

Properties of the network of the hydrogen bonds of water

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Networks of the hydrogen bonds and those consisting of lines connecting nearby molecules were constructed using configurations of water molecules obtained by the Monte-Carlo method. The concentrations of closed cycles of hydrogen bonds were established to be determined only by the probability of hydrogen bond formation. Characteristics of a model ideal water network were determined. Topological properties of the Polk model and those of the network of nearest neighbors substantially differ from the properties of the ideal network. The totality of the hydrogen bonds in pure water was proposed to be considered as a hierarchical system. Three topologically different structures of water associates were determined.

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

Liquid H_2O and aqueous solutions have always attracted the attention of experimentalists and theoreticians. This was mainly associated with two factors. Firstly, many technological and biological processes proceed either in aqueous medium or with participation of water. Secondly, water and aqueous solutions possess unique physicochemical properties, which can only be explained using information on the supramolecular structure.

It is impossible to obtain an unambiguous picture of the mutual arrangement of water molecules based only on the data of experimental methods. Several tens of phenomenological models of the water structure have been suggested, which are based on essentially different postulates, and, hence, properties of water and those of aqueous solutions are naturally explained by different reasons. As a result, none of those models can describe all the known information on water as a whole.¹⁻⁴ The model of a random network of bonds³ occupies a particular place among the phenomenological models of the structure of liquid H_2O . It is widely used for describing experimentally determined properties of water. The percolation model has played an important role in gaining insight into regularities of constructing a network of water hydrogen bonds.⁵ The network of hydrogen bonds was shown to correspond to the state of the nonstationary gel, which structure can be described using methods developed in the polymer physics.^{6,7}

We believe that the structure of water can only be described in the framework of a systematic-structural approach where the term *system* implies any finite set of elements with connections, and the *structure* is the totality of stable connections among the elements. Assuming such a concept of the structure, one must choose for its descriptions the elements and connections, and

determine characteristic, stable relations between the elements, i.e., find the regularities.

Recently, numerous intensive studies of the properties of liquids have been carried out using computer simulation methods. Using the Monte-Carlo and molecular dynamics methods based on the potentials of intermolecular interactions, one can obtain and analyze the coordinate sets of the species both in I and in V ensembles. The drawbacks of the methods include the small number of species simulating the behavior of the macrosystem, difficulties in achieving convergence of the results to the statistic mean value, and problems associated with ergodicity of simulation.

Method of Calculations

In this work the systems were constructed on the basis of configurations obtained by the Monte-Carlo method. Closed cycles of intermolecular bonds were taken as structural elements, while the quantitative ratios of concentrations of the cycles with the number of vertices from three to eight were considered as connections. The spatial structure of the system was described by the functions of radial distribution (FRD) of geometric centers of the cycles. Averaging over the generated ensemble ensured stability of the totality of element ratios.

Simulations of the water structure were performed by the Monte-Carlo method in the NTV ensemble at 298.15 K. The procedure of simulation and processing of results was described previously.⁸ The SPC/E, TIP4P ($N = 125$), and ST2 ($N = 216$) potentials were used to describe the intermolecular interactions.

Results and Discussion

Our previous studies showed that the topological properties of the network of the hydrogen bonds of

water, in particular the concentrations of closed cycles, depend on the parameter of connectivity (n), the average number of bonds per one molecule.⁸⁻¹⁰ If one assumes that a water molecule can participate in a maximum of four bonds, then the relation $p = n/4$ for the probability of the bond formation (p) will be valid. There is no physically decisive criterion of formation of the hydrogen bond; therefore, when studying the properties of the network it is conventional to use several criteria. In accordance with the energy threshold criterion two molecules are considered to be involved in the hydrogen bond if the energy of their pair interaction is less than a fixed negative value E_{HB} . Weaker bonds are excluded from consideration if E_{HB} is successively decreased, which results in decreasing the n and p parameters.

