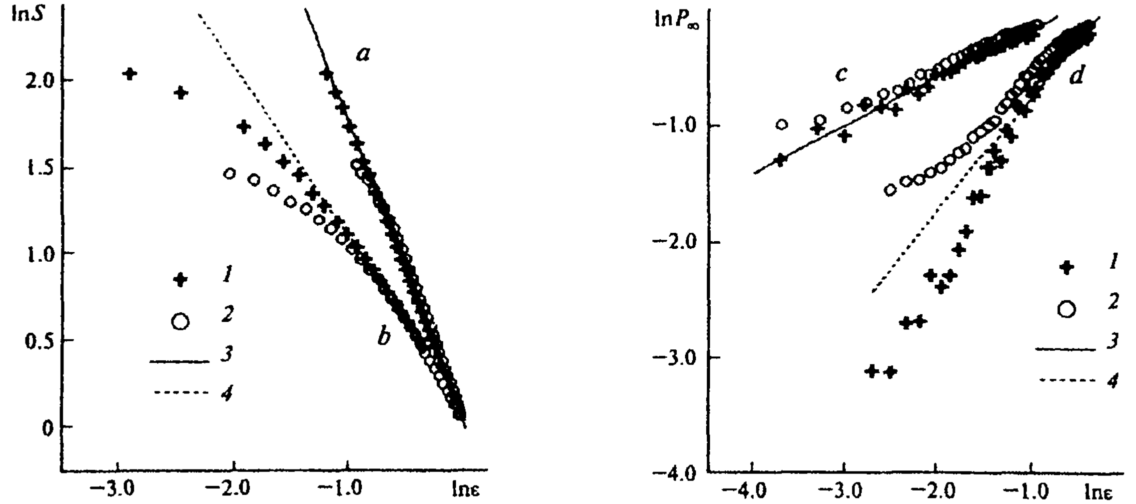

Fig. 4. Dependence of the average number of molecules in the finite cluster (S) and the fraction of molecules belonging to the infinite cluster (P_∞) on the parameter ε: calculations at p_c = 0.448 (*a*), 0.41 (*c*), and 0.333 (*b*, *d*); N = 1000 (*1*) and 125 (*2*). Approximation using relationships (2) with percolation (*3*) and classical (*4*) parameters.

two fixed percolation parameters lead to the substantial increase in the approximation error. Most likely, the system overcomes the gelation threshold at a higher value of the degree of connectivity of the network n ($n = 4p$) than was assumed before.

The results of approximation of the calculated characteristics of clusters using relationships (2) are shown in Figs. 4 and 5 on a log-log scale. In the region distant from the gelation point ($-1 < \ln \varepsilon < 0$), the behavior of the S and P_∞ values is well described in the framework of both the percolation and classical theory. Appreciable deviations of the dependences from the functions with classical parameters are observed as the argument values decrease. The increase in the number of species in the unit cell up to 1000 made it possible to extend the approximation range and to increase the reliability of the determination of parameters.

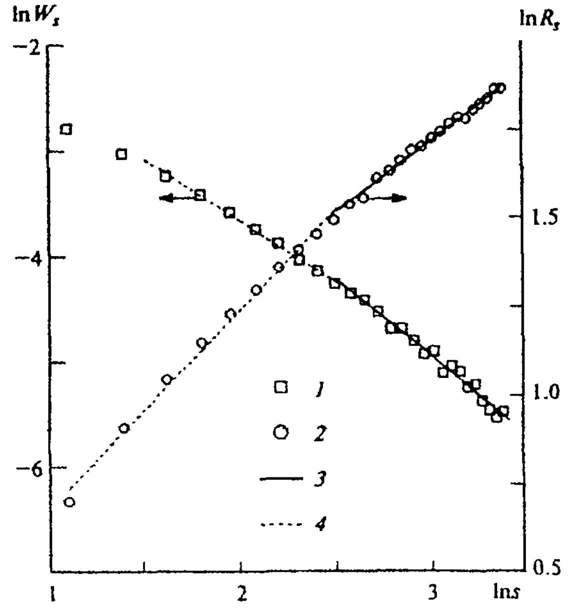

Fig. 5. Dependence of the weight fraction of clusters W_s (*1*) and the radius of gyration R_s (*2*) in the vicinity of the gelation threshold on the cluster size s. Linear approximation using relationships (2) with percolation (*3*) and classical (*4*) parameters.

