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Structural and dynamic heterogeneity of computer simulated water: ordinary, supercooled, stretched and compressed

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Molecular dynamics simulation revealed structural and dynamic heterogeneity of water in a wide range of temperatures and densities. Dynamic heterogeneity is exhibited by a very broad distribution of the lifetimes of hydrogen bonds and of types of water molecule coordination. Another manifestation of dynamic heterogeneity is related to the dependence of dynamic characteristics of the molecules on their local environment. The structural heterogeneity is manifested in non-uniform space distribution of the molecules with different values of the parameters describing this local environment.

1. INTRODUCTION

Structure of water was one of the problems that interested O.Ya. Samoilov during all his life. As early as in 1946 [1] (see also [2]) he put forward the idea that water could be regarded as distorted by thermal motion ice, with cavities in its structure partially filled by water molecules. This model accounted for the increase of density during melting of ice and reconciled two-state model with the idea of the existence of an infinite three-dimensional hydrogen bond network in water. Two-state models naturally and without restrictions explain many anomalies of water. The earliest version of such a model was proposed by W.C. Röntgen [3]. The idea of infinite network in water was put forward by J. Bernal and R. Fowler [4]. It was developed by Pople [5] and by Bernal [6]. The most popular picture of water structure in 1950s–1960s represented water as mixture of hydrogen-bonded clusters floating in the "ocean" of non-bonded molecules [7,8,9]. In the most vivid form this picture was represented in the models by Frank and Wen [10] and Némethy and Scheraga [11]. Samoilov's model actually was the first example of clathrate models where water was considered as hydrogen-bonded framework containing cavities partially filled by water molecules. "Water is a clathrate hydrate of water". In L. Pauling's model [12] it was supposed that the framework in water is not ice-like, but is similar to that found in gas hydrates. Both Samoilov's and Pauling's models are quasi-crystalline. One of the authors of the present paper proposed an utterly non-crystalline clathrate model [13], similar to the model of silica glass proposed by Tilton [14].

The 1960s were marked by mutual rapprochement of the models. In the case of clathrate models it was supposed that molecules in the cavities form hydrogen bonds with the framework [15,16]. Versions of cluster models were proposed which implied that less dense hydrogen-bonded clusters were not floating in the "ocean" of the non-bonded molecules,

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but rather that the molecules in the denser microphase are also connected to the environment by hydrogen bonds [17,18]. A notion appeared that classical cluster models of Némethy and Scheraga type are topologically impossible [19]. The conclusive death warrant to these models was signed when H.E. Stanley and his co-workers introduced ideas of percolation theory in the science of water structure [20,21]. The picture of water as random hydrogen bonded network triumphed.

A powerful momentum in the study of water and its structure was given by the discovery of the existence of the dense form of amorphous ice [22] and the possibility of a first-order transition [23] between this form and earlier known [24] amorphous ice of low density. These findings attracted attention to properties of supercooled water and generated ideas about the possibility of phase separation of water below the hypothetical low-temperature critical point far below the temperature of ice melting [25,26,27] (see the review in [28]). The interest in two-state water models revived [29]. This time, naturally, low- and high-density amorphous ices were chosen as prototypes for the two states. In any case it became clear that random network is not uniform, but structural heterogeneity of water is much more interesting and subtle than it was implied in the early models.

O. Ya. Samoilov has always insisted that structure and dynamics of a liquid are closely related and determine each other. In this paper we present some of the results of our study of structure and dynamics of water over a wide range of temperature and density including deeply supercooled states, which may be regarded as models for amorphous ices of high and low density.

2. METHODS

The rigid water molecule model, proposed in [30] was used in our simulation. The OH distances were 0.98Å, the partial charge q on hydrogen atoms was assumed to be $0.34e$, the corresponding value for oxygen was $-2q = -0.68e$. The main contribution to the intermolecular interaction was due to the electrostatic interaction between the point charges on the atoms. The non-Coulomb interactions were described as atom-atom potential functions in the form $B/R_{ij}^{12} - A/R_{ij}^{n}$, n being 6 for H-H and O-O interactions, and 10 for O-H interactions. The parameters of the functions are given in [30] and other ones of our publications [31-33]. This interaction model was designed for the simulation of polynucleotide hydration shells [30,32,33], but it describes sufficiently well condensed phases of pure water: liquid water [34] and crystalline [35,36].

The molecular dynamics of all studied systems was simulated in the *NVE* (microcanonical) ensemble. The periodic boundary conditions were applied in all cases except the study of the co-ordination type lifetimes. In the latter case an $(H_2O)_{216}$ microdroplet was simulated. The equations of motion were integrated using Verlet algorithm (see, e.g. [37]) and Grivtsov-Balabayev method of treating constraint equations for bonds of fixed lengths [38]. The total energy per molecule was conserved during the run with the accuracy better than 0.002 kJ/mol. The temperature was calculated by averaging instantaneous temperatures over the part of the phase-space trajectory after equilibration. The integration step was 1 fs for the systems with periodic boundary conditions and 2 fs for the droplet. Initial configurations were obtained by melting the crystalline phases: ice-II (576), ice-III (768), ice-XII (648) and the hypothetical ice modification with the structure

of high pressure Si modification BC8 (432, for the structure see [39]). The numbers of water molecules in the unit cells are given in brackets. After the melting of the crystals the cells were converted into cubic ones and the parameters were adjusted to obtain the required density. The densities of the simulated systems varied from $0.94\,g/cm^3$ (low-density amorphous ice at normal pressure) to $1.3\,g/cm^3$ (high-density amorphous ice at high pressure). The temperature of the simulated systems varied from 50 to 356 K. The cluster was simulated at 300 K only.

