

Liquid water and ices: understanding the structure and physical properties

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TOPICAL REVIEW

Liquid water and ices: understanding the structure and physical properties

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Abstract

A review of the structure and some properties of condensed phases of water is given. Since the discovery of the polymorphism of crystalline ice (beginning of the twentieth century), 15 ice modifications have been found and their structures have been determined. If we do not take into consideration proton ordering or disordering, nine distinct crystalline ice modifications in which water molecules retain their individuality are known. In the tenth, ice X, there are no H₂O molecules. It contains ions (or atoms) of oxygen and hydrogen. The structure of all these modifications is described and information about their fields of stability and about the transition between them is given. It is emphasized that there are ice modifications which are metastable at any temperature and pressure (ices Ic, IV and XII), and many modifications can exist as metastable phases beyond their fields of stability. The ability of water to exist in metastable states is one of its remarkable properties. Several amorphous ice modifications (all of them are metastable) are known. Brief information about their properties and transitions between them is given. At the end of the 1960s the conception of the water structure as a three-dimensional hydrogen-bonded network was conclusively formed. Discovery of the polymorphism of amorphous ices awakened interest in the heterogeneity of the water network. Structural and dynamical heterogeneity of liquid water is discussed in detail. Computer simulation showed that the diffusion coefficient of water molecules in dense regions of the network is lower than in the loose regions, while an increase of density of the entire network gives rise to an increase of diffusion coefficient. This finding contradicts the conceptions associated with the primitive two-state models and can be explained from pressure dependences of melting temperature and of homogeneous nucleation temperature. A brief discussion of the picture of molecular motions in liquid water based on experiment and on computer simulation is given. This picture is still very incomplete. The most fascinating idea that was put forward during the last 20 years was the second critical point conjecture. It is still not clear whether this conjecture corresponds to reality.

(Some figures in this article are in colour only in the electronic version)

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Water equals time and provides beauty with its double. Part water, we serve beauty in the same fashion.

Joseph Brodsky. Watermark

1. Introduction

Water is a chemical substance consisting of hydrogen, the most abundant element in the Universe, and oxygen, the most abundant element on the Earth. The water molecule is the smallest molecule containing more than one atom. The water molecule behaves in crystals practically as a spherical particle with effective radius about 1.4 Å (see, for instance [1]). Even the H₂ molecule shows itself as a larger particle: the shortest distance between centres of H₂ molecules in a crystal is about 3.7 Å (the effective radius is half the size). Water is often said to be a very anomalous substance. These ‘anomalies’ are enumerated in M Chaplin’s well known internet site [2], consecrated to water. Sixty-three of them are counted there. I do not think that most of these ‘anomalies’ should be called so in the present state of the art. What is unusual in the high temperatures of melting and boiling of water? They are quite normal for a substance with hydrogen bonds. It is hardly surprising that, say, methanol boils at a much higher temperature than ethane. The first ‘anomaly’ in M Chaplin’s list (section ‘Physical anomalies’) is ‘water has unusually high viscosity’. To my mind, the viscosity of water is normal for a liquid with hydrogen bonds. But water is not simply a liquid with hydrogen bonds between its molecules. These bonds form a three-dimensional network. Rodnikova suggested setting apart such liquids from other solutes with hydrogen bonds [3–5]. They constitute a special class of liquids. High viscosity is typical for most such liquids (ethylene glycol, glycerol, ethanolamine etc). The viscosity of water is unusually low for the liquids belonging to the class of liquids with three-dimensional hydrogen-bonded network. But water is not the only exception. For instance, the viscosity of ethylenediamine is close to that of water [5]. I do not like to call unusual and peculiar properties of water anomalies. Most of them are fairly typical for the class of liquids to which water belongs. Many of them can be found in substances in which particles are not connected by hydrogen bonds, but are structurally similar to water (tetrahedral substances, such as SiO₂, Si and Ge). But, anyhow, the set of unusual properties of water is too large for one substance. I mean, in particular, that too many properties depend non-monotonically on temperature or pressure: volume, heat capacity, compressibility, viscosity, diffusion coefficient and others. And this applies not only to liquid water. Everyone knows that the density of water is maximal at 4 °C (at normal pressure). But the density of ordinary ice (ice Ih) at ambient pressure depends on temperature non-monotonically as well

and reaches its maximum at about 80 K. This fact was known rather long ago. The latest very precise measurements can be found in [6]. Similar behaviour is typical for other crystals in which particles are tetrahedrally coordinated (Si, Ge, ZnS, GaAs etc [7]), though interparticle interactions in semiconductors and ice are utterly different. This refers to the contraction of volume on melting and some other properties as well. So not only hydrogen bonds are responsible for the peculiar properties of condensed phases of water. Some of them can be connected with the actual arrangement of the particles irrespective of the nature of interactions between them. In my opinion the most interesting property of water is its polymorphism. At least 15 crystalline modifications of ice are known, as well as several amorphous ones. In this respect water seems to be the champion. The number of crystalline modifications of Si and Ge is a little smaller than that of ice and several amorphous modifications are known for these substances. But this structural diversity is partially connected with the transition from semiconductors to metals, whereas the nature of intermolecular interactions in ice modifications is the same (except ice X). Water molecules retain their individuality and are connected with each other by hydrogen bonds. Only in ice X are there no molecules. This modification can be considered as an ionic crystal (other interpretation: oxygen atoms are connected by strong symmetric hydrogen bonds).