Regularities of the cluster growth in the vicinity of the percolation threshold are characterized by the last two dependences (2) (see Fig. 5). The changes in the W_s values in the cluster size range $5 < s < 12$ ($1.5 < \ln s < 2.5$) are best described by the equation with the coefficients $c = 0.27$ and $\tau = 2.18$, while those observed in the interval $12 < s < 27$ ($2.5 < \ln s < 3.3$) are best described by the equation with the coefficients $c = 0.76$ and $\tau = 2.57$. Geometric size of a cluster is characterized by the radius of gyration R_s. Within the latter interval the cluster size increases following the percolation law with an exponent of 0.405 (the theoretical value is 0.409). The average potential energy per molecule in the cluster in the vicinity of the gelation threshold is approximately −100.5 kJ mol^{-1}, which is 2.5 kJ mol^{-1} lower than the value averaged over the ensemble. Hence, the clusters have low energies.

The clusters A—C randomly selected from molecular configurations in the vicinity of the percolation threshold are shown in Fig. 6. Each cluster consists of 20 water molecules. The average statistical value of the radius of gyration for such associates is 0.56 nm, while the average distance between the most distant molecules in these associates is 1.65 nm. The clusters have a shape of bent chains with small numbers of branching points. Closed cycles of H-bonds or associates of cycles occur in some clusters (see Fig. 6, **B** and **C**, respectively). The clusters strongly differ in shape from the ice-like aggre-

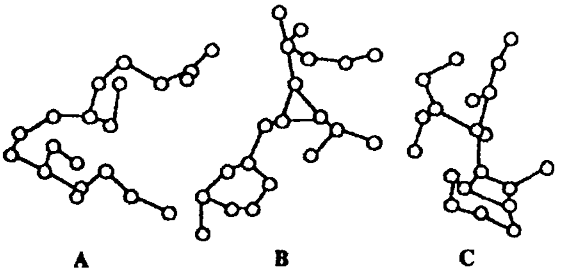

Fig. 6. Clusters (A—C, see text) formed by water molecules bonded by H-bonds at $s = 20$.

gations ("icebergs") in a medium of monomeric molecules, as is generally agreed in the phenomenological cluster model of water structure.[34]

Thus, investigation of the properties of molecular clusters has shown that they can be described more precisely in the framework of percolation theory with a percolation threshold value of ~0.42. However, the calculated $S(\varepsilon)$, $P_\infty(\varepsilon)$, $W_s(s)$, and $R_s(s)$ values are fairly well approximated by relationships (2) with classical parameters on certain intervals of the argument values. It is likely that the effects of excluded volume and cycle formation are insignificant for the clusters with minimum energy.

If clusters are elements of low-energy supramolecular structure, the closed cycles of H-bonds are natural structural elements in the range of intermediate energies of intermolecular interaction. We calculated the dependences of the concentrations of cycles (c_i, where i is the number of vertices in the cycle) in the network of H-bonds of water on the probability of bond formation p. The calculated values were approximated by the least squares method using the following functions

$$c_i = a_i p^{bi}. \qquad (3)$$

The smallest errors were obtained in the case of simultaneous fitting of two free parameters, *viz.*, a_4 = 0.162 and b_4 = 5.55 (0.002) (hereafter the concentrations c_i and the a_i values are expressed as the numbers of cycles per molecule; the standard deviation of the approximation, σ, is given in parentheses); a_5 = 0.398, b_5 = 5.5 (0.001); a_6 = 0.691, b_6 = 6.63 (0.002); a_7 = 1.278, b_7 = 7.86 (0.003); and a_8 = 2.572, b_8 = 9.09 (0.005). However, quite satisfactory results were also obtained under the condition $b_i = i$, *viz.*, a_4 = 0.129 (0.006); a_5 = 0.372 (0.005); a_6 = 0.640 (0.007); a_7 = 1.157 (0.014); and a_8 = 2.284 (0.026). In this approximation the probability of cycle formation is proportional to the probability of bond formation raised to the power equal to the number of cycle edges. The values of the coefficients listed above are in good agreement with those determined earlier[15,16] for systems with different potentials of intermolecular interactions, numbers of species in the unit cell, and criteria of H-bond formation utilized.