The connectivity of the network can also be changed in another way. In the system under study a network ($n = 3$) is constructed using one criterion, and then several bonds break up randomly with retention of the initial molecular configuration. If the distribution of the bonds in the network does not depend on energy, then in both cases, the topological properties of the networks will coincide at the same p values.

Dependences of $\ln c_i$ on $\ln p$, where c_i is the ratio of closed cycles with i vertices to the number of species, i.e., the concentrations of closed cycles, are shown in Fig. 1. For the water models with the potentials of interspecies interactions TIP4P, SPC/E, and ST2 and for two ways of the bond cleavage the calculated points appeared to lie on the lines having the slope i . Hence, the relationships are fulfilled

$$c_i = a_i \cdot p^i, \quad (1)$$

$$a_4 = 0.068 \pm 0.01, a_5 = 0.33 \pm 0.04, a_6 = 0.61 \pm 0.05, \\ a_7 = 1.04 \pm 0.08, a_8 = 2.92 \pm 0.7.$$

As is known,^{5,11} another important characteristic, fraction of molecules having a certain number of bonds, is given by the binomial distribution. Thus, the most important topological properties of the network of water bondings are defined by one parameter p , the probability of their formation. The bonds are generated randomly, i.e., they are noncorrelated. A set of numbers a_i characterizes basic properties of the network. Assuming $p = 1$, we get an ideal hypothetical network where each of the molecules forms four H-bonds and $c_i = a_i$.

In the framework of the conducted investigations the mentioned properties of the network depend neither on the kind of the potential nor on the bond criterion or on peculiarities of the procedure of simulation. Small deviations of the results of calculations of concentrations of the cycles from dependence (1) at small p values, observed using the threshold energy criterion of the bond, indicate some correlation in the mutual spatial arrangement of the molecules with strong H-bonds. In this case the system of the bonds is above the percolation threshold ($p = 0.4$, $\ln p = -0.92$), and the network

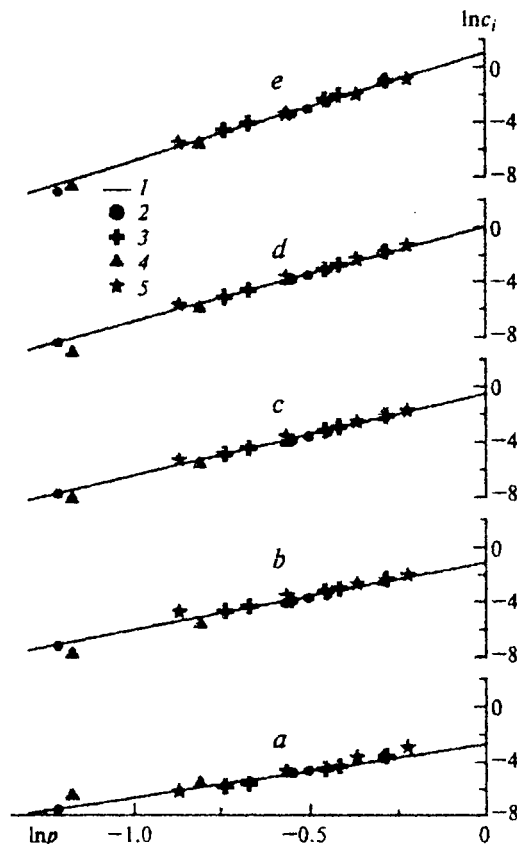


Fig. 1. Dependences of concentrations of closed cycles (c_i) on the probability of the bond formation (p); i is the number of vertices in the cycle: $i = 4$ (a), 5 (b), 6 (c), 7 (d), and 8 (e); 1, calculation using Eq. (1); 2 and 3, simulation of a random rupture of bonds with the SPC/E and TIP4P potentials, respectively; 4 and 5, taking into account of changes in E_{HB} values in the SPC/E and ST2 models, respectively (the plots are mutually shifted along the ordinate axis for clarity).

breaks up into noncorrelated clusters. It should be noted that transition of the system over the percolation threshold does not affect the character of the dependence.