The time dependence of the mean square displacement $\langle Deltar^2 \rangle$ of the centers of mass of the water molecules was calculated to determine the diffusion coefficient. The whole trajectory was divided into several segments whose length was two or three thousand steps each. The values of $\langle Deltar^2 \rangle (t)$ were calculated for each segment, and the average of all the segments was determined.

A non-uniform space distribution of some characteristics of water molecules in the simulated hydrogen-bonded networks has been found in our study. These characteristics are: tetrahedricity (τ), Voronoï polyhedron volume (VVP), potential energy (energy of interaction of a particular molecule with all the others, E_{pot}), and type of co-ordination (TC). Tetrahedricity is the measure of deviation of the immediate surrounding of a molecule from the ideal tetrahedral one. It is calculated according to the formula [40]:

$$\tau = \sum_{i=1}^{5} \sum_{j=i+1}^{6} \frac{(l_i - l_j)^2}{15\,\langle l^2 \rangle} \tag{1}$$

where l_i and l_j are the lengths of the edges of the tetrahedron formed around a particular molecule by the four nearest oxygen atoms. The tetrahedricity is zero if the tetrahedron is ideal (all the edges are equal to each other). VVP is the measure of local density. Its reciprocal corresponds to the density of the smallest portion of the condensed system with respect to which the notion of density can still be used. Figuratively speaking, inverse VVP is "the density of one molecule". The program for computing VVP was provided by V.P. Voloshin. For the algorithm, see, e.g. [41]. The type of co-ordination [31,38,42] indicates, in how many hydrogen bonds a particular molecule participates as donor and acceptor of protons. TC is denoted by the index A_mD_n where m is the number of bonds in which a molecule participates as an acceptor of proton and n is the corresponding number of bonds in which our molecule acts as a proton donor. A_2D_2 is the most common TC. All molecules in the ideal ice I structure are of the A_2D_2 type. If $n \geq 3$, the molecule participates in bi- or polyfurcated bonds [38]. It must be noted that the correlation between VVP, τ and E_{pot} is very weak, if any (Fig. 1). TC and the other characteristics of the environment of the molecules also are very weakly correlated. It can be illustrated by Fig. 2, where the correlation between the number of hydrogen bonds and τ, VVP or E_{pot} is shown.

3. DYNAMICAL HETEROGENEITY

We consider two aspects of dynamic heterogeneity of hydrogen bonded network. The first one is due to broad distribution of hydrogen bond lifetimes [31,43]. The longest hydrogen bond lifetime observed in a $(H_2O)_{216}$ microdroplet was a little less than 30 ps. The geometry criterion $R_{OO}^{max} = 3.3\,Å$ and $R_{OH}^{max} = 2.6\,Å$ was used as the hydrogen bond

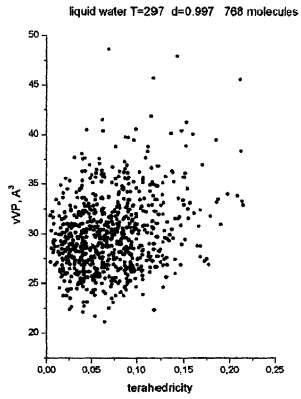


Figure 1a. Poor correlation between parameters describing the environment of water molecules: VVP and tetrahedricity. Each dot represents one molecule in an instantaneous configuration of simulated water. All pictures refer to the same configuration obtained during simulation of a system containing 768 molecules in an independent cell at $T = 297\,\mathrm{K}$ and $d = 0,997\,\mathrm{g/cm^3}$ (stretched molten ice III).

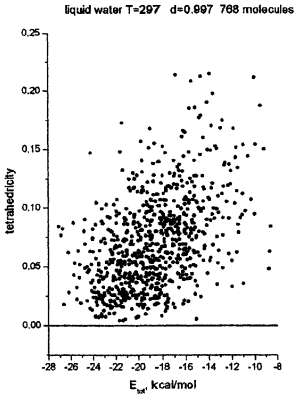


Figure 1b. Poor correlation between parameters describing the environment of water molecules: tetrahedricity and E_{pot}. The instantaneous configuration is the same as on Fig. 1a

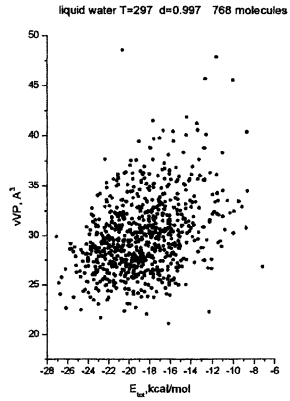


Figure 1c. Poor correlation between parameters describing the environment of water molecules: VVP and E_{pot}. The instantaneous configuration is the same as on Fig. 1a

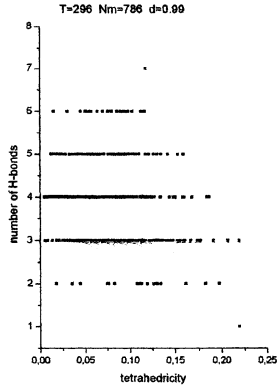


Figure 2a. Poor correlation between the number of hydrogen bonds and other characteristics of the environment of the water molecules: tetrahedricity. The same system as on Fig. 1, but another instantaneous configuration.