At $p < p_c$ (below the gelation threshold) the number of cycles is very small. There is approximately one four-membered and one five-membered cycle per configuration consisting of 1000 molecules. The octagon can be found only after exhausting 10 configurations. Thus, in the vicinity of the gelation threshold the effects of the self-closure of chains of H-bonds are insignificant, which partly explains the fact that the classical theory can fairly well describe some intervals of p values. Mention may be made that at $p = 0.576$ the concentrations of all cycles with i values in the range $4 \le i \le 8$ are approximately equal (0.019 cycle per molecule).

Let us consider the problem of the mutual arrangement of cycles and long-range spatial correlations in liquid water. In the case of simulation at $N = 1000$, the geometric size of the unit cell makes it possible to calculate the RDF values at a maximum distance between the molecules no longer than 1.55 nm (~5 molecular diameters). As follows from the plots of the functions shown in Figs. 2 and 3, weakly damped oscillations of the curves are observed in the range 1.2—1.5 nm. Mutual compensation of the values of the $g^H(r)$ and $g^L(r)$ functions at the extreme points at $r > 0.8$ nm leads to virtually complete absence of peculiarities of the $g(r)$ function. Such behavior of the functions explains the negative results[5] of the search for long-range correlations by the SAXS and SANS methods. The small angle scattering of radiation by low-energy tetrahedrally coordinated molecules constituting the clusters of chain and dendritic structure is complemented with scattering by high-energy molecules that are characterized by another type of spatial ordering. This explains the observed homogeneity of liquid at the above-mentioned distances.

There exist clearly seen correlations in the mutual arrangement not only for molecules, but also for closed cycles of bonds. Let us define the points in the unit cell, corresponding to the geometric centers of cycles, by calculating the arithmetic mean values of the coordinates of the oxygen atoms of the molecules constituting the cycles. Regularities of the arrangement of points for the cycles with i and j vertices are characterized by the $G_{ij}(r)$ radial distribution functions. By definition they are equal to the ratio of the local numerical density of points of type j in a spherical layer of thickness dr at a distance r from the point of type i to the average statistical density of the points of type j. Fast change in the concentrations of cycles occurring as the p value decreases leads to appreciable increase in statistical noise when determining the G_{ij} RDF, whereas the fraction of bifurcated bonds increases as the p value increases. It is these factors that are responsible for the choice of a p value of 0.92 for calculating the functions shown in Figs. 7 and 8.

Oscillations of the G_{ij} RDF are rapidly damped out as the intercycle distances increase and are not traced at $r > 1.4$ nm. Spatial distribution of the cycles tends to

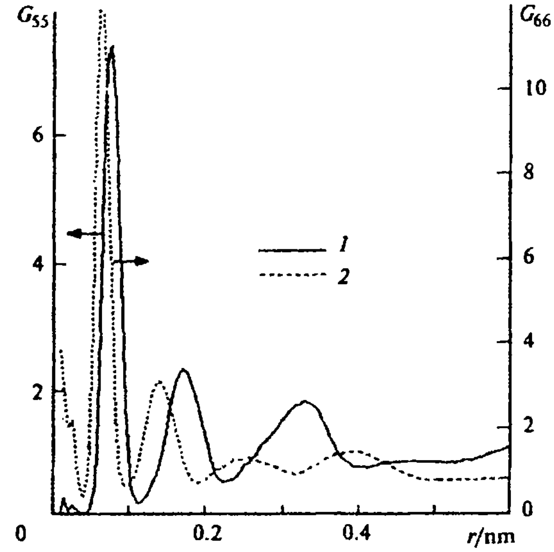

Fig. 7. Radial distribution functions of the geometric centers of five-membered (G_{55}, *1*) and six-membered (G_{66}, *2*) closed cycles of H-bonds in the region of short intercycle distances.