It is obvious that the topology of the network of bonds is not only determined by the ratio of concentrations of the cycles of different kinds, but also by the manner in which they are joined into the network. The observed variety of the networks of the hydrogen bonds of ice, where each water molecule forms four hydrogen bonds, indicates a multitude of possible combinations of mutual arrangements of the cycles. The power of this set is strongly increased in liquid H_2O . As was shown previously,⁸⁻¹¹ a mutual spatial arrangement of the cycles can be described by means of the FRD of their geometric centers. For the TIP4P and SPC/E potentials these functions virtually coincide at equal p values, while small distinctions appear for the ST2 potential. The position of each maximum of the function can correspond to the distance in an ideal model associate or to a set of distances in several associates of the cycles.

The network of bonds in the computer model of water essentially differs from the networks of the hydrogen bonds of ice and crystal hydrates in both the ratio of concentrations of the cycles of different kinds and in the manner of their association. It cannot be thought as an ice-like framework with partially filled voids. It is random in the sense that the topological characteristics are determined by the probability of the bond formation; however, at the same time there exist pronounced regularities in its construction. Let us try to answer the question on the sufficiency of the randomness concept for constructing a water network, keeping in mind that a concrete molecular realization of a random network with a minimum distortion of the tetrahedral bonds^{3,12,13} corresponds to the Polk model (PM) in the form of a coordinate list and a connectivity matrix.

An analysis of the PM network we carried out showed that 519 molecules form 137 pentagons ($c_5 = 0.264$) in the absence of tetragons, 307 hexagons and 307 heptagons ($c_6 = c_7 = 0.591$), and 516 octagons ($c_8 = 0.99$) at $n = 3.44$. The connectivity parameter differs from four due to molecules located in the vicinity of the cluster surface. If the ideal network of the computer model of water and that of PM have a fairly close number of penta- and hexagons, then they appreciably differ in the number of the cycles of other types.

Some of the FRD of the geometric centers of the cycles G_{ij} , calculated for the model of water at $n = 3$ and for the PM are shown in Fig. 2. Several common

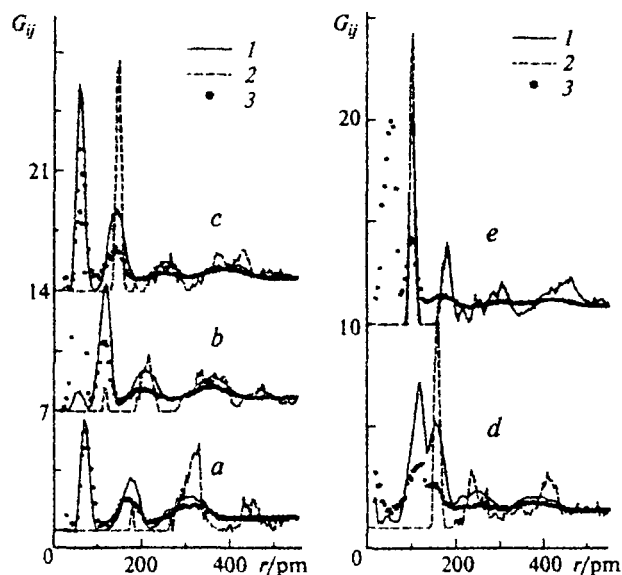


Fig. 2. Functions of the radial distributions of geometric centers of closed cycles of hydrogen bonds, $G_{ij}(r)$; r is the distance between the cycles; i, j are the numbers of vertices in the cycles: $ij = 55$ (a), 56 (b), 66 (c), 57 (d), and 67 (e); 1, for the SPC/E model at $n = 3$; 2, for the network of bonds of the Polk model; 3, for the network of bonds between nearest neighbors according to the SPC/E model (the plots are mutually shifted along the ordinate axis for clarity).

features as well as essential differences are seen in the behavior of the plotted functions. Since there are no cycles with three or four vertices in the PM network, some FRD maxima are absent in the region of short distances.⁸⁻¹⁰ An increased correlation of planar pentagons (G_{55} , $r = 330$ pm) and hexagons having a twist-boat conformation (G_{66} , $r = 147$ pm) is characteristic of this network. Several functions of the models (G_{67}) nearly coincide, while the other ones (G_{57}) are essentially different.