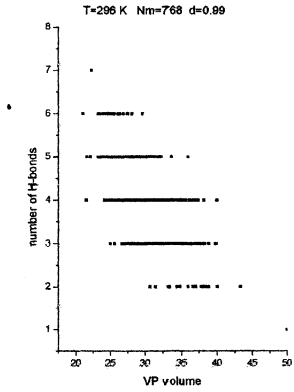


Figure 2b. Poor correlation between the number of hydrogen bonds and other characteristics of the environment of the water molecules: VVP. The instantaneous configuration is the same as on Fig. 2a

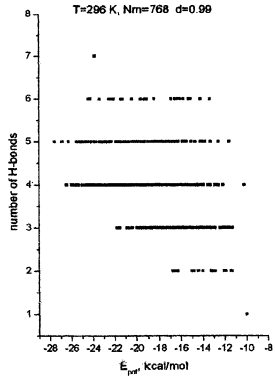


Figure 2c. Poor correlation between the number of hydrogen bonds and other characteristics of the environment of the water molecules: VVP. The instantaneous configuration is the same as on Fig. 2a

definition [31]. The upper limits of R_{OO} and R_{OH} correspond to the inflections of the rank distributions of these distances [31] (see [43] about the rank distributions). The values of lifetimes were corrected by a dynamic criterion [44]. According to the dynamic criterion a hydrogen bond is not considered broken if the period during which R_{OO} and/or R_{OH} exceeds the limits, is shorter than τ^{min}. The latter value was determined from the inflection on the rank distributions of hydrogen bond lifetimes plotted without taking into account the dynamic criterion. The same inflection was found for the distributions of periods of time during which the proton did not participate in the hydrogen bond. The inflexions of both distributions correspond to the same time, 0.08 ps; hence τ^{min} = 0.08 ps [44]. This time is a little shorter than the typical period of oscillations of the R_{OO} distance. As follows from the rank distributions of hydrogen bond lifetimes, a small number of hydrogen bonds exist for rather long time, more than 20 ps. The molecules connected by these long-living bonds constitute complexes which move within the network during the lifetime of these bonds. It can be said that the hydrogen bonded network in water is not homogeneous with respect to lifetimes of the individual bonds. But this heterogeneity cannot be seen from the analysis of instantaneous structures only. One must know the past and the future of the system in order to see this heterogeneity. This situation is similar to the case of the dynamic criterion for hydrogen bonds.

A more trivial case of dynamic heterogeneity lies in the dependence of dynamical properties of water molecules on their local environments. We have studied such dependence for crystalline [35,36] and amorphous ices [45–47] as well as for liquid water [34,48]. The time dependence of the center of mass mean square displacement for the molecules with different values of VVP is shown in Fig. 3 for water at ambient temperature and density. The main difficulty for the study of dynamical heterogeneity of this kind consists in the time dependence of characteristics of the local environment. It was necessary to choose the molecules, which retain values of the corresponding characteristics for rather long time to be able to calculate dynamic properties. How it was done we described in our earlier publications [34,48]. It was shown there, that not only mean square displacement depends on local environment, but the density of vibration states as well. Let us discuss the time dependence of local environment of the molecules using the type of coordination as an example.

4. DYNAMICS OF TYPE OF COORDINATION

We already discussed the lifetimes of various types of coordination in one of our previous papers [31]. Since then we have done more detailed computations and some of their results will be given here. Types of coordination were searched during the simulation of a $(H_2O)_{216}$ microdroplet at the temperature 300 K. The length of the trajectory was 80 ps. Geometrical and dynamical hydrogen bond criteria were used. The rank distributions of some TC are shown on Fig. 4.18 different TC were recorded. The information about them is summarized in Table 1.