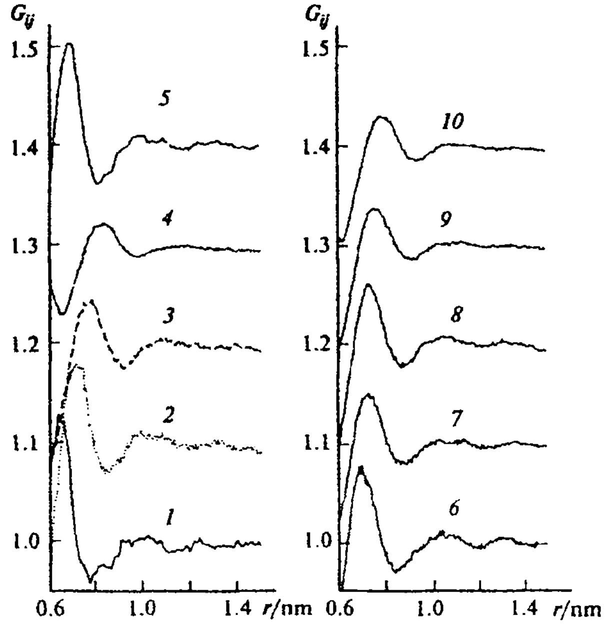

Fig. 8. Radial distribution functions of the geometric centers of closed cycles of H-bonds ($G_{ij}(r)$) in the region of long intercycle distances: *1*, G_{55}; *2*, G_{66}; *3*, G_{77}; *4*, G_{88}; *5*, G_{56}; *6*, G_{57}; *7*, G_{58}; *8*, G_{67}; *9*, G_{68}; and *10*, G_{78}. For clarity, the intervals of the plots along the ordinate axis are enlarged.

the mean statistical one. To reveal discrete structural units formed by associates of cycles, we compared the spectrum of distances at which maxima of the functions are observed with the distances between the cycles in ideal associates. The structure of a series of specially selected alkanes was determined by the molecular mechanics (MM2) method. By ignoring H atoms, replacing C atoms by O atoms, and increasing the C—C bond length in the alkane molecules by a factor of 1.8 one can obtain a set of elements that simulate the arrangement of oxygen atoms in the network of H-bonds of water.

Previously,[14] we established a regularity of mutual arrangement of cycles in the region $r < 0.6$ nm: if two cycles share n edges, the maximum of the function corresponds to each n value. If there are several conformations of cycles, the G_{ij} maxima can overlap. The network of H-bonds of liquid water is characterized by the presence of all theoretically possible types of associates of cycles and the absence of explicit domination of particular types of associates, and so it is impossible to distinguish elongated fragments characteristic of crystalline modifications of water or crystal hydrates.

The idealized structures (**1—17**) of associates in which the intercycle distances correspond to the positions of maxima of the G_{55} and G_{66} functions are shown in Fig. 9. In addition to previously found structures,[14] a number of new structures (**4—8**, **14—17**) are shown in Fig. 9. For the associates of cycles separated by H-bonds there exists a large set of possible conformations with differing intercycle distances. Nevertheless, a general regularity of the construction of the network of bonds in water persists. The probabilities of the appearance of fragments **4** and **14** in the network are low and they cause very small changes in the behavior of the RDF. The low statistical weight factors of these fragments can partly be explained by obligatory presence of a molecule participating in four H-bonds; the probability of the appearance of this molecule is proportional to p^4 at $p < 1$. Of the two conformations of the pentagons connected by a chain of two bonds (see Fig. 9, structures **6** and **7**) the former is preferably observed. The arrangement of hexagons in the network, analogous to structure **16** in Fig. 9, is atypical. More characteristic are conformations with shorter intercycle distances.

Two maxima are observed on the plots of the G_{ij} functions in the range $r > 0.6$ nm (see Fig. 8). The first peak is shifted towards long distances as i (at $i = j$) or j (at a fixed i) values increase. An increase in the size of one or both cycles causes lengthening of intercycle distances. It is likely that in all cases the major contribution to the first peak comes from the configurations in which the cycles are separated by one H-bond and "open" structures are dominating. However, it should be noted that in the framework of ice Ih (see Fig. 9, structure **12**) the distance between the two six-membered cycles in the "chair" conformation is approximately halved (from 0.70 to 0.38 nm) as compared to that in structure **15**. Analogously, two pentagons on the opposite faces of a dodecahedron are separated by three H-bonds similarly to structure **8** in Fig. 9; however, the intercycle distance corresponds to the positions of the extrema of the G_{55} function and is 0.61 nm.