So much has been said about crystals because crystals are the only condensed phases where the actual positions of atoms and molecules can be precisely known experimentally. My understanding of what structure is on an atomic level of organization of matter can be found in [8–11]. In these papers I tried to support idea that the structure of non-crystalline condensed phases is not reduced to a set of radial distribution functions as some physicists think (see, for instance, [12]), but can be described as a structure of crystals in terms of a particular arrangement of atoms or molecules.

This survey cannot cover, of course, all the problems connected with the condensed phases of water. I shall not touch on, for instance, water at high temperatures, including supercritical water, though it is extremely interesting and very important matter.

The well known book by Eisenberg and Kauzmann about water in all three states, gaseous, liquid and solid, was published 40 years ago [13]. A great number of new facts about water have come to light since then. Many new ideas have been put forward. But I still think that it is a great book. It summed up in a brilliant way the achievements of science concerning water on the eve of the era of computer simulation of this substance. A significant coincidence: the book [13] was published in the same year as the first paper on computer simulation of water [14]. I think that the start of computer simulation was one of the most important milestones in the history of studying water. Now I should like to name the other milestones. Their choice is, of course very personal. I want to start with the paper of Röntgen (1891, [15], see also [16]), in which he summarized experimental studies of water performed earlier and proposed the first two-state model of water. Of course, many important findings were made before made Röntgen. Water is not an element but consists of oxygen

Table 1. Triple points of water and thermodynamic data for phase transitions.

Phases			P (MPa)	T (K)	Transitions	ΔS (J mol ⁻¹ K ⁻¹)	ΔV (cm ³ mol ⁻¹)
Gas	Liquid	Ih	6.117×10^{-4}	273.16	Gas \rightarrow liquid	-132.5	-22 050
					Gas \rightarrow Ih	-154.5	-22 048
					Liquid \rightarrow Ih	-22.0	1.634
Liquid	Ih	III	207.5	251.1	Liquid \rightarrow Ih	-14.9	2.434
					Liquid \rightarrow III	-13.9	-0.839
					Ih \rightarrow III	1.0	-3.273
Ih	II	III	212.9	238.4	Ih \rightarrow II	-2.1	-3.919
					Ih \rightarrow III	1.0	-3.532
					II \rightarrow III	3.2	0.387
II	III	V	344.3	248.8	II \rightarrow III	3.1	0.261
					II \rightarrow V	3.3	-0.721
					III \rightarrow V	0.1	-0.982
Liquid	III	V	346.3	256.1	Liquid \rightarrow III	-13.2	-0.434
					Liquid \rightarrow V	-13.1	-1.419
					III \rightarrow V	0.1	-0.985
II	V	VI	~620	~218			
Liquid	V	VI	625.9	273.0			
					-15.7	-0.949	
					-16.2	-1.649	
					-0.5	-0.70	
VI	VII	VIII	2 100	~278			
Liquid	VI	VII	2 200	254.7			
VII	VIII	X	62 000	100			
Liquid	VII	X	43 000	~1600			

and hydrogen (last quarter of the 18th century). The formula of water is H₂O (middle of the 19th century). It was known in the Stone Age that the density of ice is less than the density of liquid water. Here are the milestones.

1891. Röntgen's model.

1900. Discovery of polymorphism of crystalline ice [17].

1922. Determination of crystal structure of ordinary ice [18].

1933. Bernal and Fowler's model [19]. Water is a continuous three-dimensional network of hydrogen-bonded molecules. It is very peculiar that the term 'hydrogen bond' is not used in this paper.

1936. Discovery of cubic and amorphous ices [20].

1969. Start of computer simulation of water on molecular level [14].

1979. Application of methods of percolation theory to structure of water [21].

1984. Discovery of pressure-induced amorphization of ice [22].

Of course many other remarkable discoveries were made and noteworthy ideas were suggested. But I have tried to enumerate the most important events, though, of course, not all of them were highly appreciated by their contemporaries.

2. Crystalline water

The number of publications dedicated to crystalline ice is enormous. Two good books were published in the 1970s [23, 24]. Much information can be found in corresponding chapters of multi-volume editions edited by Franks [25, 26]. A good book on ice physics appeared not so

long ago [27]. A collection of papers in which the present state of the art is covered was published recently [28]. An interesting review paper [29] contains much information about properties of crystalline and amorphous ice. In our survey [30] we cover mainly transitions between ice modifications, and their physical properties. In the present paper more attention will be given to their structure. Since the publication of our paper on crystalline water ices [30] two new modifications have been discovered and called ice XIII and ice XIV [31–34]. According to tradition, dating back to Tammann, to each newly discovered ice modification the next roman number is given. Thus Tammann called ordinary ice ice I and gave to modifications found by him numbers II and III. Ices IV, V, VI and VII were found and studied by Bridgman. The only exception is cubic ice, which is called ice Ic. After the existence of cubic ice was accepted by the scientific community, ordinary ice began to be called ice Ih (hexagonal). Ices VIII–XII were discovered in the second half of the 20th century; ices XIII and XV were found recently. Sometimes a number was assigned to a hypothetical modification, whose existence was not confirmed later. Thus along with 'normal' ice XI (the proton-ordered form of ice Ih) non-existing high pressure ice XI is discussed (the hexagonal analogue of ice X [35]). Holzapfel [36] mentions ice XII ('heavy fermion ice'), and calls it fictitious. Still more fictitious is ice IX from the excellent novel by Kurt Vonnegut *Cat's Cradle*.