The data on probabilities and lifetimes in this table differ from those given in Ref. [31], because here we give information about the whole cluster and in [31] the data refer to its inner part only. For instance, the probability of TC A_2D_2 in the central part of the cluster is 52% [31]. Probabilities of TC in the central part of the cluster are practically

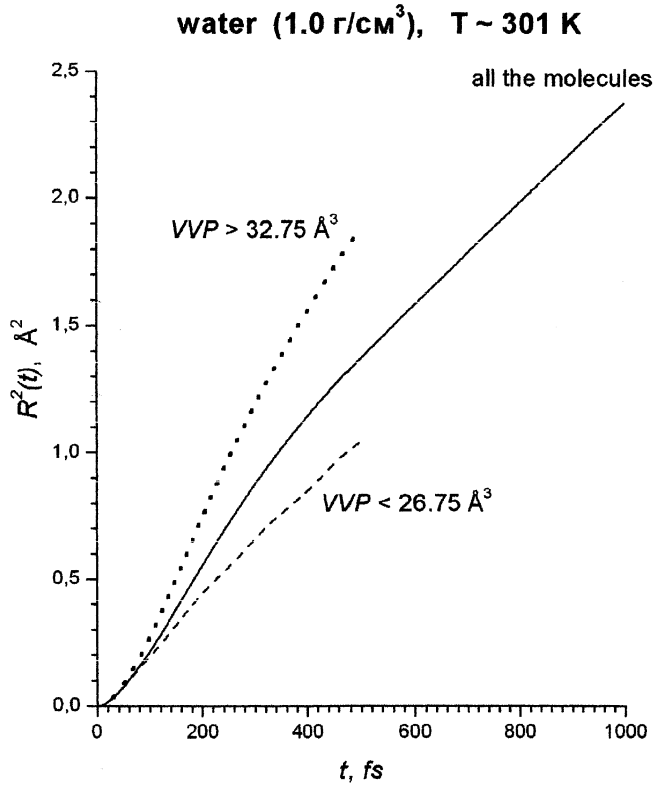


Figure 3. Dependence of the mobility of water molecules on the local density. The diffusion of molecules with small values of VVP (higher local density) is slower. A qualitatively similar dependence was found for water molecules with different values of τ [34,44,45]

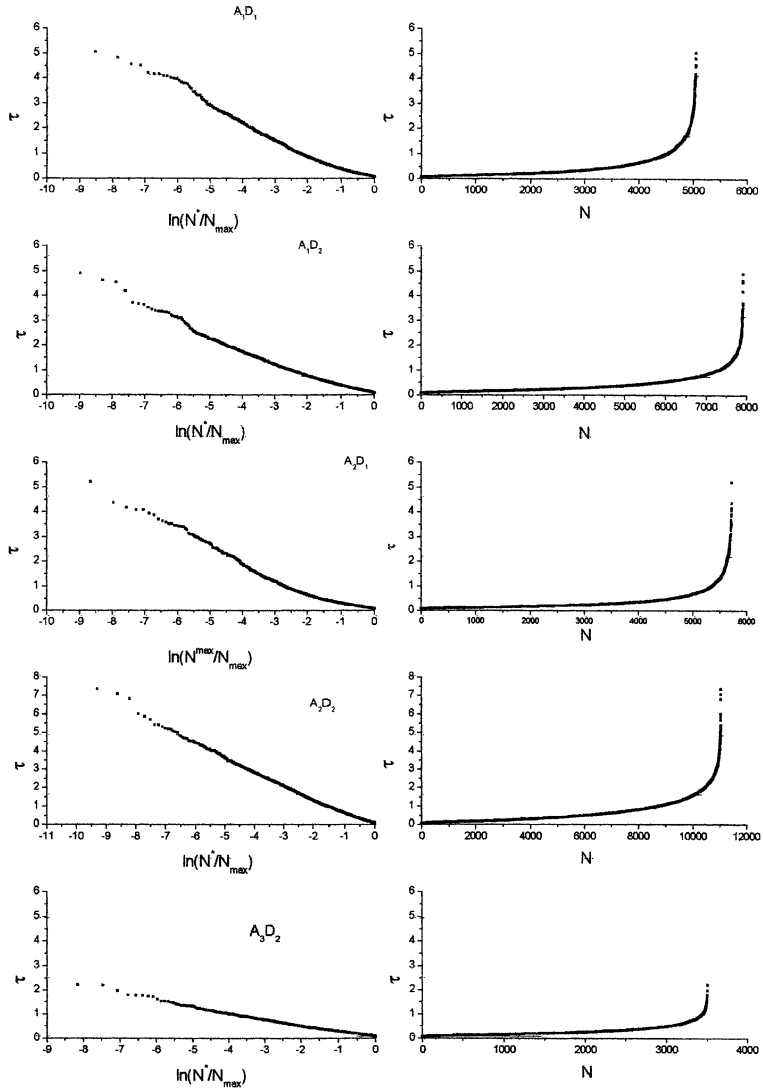
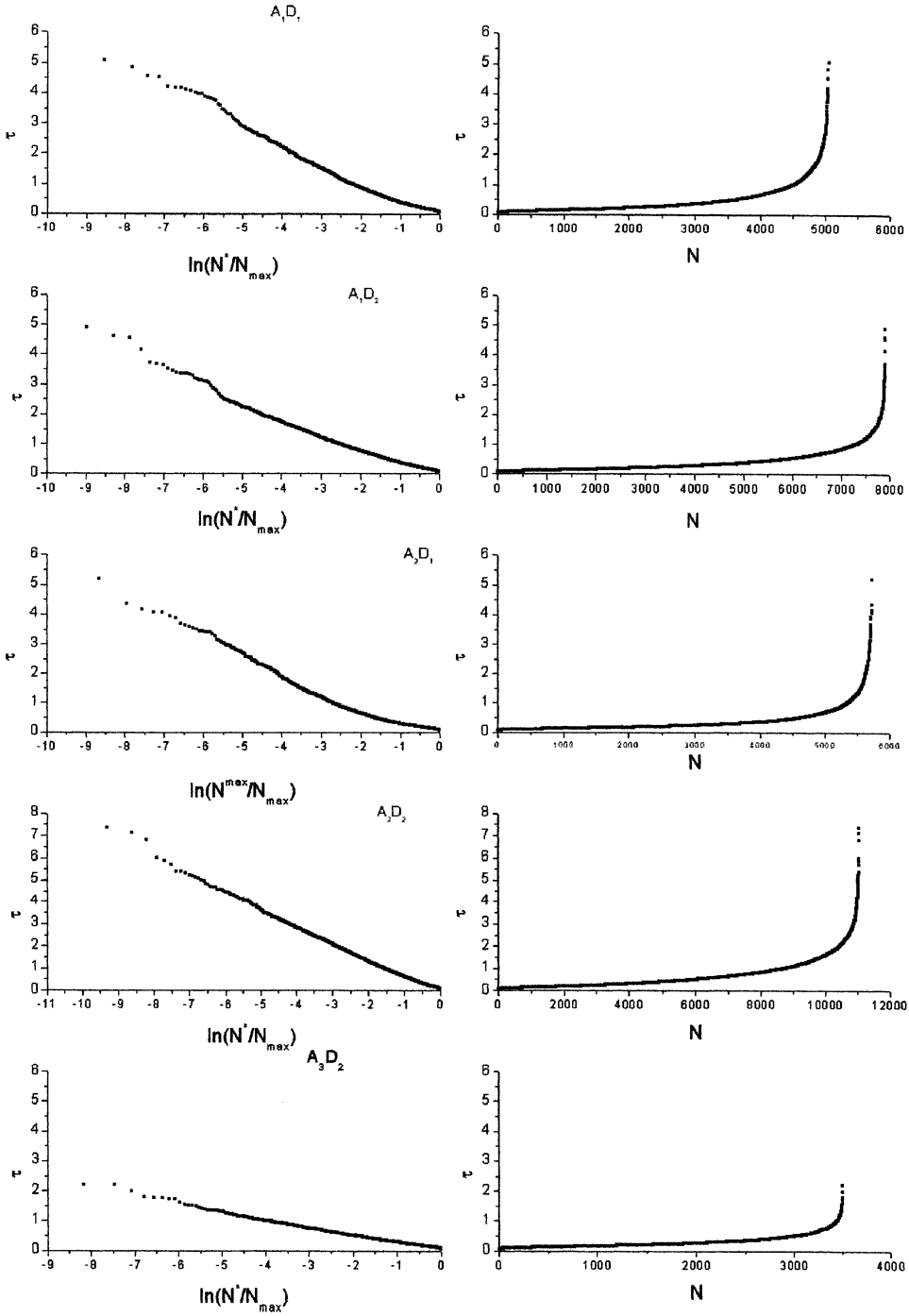