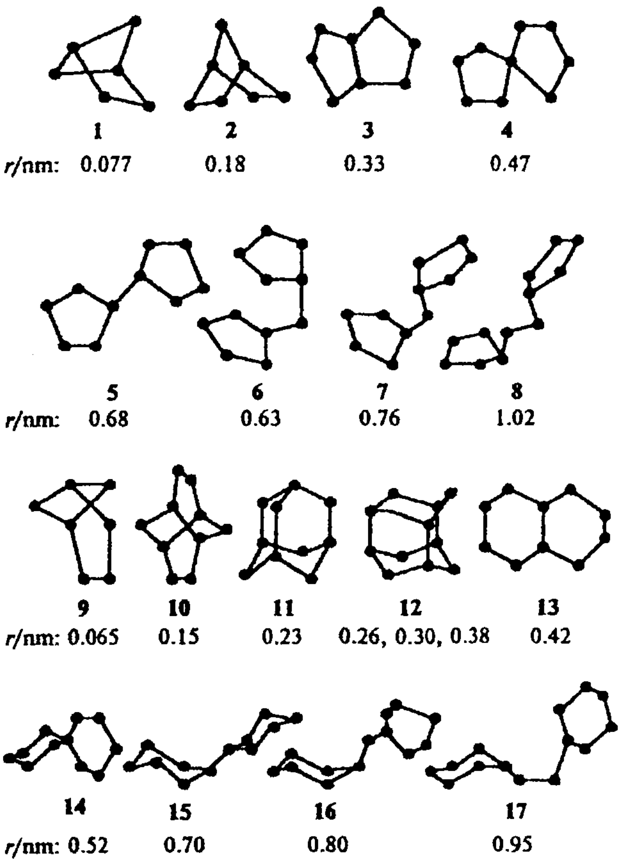

Fig. 9. Structures of molecular associates reproducing the mutual arrangement of closed cycles in the network of H-bonds of water (**1** —**17**); r are intercycle distances corresponding to the positions of maxima of the G_{55} and G_{56} functions. For structure **12**, the distances between the centers of six-membered cycles for three conformations (boat-chair, boat-boat, and chair-chair) are given.

Thus, in the region above the percolation threshold ($p > p_c$) the network of bonds of water is a three-dimensional, tetrahedrally coordinated framework and the molecules located in the nodes and internodes (high-energy molecules) can be distinguished. Therefore, numerous clathrate models of the structure of water are theoretically substantiated. However, the results of computer simulation show that the topological properties of the framework appreciably differ from those of the frameworks of the known water-containing crystalline compounds.

Previously,[35–37] we have shown that regularities of the formation of spatial structure of liquid methanol, N,N-dimethylformamide, and acetone are determined by universal repulsive interactions, the molecular shape, and packing factors. The networks built of the lines connecting the nearest central atoms of molecules in liquids are similar in topological properties to the networks in random closely packed systems of soft spheres. The main structural elements of the system of bonds are cycles with three and four vertices. However, it is impossible to describe the structure of liquid water using a close packing of spheres even to a first approximation.[15,20] In this connection the question arises: Can other geometric figures be chosen so that their close packing could reproduce the characteristic features of the structure of water?

Previously,[20] thermodynamic and structural properties of a model liquid whose molecules have the shape of solid tetrahedra were calculated. Five-membered cycles appeared to be dominating elements in the network of lines connecting the centers of adjacent tetrahedra. In the simple model of water[8,12–14] (the 3D potential) the short-range spherically symmetric interactions are described by the Lennard-Jones (12-6) function, while anisotropic tetrahedrally symmetric interactions are described by a specially developed function dependent on the mutual orientation of molecules. We have shown[8] that the topological properties of the network of H-bonds of water approach those of the lattice of ice Ic as the length of the Markovian chain increases up to 200 million configurations. In this model, the network of H-bonds of water is built mainly of six-membered cycles that are in "chair" conformation. In the model that describes an intermediate variant in which the molecule has the shape of a tetrahedron with four truncated vertices, five- and six-membered cycles must occur in the network of bonds of a closely packed system. It is likely that, to a first approximation, its topological properties will correspond to those of the network of H-bonds of water.