Most ice modifications are formed when water is subjected to high pressures. In table 1 triple points of the water phase diagram are given. Most of the data are borrowed from Chaplin's site [2]. They were checked against original publications. Values of temperature were converted into kelvin. Triple points in which metastable phases participate were

excluded. I decided not to give the phase diagram of water in the graphic form. It is studied up to 100 GPa. If logarithms of pressure are plotted the diagram loses its lucidity. The data on the triple points can give a clear idea about the fields of stability of the phases.

It is seen that ices Ic, IV, XI, XII, XIII and XIV are not included in the table. The first four are metastable at any temperature at pressure. This is another interesting property of water—existence of phases which are metastable in the whole studied range of thermodynamic conditions. Most of the high pressure ice modifications can exist as metastable phases at ambient pressure and low temperatures. Information about stability of ices XIII and XIV is incomplete yet, but the latter is the proton-ordered form of ice XII and should be metastable. Information about the ice Ih–ice XI transition is contained in Chaplin’s table; I have excluded it. Ice XI is the proton-ordered form of ice Ih as ice XIII is the proton-ordered form of ice V. It is high time now to say some words about proton order in ice.

2.1. Proton order

As in early x-ray diffraction works on ice proton positions could not be determined, only speculative considerations about this problem could be put forward. In the 1920s some authors assumed that ice was an ionic crystal in which protons were placed on the lines connecting two neighbour oxygen atoms and were equidistant from them. Others admitted that H₂O molecules remain in the crystal. Bernal and Fowler were of the latter opinion. They wrote in their famous paper [19] that ice was a crystal with respect to the position of oxygen atoms and a glass with respect to the position of the hydrogen atoms. Bernal–Fowler rules were formulated: two hydrogen atoms are near each oxygen atom (1); on each line connecting nearest oxygen atom there is only one hydrogen atom (2). These rules refer to ideal crystals of course. In real crystals defects are always present. Violation of the first rule gives rise to formation of H₃O⁺ and OH[−] ions. When the second rule is violated, L and D Bjerrum defects arise (L means that there is no proton on the bond, D means that there are two of them between a pair of oxygen atoms). In 1935 Pauling [37], supposing that protons are distributed at random and Bernal–Fowler rules are followed, calculated residual entropy of ice. It is equal to $\ln 2/3$. All this is well known and has been discussed many times in the literature. In proton-disordered modifications each of the two possible positions on the bond is occupied with probability 1/2, while in proton-ordered ones only one of these positions is occupied with probability equal to unity. Proton-ordered forms have no residual entropy. This is why the entropy (table 1) and enthalpy of their transformation into proton-ordered forms is greater than that of transformation of one proton-disordered into another. The static dielectric permittivity of proton-ordered forms is low, while that of proton-disordered forms is high. Of course neither ideally disordered nor completely ordered ice crystals exist in nature. In table 2 proton-ordered and proton-disordered modifications are enumerated.

It is seen that ice II has no proton-disordered analogue, while no proton-ordered forms of ices Ic, IV and VI are known.

Table 2. Proton-ordered and proton-disordered ice modifications.

Proton-disordered modifications	Corresponding proton-ordered modifications
Ice Ih	Ice XI
Ice Ic	—
—	Ice II
Ice III	Ice IX
Ice IV	—
Ice V	Ice XIII
Ice VI	—
Ice VII	Ice VIII
Ice XII	Ice XIV

Ice X, of course is not included in the table because it does not contain water molecules in its structure (though, as will be noted below, the question of the existence of proton-disordered and proton-ordered forms of ice X is widely discussed in the literature; the difference between these two forms is of not the same nature as the difference between the modifications placed in the same row of table 2).

Ice IX exists within the field of ice II stability of the phase diagram and can be metastable at low pressure and temperature. As already pointed out, completely proton-ordered ice crystals do not exist. One of the first publications about ice IX is called ‘on nearly proton-ordered structure for ice IX’ [38]. But in ice III protons are partially ordered as well [39, 40]. Knight and Singer assert [41] that at very low temperature practically fully ordered ice IX exists. Ice IX is formed from ice III when it is cooled very quickly. It can be kept at a temperature below ~ 100 K. When heated it converts into ice II. Unlike the ice III \rightarrow ice IX transition, transformation of ice VII into ice VIII is a normal reversible phase transition [42]. This transition has been studied by many authors. As far as I know, the most detailed and thorough study of it was done using infrared spectroscopy [43]. The authors compare their results with those obtained by other authors who used different experimental techniques. At comparatively low pressures the transition temperature only slightly depends on pressure and occurs at about 270 K. When pressure reaches some 12 GPa, the transition temperature begins to decrease sharply and reaches 100 K at 62 GPa (the VII–VIII–X triple point, see table 1). The mechanism of the VII \leftrightarrow VIII transition was proposed in [44]. In [45] rearrangement of protons during this transition was considered. It was shown that the transition is of the first order and the entropy difference between phases should be equal to that calculated by Pauling.