Figure 4. Rank distribution of lifetimes of some types of coordination. Graphs in the left are plotted in coordinates: $\log(N/N_{max})$ versus lifetime τ, N_{max} being the number of terms of the series with highest lifetime [43]. Graphs on the right part are usual rank distributions plotted in the coordinates: number of terms of the series versus lifetime


A1D1
τ
ln(N*/Nmax)
N
A1D2
τ
ln(N*/Nmax)
N
A2D1
τ
ln(Nmax/Nmax)
N
A2D2
τ
ln(N*/Nmax)
N
A3D2
τ
ln(N*/Nmax)
N

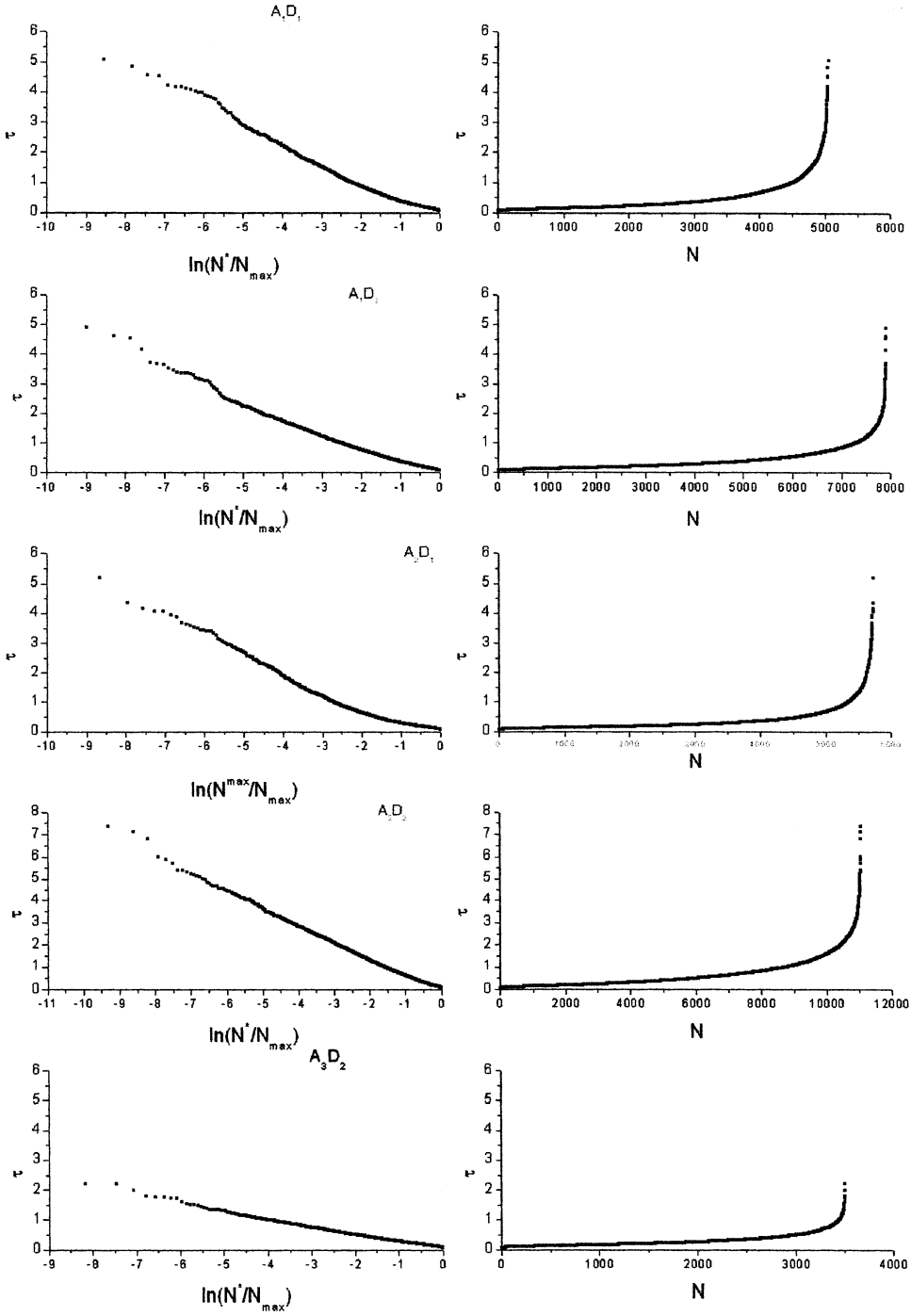

A1D1
τ
ln(N*/Nmax)
N
A1D2
A2D1
ln(Nmax/Nmax)
A2D2
A3D2

Table 1
Types of coordination of water in a $(H_2O)_{216}$ microdroplet

TC	Probability, %	The longest lifetime observed, ps	Average lifetime, ps	Fraction of lifetimes longer than 1 ps, %
A_0D_2	0.65	1.84	0.30	4
A_0D_2	0.47	1.07	0.24	0.6
A_1D_2	1.19	2.73	0.31	4.8
A_1D_2	13.78	5.06	0.47	10.9
A_1D_2	19.45	4.89	0.43	8.0
A_1D_2	0.16	0.41	0.16	0
A_2D_2	0.44	1.89	0.22	1.7
A_2D_2	12.43	5.21	0.38	6.7
A_2D_2	43.79	7.35	0.69	21.1
A_2D_2	0.75	0.62	0.19	0
A_2D_2	0.0007	0.13	0.13	0
A_3D_2	0.009	0.33	0.16	0
A_3D_2	0.54	0.79	0.19	0
A_3D_2	6.16	2.23	0.31	1.8
A_3D_2	0.09	0.43	0.16	0
A_4D_2	0.002	0.25	0.24	0
A_4D_2	0.06	0.67	0.18	0
A_4D_2	0.002	0.25	0.2	0

Table 2
Probabilities of different types co-ordinates in deeply supercooled (glassy) water (%). NHB is the average number of hydrogen bonds between molecules.

TC	$d = 1.3$ $T = 105$	$d = 1.17$ $T = 105$	$d = 1.0$ $T = 99$	$d = 0.94$ $T = 109$
A_1D_1	0	0.13	0	0.91
A_2D_1	0.15	0.65	1.95	2.21
A_3D_1	0	0	0.13	0.26
A_1D_2	8.18	9.37	9.11	9.11
A_2D_2	67.28	73.18	80.08	80.08
A_3D_2	15.74	12.5	7.68	6.90
A_4D_2	0.46	0.13	0.13	0
A_1D_3	0.15	0.26	0.13	0
A_2D_3	7.1	3.0	0.78	0.52
A_3D_3	0.31	0.52	0	0
A_2D_4	0.62	0.26	0	0
NHB	4.82	4.40	4.06	4.00

the same as found in bulk water at normal density and temperature. In the last column of the table the fractions of lifetimes longer than 1 ps are given. The value of 1 ps is, of course, arbitrary. But it gives some idea about the number of relatively long-living types of local coordination.

It was demonstrated rather long ago [42] that in the inherent structures (F-structures in [42]) the number of different TC is smaller and the fraction of more abundant TC is greater in comparison with the ensemble of instantaneous structures. The distribution of all structural characteristics obtained at low temperatures is close to the one found for inherent structures. We demonstrate the dependence of the probabilities of TC on the density of water using the results of simulations at low temperatures as an example (Table 2).