Structural inhomogeneity (microheterogeneity) of liquid water justifies the existence of a set of phenomenological models. By considering a limited number of structural states as basic ones and ignoring all other states one can describe many experimental dependences of the properties of water and solutions in the framework of these models. In this case the same phenomena are explained by different reasons. Most likely, it is possible to define an infinite number of structures in the system of H-bonds of water, each of them being characterized by its own structural elements and bonds (relations) between them. Using modern computers, the behavior of systems consisting of hundreds (at most, thousands) of species can be studied. Correspondingly, the elements of supramolecular structures can be constructed of only a very small number of molecules. Studying the response of the system of H-bonds of water to changes in external conditions or to dissolution of other substances (especially, biologically active macromolecules) on the supramolecular level is topical and it is already possible to outline some ways of solving this problem.

Previously,[15] it was suggested to consider the totality of bonds in pure water as a hierarchic system in which three topologically different structures can be distinguished by convention. At $p < 0.4$, finite clusters (structure I) play the role of basic structural elements. The clusters are united to form a loose three-dimensional network (structure II) as p values increases ($0.4 < p < 0.6$). Topologically, the system of H-bonds is a "tree-like" structure with dangling groups of cycles. The subsequent increase in the *p* values leads to an intense association of cycles and the formation of a large number of polyhedral frameworks (structure III).

It is likely that the response of the system of H-bonds of water to changes in external conditions or to dissolution of molecules of another compound will be determined by those structural elements that are affected to the greatest extent. Changes in temperature and pressure shifts the dynamic equilibrium between low-energy and high-energy states of the molecules, thus affecting structure I. We have shown[16] that the network of H-bonds of water that is destroyed as the content of organic component in dilute aqueous solutions of methanol, acetone, and DMF increases, becomes more patterned due to a relative decrease in the fraction of acyclic associates. Compact fragments of the network are stabilized rather than elongated acyclic fragments. Weak intermolecular interactions between hydrophobic groups of molecules initially affect structure III, and if the concentration of organic component increases (at $X < 0.4$ mole fraction), they affect structure II of water. The destruction of the network by hydrophilic groups of molecules of organic compounds requires further investigation.

It cannot be ruled out that hydration of molecules will cause stabilization of certain types of associates of water molecules similar to those shown in Fig. 9 and destruction of other types of associates in the labile system of H-bonds characterized by the presence of many dynamic equilibria between structural elements. In particular, configurations with the arrangement of cycles corresponding to structures **2** and **10** (see Fig. 9) are obviously stabilized in dilute aqueous solutions of acetone, whose molecules possess mostly hydrophobic properties.[16] Thus, the idea[38] of mutual complementarity of the structure of biological macromolecules to fractal configurations built of "twist-boats" (see Fig. 9, structure **10**) has some validity. Considerable increase in the potential energy of the water matrix (energy storing therein) can be observed in the case of such a structural transformation of the system of H-bonds. Under particular conditions the stored energy can be liberated, thus strongly affecting the occurrence of chemical reactions.

The results of computer simulation of liquid water not only confirm, but also substantially complement many of the known concepts of water structure.[1—4] Thus, assuming that bending of the bonds appreciably dominates over their cleavage, we get continuum models of the structure of water. However, by introducing the criterion of the H-bond and varying its value, thus separating more "perfect" bonds from less "perfect" ones, it is possible to obtain systems whose properties are best described in the framework of "mixed" (*e.g.*, two-structure, cluster, or clathrate) models. Each dissolved compound can belong to a certain class of substances that has a selective effect on particular elements of the system of H-bonds of water.

Thus, we have shown that there exist spatially localized low-energy states of molecules that are in a less tetrahedrally coordinated medium formed by molecules with higher potential energy. The properties of clusters are described by basic scaling dependences whose parameters are close in value to the percolation parameters determined for the diamond-like lattice. The classical self-consistent field theory can also be used on particular intervals of argument values. To a first approximation, the properties of low-energy clusters, the fraction of molecules with a given number of H-bonds,[16,29] and the number of closed cycles of bonds are determined by a set of fundamental constants and one free parameter, *viz.*, the probability of bond formation. From this point of view the network is random; however, statistical regularities are clearly seen when describing its properties. All possible types of association of closed cycles occur in the network of H-bonds of water molecules. There exist long-range (1.0—1.5 nm) correlations in the mutual spatial arrangement of both the molecules and the cycles of bonds. We believe that the networks generated by methods of computer simulation and the network of H-bonds in natural water belong to the same type of structures. Hence, the models reproduce basic regularities of the formation and structure of the network of bonds of water.

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