The center of the cycle is defined as the arithmetic mean of atomic coordinates of oxygen. Noncorrelated vibrations of the molecules in the cycle can not result in an appreciable shift of its center. Hence, the FRDs of the centers of the cycles to a certain extent characterize the V structure of water. Thus, taking into account that there are differences between the V structure of water in the PM and the I structure in computer simulation, the FRDs of the cycle centers should be close. Nevertheless, the results of comparison of the topological properties show that the network of the computer model of water and that of the PM substantially differ.

The increased E_{HB} value results in a sharp increase in the number of molecules with five and more hydrogen bonds due to bifurcated bonds. Such a network cannot serve as an example of an ideal network where each center has only four bonds. Let us see whether the network designed of lines connecting adjacent water molecules can be ideal. For this purpose, let us construct the networks using the SPC/E potential in such a way that each O atom will be connected by four lines to adjacent O atoms of other water molecules. In the case of such definition of bonding the concentrations of the closed cycles in the system are: $c_4 = 0.16$, $c_5 = 0.42$, $c_6 = 0.72$, $c_7 = 1.40$, and $c_8 = 3.75$. They substantially differ from those characteristic of an ideal network (see Eq. (1)). The functions of radial distribution of the cycle centers in a network formed by nearest neighbors are shown in Fig. 2. Mutual arrangement of the cycles in this network does not coincide with their arrangement in both the network of the hydrogen bonds of water at $n = 3$ and in the PM.

Thus, the question of the procedures of constructing a model of an ideal network of the bonds of water remains unclarified. It seems to be important to learn to generate such networks without resorting to a computer simulation using the molecular dynamics or Monte-Carlo methods. This could allow elimination of limitations inherent in the methods in question and a more detailed understanding of the structure and properties of liquid H_2O and aqueous solutions.

In the case of interpretation of experimental results it is convenient from the methodological viewpoint to consider the totality of bonds in pure water as a hierarchical system, arbitrarily selecting three topologically different structures. The first structure is formed by strong hydrogen bonds and can be observed at $n < 1.6$. Since the system is below the percolation threshold, the

pertinent graph consists of clusters among which the dominating fraction has a tree shape (the connection graphs with no cycles).

The second structure is a result of adding weaker bonds ($1.6 < n < 2.5$) to the first one. This results in increasing the size of clusters, their association into a three-dimensional loose network, and formation of an appreciable number of cycles with a tendency toward mutual association, which is distinctly seen in the behavior of the FRDs of their geometric centers. In this case the system of the hydrogen bonds of water resembles trees with pendent groups of cycles. The experimentally observed inhomogeneity of the network polymers, to which (with certain reservations) water can be referred, can be explained by larger conformational entropy of the like substances as compared with the structures of the regular lattice types.^{14,15}

The connectivity of the network increases when even weaker bonds ($n > 2.5$) are successively added. The cycles intensively unite with the formation of a variety of polyhedral structures. In the network of the third structure triangles and tetragons appear in appreciable amounts, while the concentration of octagons is considerably higher than that of penta- and hexagons. If the point $n = 1.6$ in this classification is physically justified, then the point $n = 2.5$ is rather conventional.

Thus, an analysis of the supramolecular structure of the computer models of water revealed a number of regularities in construction of the network of bonds independent (within the framework of the performed investigations) of the type of the potential used and the characteristic features of simulation.

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