No one managed to obtain other proton-ordered forms of ice from corresponding proton-disordered modifications without contamination of the samples. As already mentioned, many facts pointed to the possibility of partial ordering of protons in ices, especially at low temperature. The most compelling evidence was given by Johary and Wahalley for ice V [46] (see also [40]). It is necessary to add something to the system if one wants to obtain more or less fully proton-ordered forms of ices Ih, V and XII. Ice Ih doped with KOH converts into ice XI when cooled [47–49]. The transition is reversible and occurs at 72 K (at atmospheric pressure). Ices XIII and XIV have been prepared recently by cooling ice V and

XII respectively [32–35]. The transition occurred only in the samples doped with HCl. Addition of alkalis did not facilitate this transition. Neither did acid in the case of transformation of ice Ih into ice XI. This fact still needs comprehension.

I am not aware whether anyone has managed to prepare proton-ordered forms of ices IV and VI. Nothing is known of whether the proton-disordered form of ice II exists. The possibility of the existence of proton-ordered ice VI at low temperature has been discussed by some authors (see, for instance, [50]).

Proton ordering in ice can give rise to permanent macroscopic dipole moment of the crystal; hence the samples of proton-ordered modifications can be ferroelectric. This problem is discussed in many publications. The most vivid treatment of this problem can be found in a short note by Bramwell [51] (see also [48]).

2.2. Structure of crystalline ice modifications

All ice crystalline modifications, except ice X, contain H_2O molecules. These molecules are connected by hydrogen bonds forming a three-dimensional network. This network is sometimes called the hydrogen-bonded framework. All the molecules are involved in four hydrogen bonds. In two of them the molecule acts as a proton donor and in two as a proton acceptor. In ices Ih, Ic, XI, VII and VIII the bonds are directed towards vertices of practically regular tetrahedra. In other modifications these tetrahedra are more or less distorted. Frameworks of ice polymorphs differ in topology. According to essential topological properties all known water hydrogen-bonded frameworks can be subdivided into three main groups. (1) *Simple*. All the bonds form a single, not self-intersecting network. To this group belong most of the ice modifications: Ih (XI), Ic, III (IX), XII (XV). (2) *Self-entangled* or *knotted*. The bonds form a single but self-entangled framework, which can be regarded as a three-dimensional knot. To this group belong ices IV and V (XIII). (3) *Catenated* or *self-clathrate*. The bonds form two independent frameworks inserted one into another. Ices VI and VII (VIII) belong to this group. In both cases the two independent frameworks are identical.

2.2.1. Simple frameworks

Ice Ih and ice XI. The arrangement of oxygen atoms in these forms of ice is a widely occurring structural motif. In the same way Zn and S atoms (if regarded as identical) are arranged in wurtzite (hexagonal modification of ZnS) and in a great number of crystals isostructural with this mineral. Lonsdaleite, an exotic carbon modification, and corresponding Si and Ge modifications have the same structure [52, 53]. Another ice Ih structural analogue is high temperature (β) tridimite. In this modification of SiO_2 silicon atoms are arranged in the same way as oxygen atoms in ices Ih and XI. Bernal and Fowler [19] supposed that at low temperature, close to melting point, a tridimite-like component can be contained in liquid water, while at higher temperature quartz-like structure predominates. Quartz is denser and more abundant than tridimite, an SiO_2

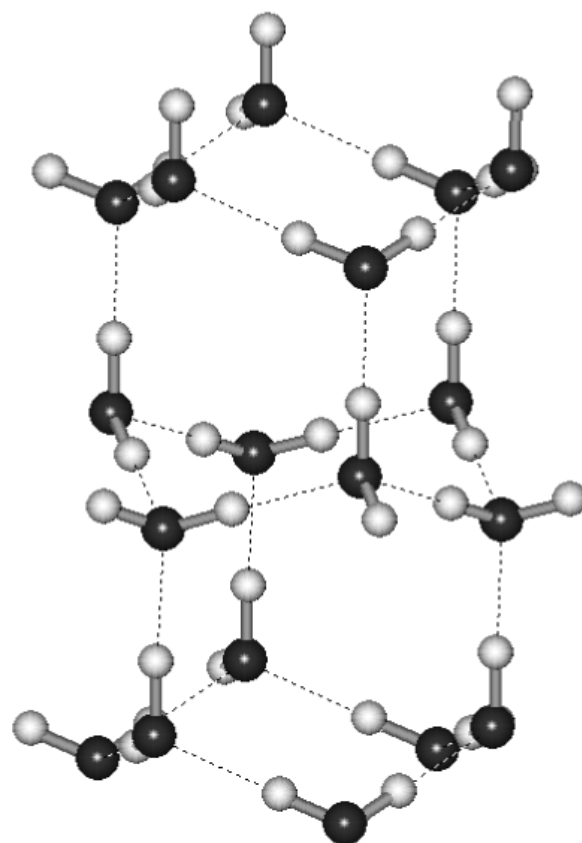


Figure 1. Fragment of the ice XI structure. Two cavities each of which is framed by 12 molecules are shown. Dashed lines are hydrogen bonds between the molecules. Positions of the oxygen atoms and of hydrogen bonds in ice Ih are the same.

modification; no form of ice isostructural with quartz is known. In the structure type to which ice Ih belongs, particles (oxygen, silicon etc atoms) are surrounded by four nearest neighbours placed in the vertices of regular tetrahedra. All particles are involved in hexagonal rings. There are two kinds of six-membered rings in this structure. Two-thirds of them have the chair conformation. Their mean planes are perpendicular to the hexagonal axis of the crystal. The rest are in the boat conformation and their mean planes are parallel to this axis (figure 1). There are channels in the structure going along the hexagonal axis (figure 2 left). These channels can be regarded as chains of cavities. Each cavity is formed by a construction of 12 particles (two chair rings put one above another). In the case of ice the cavity can accommodate such small atoms as helium. There is one cavity per two water molecules. Proton ordering in ice XI leads to lowering of symmetry from hexagonal to orthorhombic [54].