5. SELF-DIFFUSION IN WATER AT VARIOUS DENSITIES AND TEMPERATURES

The dependence of the diffusion coefficient D on temperature for water at different densities is shown on Fig. 5. The results of all runs longer than 6 ps are plotted. The length of the segments along which $\langle R^2 \rangle (t)$ was averaged, was more than 2 ps for most of the cases. For the longer runs (15 or 18 ps) the length of these segments was 3 ps. At low temperature, when diffusion is very slow, the scatter of values of D is rather high. But on the whole the dependencies are well approximated by an exponential graph. The dependence of D on temperature for water with the density corresponding to experimental density at atmospheric pressure is shown on Fig. 5d. The experimental data are also plotted. It is clear that our simulation reproduces the experiment with an error not larger than 10%. A quadratic interpolation of the computed data was performed. According

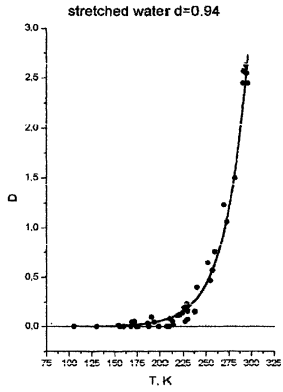


Figure 5a. Temperature dependence of self-diffusion coefficient (in $10^{-5}\,cm^2/s$) for $d = 0.94$. The results of all the runs longer than 6 ps are plotted. The solid line is the exponential approximation.

to the interpolation formula, the diffusion coefficient becomes zero at 223 K. The lowest temperature, where the diffusion can be observed in water with the density $1.17\,g/cm^3$ is about 140 K. This temperature is close to the glass transition point [28]. The diffusion in water with the density 0.94 (corresponding to the density of LD amorphous ice) starts at much higher temperature. A sharp rise of D occurs at temperatures between 120 and 130 K at all studied densities. This temperature is close to the beginning of homogeneous crystallization [28] and the hypothetical second critical point [25–28]. It is worth noting that even at low temperatures, when diffusion is so slow, that it cannot be estimated from the slope of $\langle R^2 \rangle (t)$, rare changes of hydrogen bond partners occur [47]. At the temperature about 130 K D linearly increases with density (Fig. 6). The dispersion of the values of D at this temperature is very high and the actual temperature dependence of D may be not so simple. It is necessary to stress that D increases in water at all the temperatures lower than 320 K, though not as sharp as has been found in our simulation for 230 K. As it was mentioned in Section 3 and in more detail discussed in [34], the diffusion of molecules with small values of VVP (i.e. belonging to the regions with higher density) is slower, than of molecules with large VVP. It means that the density dependence of D cannot be explained on the basis of the primitive two-state model. Water at all studied temperatures and densities is characterized by strong non-uniform distribution of molecules with high and low values of parameters describing their local environment. It is especially true for the space distribution of molecules with small and large values of VVP.

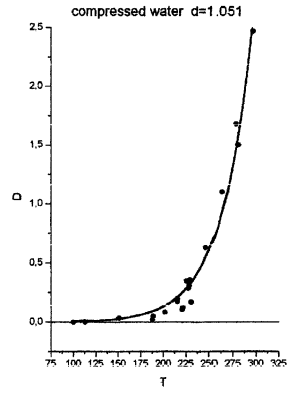


Figure 5b. Temperature dependence of self-diffusion coefficient (in $10^{-5}\,cm^2/s$) for $d = 1.051$. The simulation conditions and notations are the same as on Fig. 5a

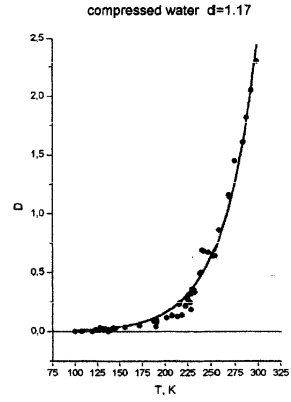


Figure 5c. Temperature dependence of self-diffusion coefficient (in $10^{-5}\,cm^2/s$) for $d = 1.17$. The simulation conditions and notations are the same as on Fig. 5a

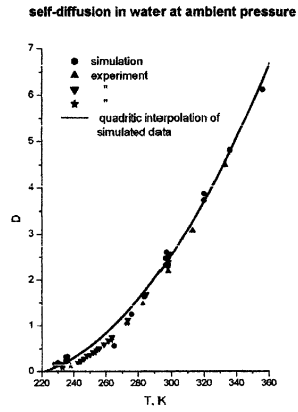


Figure 5d. Temperature dependence of self-diffusion coefficient (in 10^{-5} cm^2/s) at ambient pressure. The simulation conditions are the same as on Fig. 5a. The solid line is the quadratic approximation. •—simulations; ▲—experimental data from [48]; ▼ and ★—experimental data from [49]

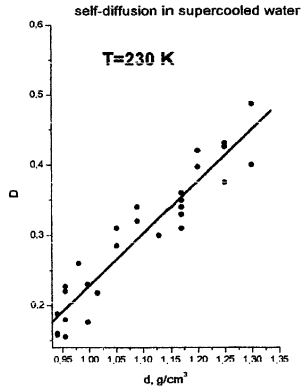


Figure 6. Density dependence of self-diffusion coefficient of water molecules at the temperature about 320 K. The straight line is the linear interpolation.