Ice Ic has the same structure as sphalerite (cubic ZnS modification), diamond and corresponding forms of Si, Ge and Sn and high temperature cristobalite. The surroundings of the particles are the same as in the hexagonal structures, but cubic ones contain six-membered rings in the chair conformation only. The structure contains cavities which are smaller than the cavities in ice Ih. There is one particle for each cavity. The cavity is formed by nine atoms, whose arrangement is

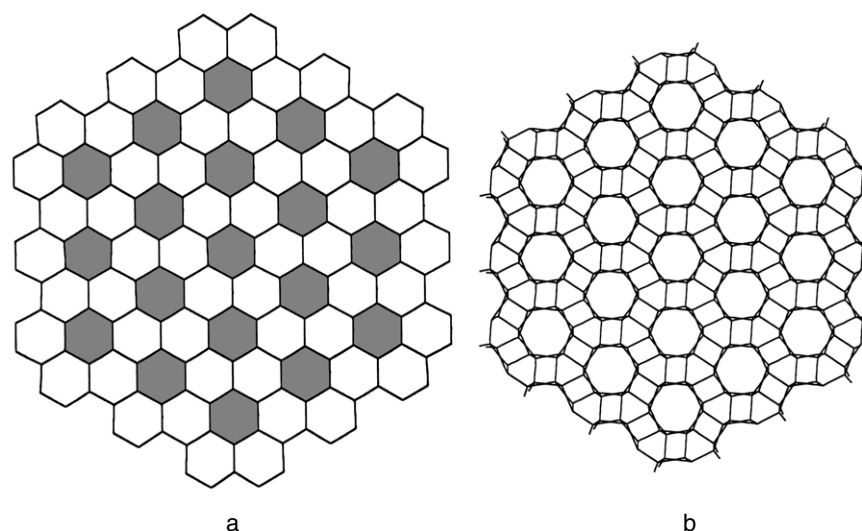


Figure 2. Left: projection of the ice Ih (IX) structure along the trigonal axis. Channels going along this axis are seen. One-third of them are marked. Right: the same for ice II. The channels marked in the left part of the figure retain their positions in ice II.

identical to the arrangement of carbon atoms in the adamantane molecule. The centres of the cavities form the same system of points as the centres of the atoms. It is not yet explained satisfactorily why in the case of ice the hexagonal modification is common and widespread in nature and the cubic one exotic, while for group IV elements the situation is the reverse. Diamond and cubic modifications of Si, Ge and Sn (white tin) are common, whereas lonsdaleite and its structural analogues of Si and Ge are exotic. The lonsdaleite form of tin has not been found yet.

Ice II. Though the density of ice II is about 25% higher than the density of ices Ih and Ic, the structure of ice II contains more roomy cavities than found in ice Ih. There is one cavity per six molecules in the ice II framework. Cavities are formed as in the case of ice Ih by two six-membered rings, but one of these rings is almost flat and the other is puckered as in ice Ih and has the chair conformation. Projections of the structures of ices Ih and II along the hexagonal (trigonal in the case of ice II) axis are compared in figure 2. It is seen that one-third of the channels in ice Ih are retained but all others are smashed and contain no cavities. I paid attention to this similarity of the structures of ices Ih and II long ago, but never thought that it was relevant to the mechanism of transformation of ice Ih to ice II. The main problem is why ice II is proton ordered and it is not known how proton order arises when ice Ih is compressed.

Ices III and IX. The density of these modifications is less than that of ice II, but there are no cavities in the ice III framework which can accommodate any atom or molecule. These modifications are the only ones among water ices which possess chirality: ices III and IX can be left and right. As in ice II there are two kinds of crystallographically nonequivalent molecules in ices III and IX. The molecules of the first kind form helices twining round fourfold screw axes; the molecules of the second kind form hydrogen bonds with molecules of the first kind, thus integrating all the molecules into a single

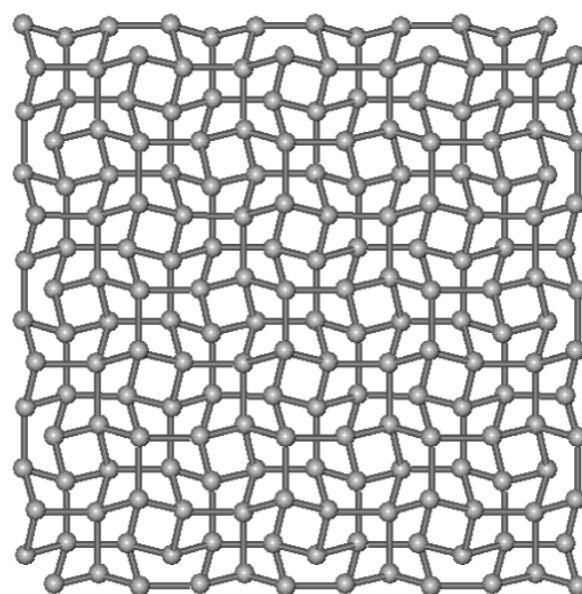


Figure 3. Projection of the ice III (ice IX) framework on the x - y plane. Oxygen atoms and hydrogen bonds are shown.

three-dimensional network. A distinguishing feature of the ice III framework is the presence of non-flat five-membered rings in formation of which molecules of both types participate (figure 3). Seven-membered rings are also present. In ice III due to proton disorder the number of types of molecules with different surroundings is, naturally, more than two [55]: each molecule can be oriented in six different ways. This applies to all proton-disordered ice phases. In paper [38] a comparison of the degree of proton order in ices II and IX was made. Ice II is almost completely proton ordered, while ice IX is partially proton disordered. Proton ordering in ices III and IX was studied thoroughly in [40, 56]. Ices III and IX are isostructural with Ge III [52, 57] and keatite, one of the SiO_2 modifications [58].

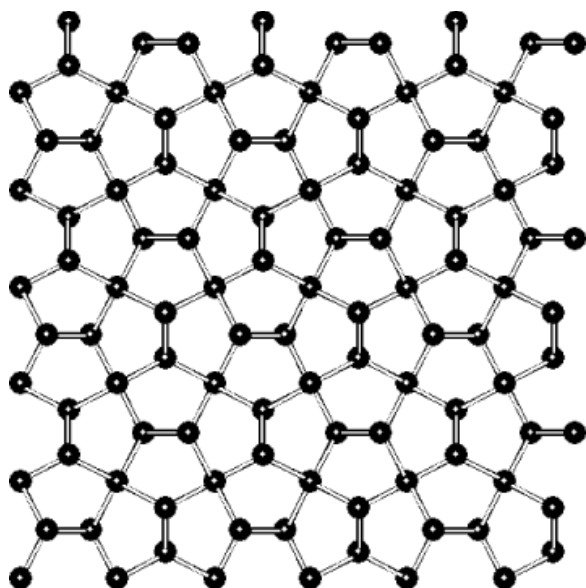


Figure 4. Projection of ice XII (ice XV) framework on the x - y plane. Oxygen atoms and hydrogen bonds are shown.

Ices XII and XIV (figure 4). These modifications are the densest ones among the forms of ice whose topology is simple [59]. There are two crystallographically different sorts of molecules. Molecules of one sort form zigzag chains along the c axis of the tetragonal unit cell. Molecules of the other sort join these chains together, forming a three-dimensional network. There are no six-membered rings in the framework, but only and seven- and eight-membered ones are present. Transition to proton ordered for ice XIV occurs with reduction of symmetry from tetragonal to orthorhombic.

2.2.2. Self-entangled (knotted) frameworks

Ice IV. An unusual property of this modification is that it is much easier to obtain it from heavy water than from ordinary water. The structure of ice IV was determined in [60] (see also [61]). The framework contains almost flat six-membered rings. These rings are connected with each other by hydrogen bonds, thus forming a three-dimensional network. All the molecules from the rings are crystallographically identical. The rings are pierced by hydrogen bonds between two water molecules, one of which is above and the other below the ring (figure 5, top). These molecules belong to another crystallographic type and are involved in hydrogen bonding with the molecules of the first type. The framework from a topological point of view can be regarded as a three-dimensional knot. It is very elegant (figure 5, bottom).

Ices V and XIII. These are the most complicated ice structures. The ice V unit cell contains 28 water molecules belonging to four crystallographically different types of molecules. The unit cell of ice XIV contains 28 molecules as well with seven crystallographically distinct oxygen atoms. The space group of ice V is $A2/a$ [40] while that of ice XIII is $P2_1/a$ [32]. It is not so easy to give a clear and intelligible description of this

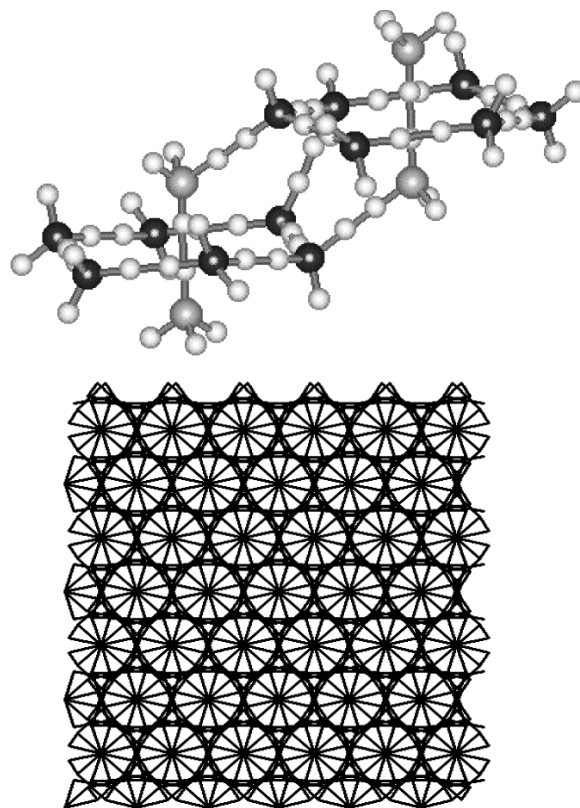


Figure 5. Structure of ice IV. Top: two six-membered rings (formed by water molecules with black oxygen atoms) pierced by hydrogen bonds between molecules with grey oxygen atoms are shown. Bottom: projection of the framework along the trigonal axis; oxygen atoms and hydrogen bonds are shown.