6. STRUCTURAL HETEROGENEITY

In our earlier publications [34, 45-48] we have demonstrated the structural heterogeneity of ordinary and supercooled water (amorphous ices) manifested in the non-uniform space distribution of molecules with high or low values of τ or VVP. Molecules with high or low values of these parameters tend to group together, forming clusters, which penetrate through the whole volume of the simulated system. These clusters can be easily visualized if we color about 20 % of the nodes of the Delaunay network (conters of the Voronoï polyhedra) with the highest or the lowest values of VVP. Similar pictures can be obtained if we color the same network according to the values of tetrahedricity of the nodes (which coincide with the oxygen atoms of the water molecules). Many examples of such pictures, illustrating structural heterogeneity of the hydrogen-bonded networks, have been given in Refs. [44-47]. Here we give a somewhat different way of visualization of the structural heterogeneity. All the molecules are divided into two equal classes in respect to one or another characteristics of their environments. 50 % molecules with lower values and 50 % with the higher values of τ, VVP, and E_{pot} are shown by different colors on Fig. 7. The picture is supplemented by the distribution in space of molecules with the TC A_2D_2 (first class, black color) and with all other TC (second class, gray color). All four pictures refer to the same instantaneous configuration of water at 298 K with the density 0.997 g/cm^3 (768 molecules in an independent cubic cell). This system has been chosen because in water at this temperature about 50 % molecules have the A_2D_2 TC. It is seen that the spheres of the same color tend to flock together. As the correlation between different characteristics of the environment is very weak, the four pictures are utterly different. The heterogeneity in respect to the space distribution of molecules with high or low values of VVP seems to be better pronounced than the other characteristics, but quantitative criteria of heterogeneity of such kind are yet to be developed.

7. CONCLUSIONS

Hydrogen bonded network in instantaneous structures of water obtained by computer simulation and built using reasonable hydrogen bond criteria seems to be rather homogeneous. But it is highly heterogeneous from the viewpoint of lifetimes of hydrogen bonds and particular types of coordination (number and type of hydrogen bonds involving the molecule). A heterogeneity of the other kind manifests in a non-uniform space distribution of molecules with close values of the parameters describing their local environments. This structural heterogeneity leads to a specific dynamic heterogeneity which is related to the difference of dynamic properties of the molecules with different local environments (regularity of surrounding, local density, number of hydrogen bonds). All these kinds of heterogeneity are inherent to the water network over a large range of densities and temperatures.

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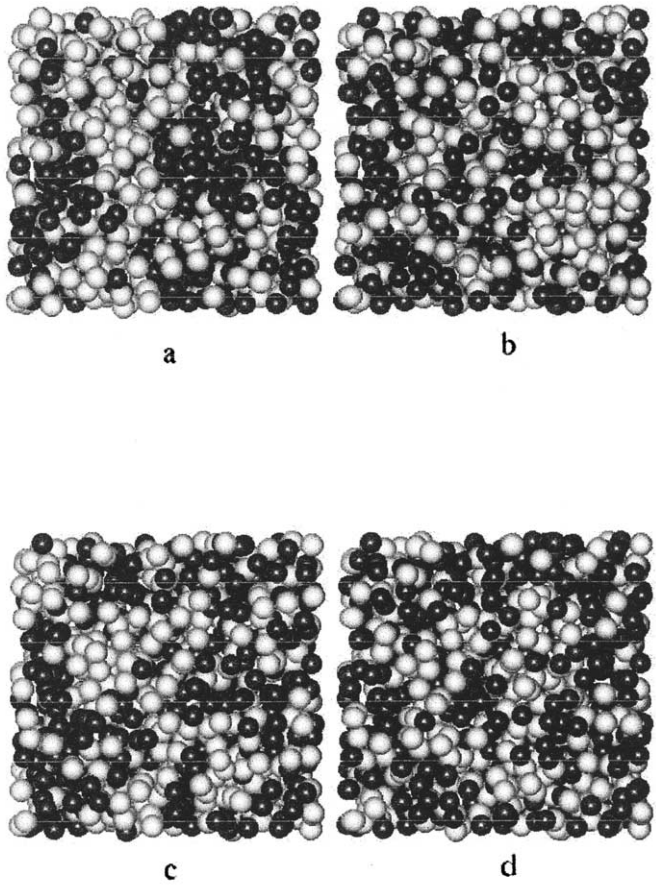

Figure 7. Space distribution of molecules with low (black) and high (gray) values of VVP (a), τ (b) and E_{pot} (c); 50% of molecules with low and other 50% of molecules with high values of the parameters are shown by different colors. On Fig. 7d the molecules with the A_2D_2 coordination are shown as black spheres (52% of the molecules). Molecules with all the other types of coordination are shown as gray spheres.

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