complicated structure. One of its structural elements is a band of fused eight-membered rings through which a zigzag chain of hydrogen-bonded molecules is threaded. The framework is remarkable for the most rich assortment of rings. Four-, five-, six- and eight-membered rings can be found in it.

2.2.3. Catenated or self-clathrate frameworks

Ice VI. Two identical frameworks are inserted one into another (figure 6). There are no hydrogen bonds between the molecules belonging to each framework. There is a structural analogue of the single ice VI framework among the aluminosilicates, eddingtonite (see [62]). Both frameworks are built of the structural elements consisting of six water molecules connected by hydrogen bonds (figure 7 right). The structural element can be treated as a distorted octahedron (figure 7, left). The octahedron must be stretched along one of the fourfold axes. This stretching leads to breaking of two of the four bonds (if we consider the edges of the octahedron as bonds) in which the molecules lying on this axis participate. The other four molecules, which occupy the vertices of the regular square in the octahedron, move up and down. They do not lie in one plane in the ice VI fragment. All four bonds between them remain. So there are eight hydrogen bonds in the fragment. The structure of this fragment is very

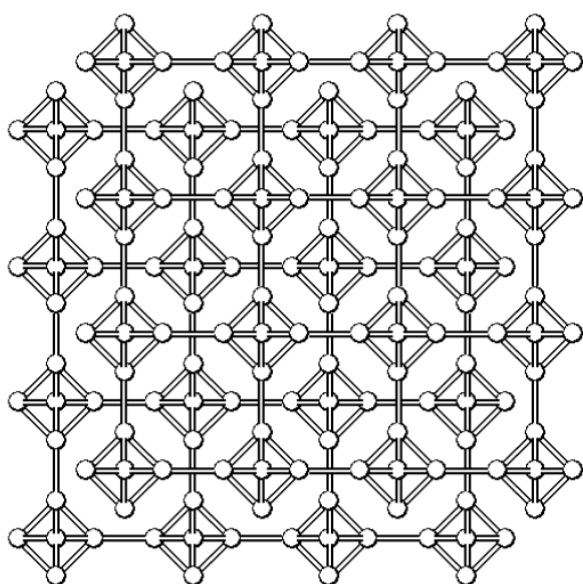
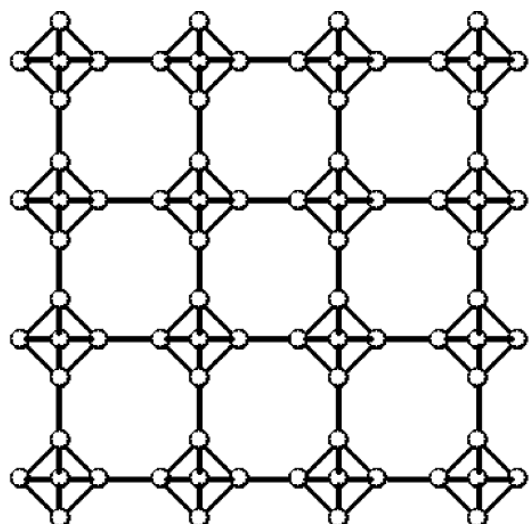


Figure 6. Structure of ice VI. Top: single ice VI framework. Oxygen atoms and hydrogen bonds are shown. Bottom: two frameworks inserted one into another. Oxygen atoms and hydrogen bonds are shown.

close to the structure of the most stable $(\text{H}_2\text{O})_6$ cluster found experimentally [63]. I obtained an $(\text{H}_2\text{O})_6$ cluster with similar structure in the course of Monte Carlo simulation of water clusters when I used a configuration in which water molecules had been placed in the vertices of a regular octahedron as the initial configuration [64]. Unfortunately in those days I did not guess that the structure of this cluster resembles a structural element of ice VI. The authors of [63] focus particular attention on this similarity. No fully proton-ordered form of ice VI is known, but as mentioned above many authors leave room for such a possibility and do not exclude the existence of fully proton-ordered ice VI [49].

Ices VII and VIII. It was noted in our description of the ice Ic structure that the system of centres of oxygen atoms and the system of cavity centres are identical. One is shifted with respect to the other along the diagonal of the cubic unit cell. If we fill all the cavities with the same particles as occupy the

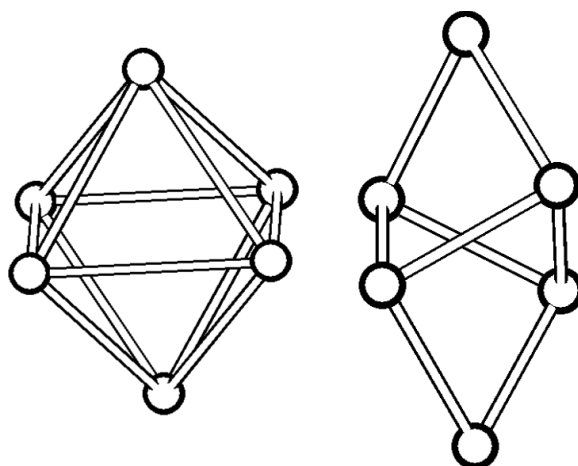


Figure 7. Right, ideal octahedron; left, structural element of ice VI.

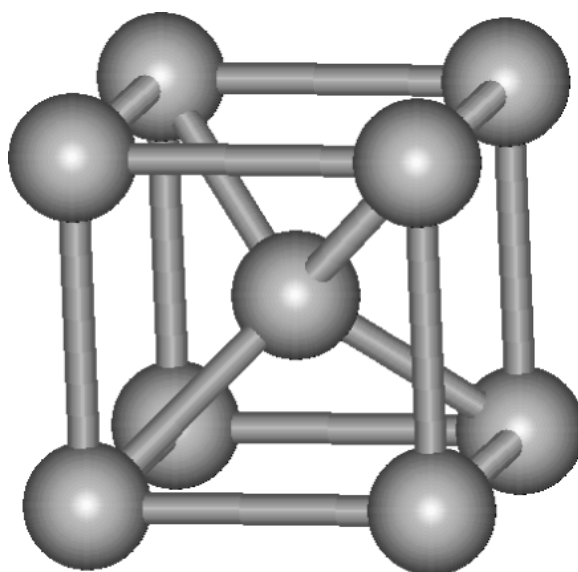


Figure 8. Body-centred cube. Unit cell in ice VII structure. Oxygen atoms, hydrogen bonds (along the diagonals of the cube) and limits of the unit cell (along the edges of the cube) are shown.

nodes of the framework, we shall obtain the well known and widespread structure in which particles are placed in the nodes of a cubic body-centred lattice (figure 8). The parameter of the cubic unit cell is half the size of the parameter of the face-centred ice Ic cell (in fact, due to repulsion between molecules in the centre of the cube and in its vertices, the parameter of the body-centred cube is a little greater than one-half of the parameter of the ice Ic face-centred cubic cell [42]). Many metals have such structure: ordinary iron (so-called α -iron), Na, K, Mo, α -W etc. If we consider such binary compounds as ZnS to be structural analogues of ices Ih and Ic, then CsCl and dozens of other salts and intermetallic compounds will be ice VII analogues. The symmetry of the proton-ordered form is lower than that of the proton-disordered one. Ice VIII is orthorhombic [65]. As already mentioned, the ice VII \leftrightarrow VIII transition is reversible and unlike many other forms of ice VII does not retain its proton-disordered structure

Table 3. Crystallographic parameters and some properties of crystalline ices.

Ice	Space group	Unit cell parameters (Å and degrees)	T, p	Z	ρ (g cm ⁻³)
Ih	$P6_3/mmc$	$a = 4.48, c = 7.31$	98 K, ambient pressure	4	0.92
Ic	$Fd\bar{3}m$	$a = 6.370$	98 K, ambient pressure	8	0.92
II	$R\bar{3}$	$a = 7.78, \alpha = 113.1^\circ$	123 K, ambient pressure	12	1.17
III	$P4_12_12$	$a = 6.73, c = 6.83$	240 K, 0.25 GPa	12	1.13
IV D ₂ O	$R\bar{3}c$	$a = 7.60, \alpha = 70.1^\circ$		16	1.272
V	$A2/a$	$a = 9.22, b = 7.54, c = 10.35, \beta = 109.2^\circ$	98 K, ambient pressure, 0.3–0.6 GPa	28	1.231
VI	$P4_2/nmc$	$a = 6.27, c = 5.79$	98 K ambient pressure	10	1.31
VII	$Pn\bar{3}m$	$a = 3.30$		2	1.66
VIII	$I4_1/amd$	$a = 4.656, c = 6.775$	10 K, 0.24 GPa	8	1.81
IX D ₂ O	$P4_12_12$	$a = 6.73, c = 6.83$	250 K, 0.3 GPa	12	1.13
XI	$Cmc2_1$	$a = 4.502, b = 7.798, c = 7.328 \text{ Å}$		8	0.93
XII	$I42d$	$a = 8.304 \text{ Å}, c = 4.024 \text{ Å}$	260 K, 0.5 GPa	12	
XIII	$P2_1/a$	$a = 9.2417, b = 7.47234, c = 10.29701, \beta = 109.6873^\circ$	80 K, ambient pressure	28	
XIV	$P2_12_12_1$	$a = 8.35, b = 8.1391, c = 4.0825$	80 K, ambient pressure	12	1.293

at low temperature and pressure. But ice VII can be obtained at a temperature below the VII \leftrightarrow VIII transition line by compressing other ice modifications at low temperature (ice Ih, via amorphous ice of high density [66], ice II [67], ice VI [68]). Most interesting in these transformations is the fact of formation of proton-disordered ice VII from proton-ordered ice II in the field of stability of proton-ordered ice VIII. This metastable ice VII is usually designated ice VII'. It transforms into ice VIII when heated at high pressure. The structure of ice VII' obtained from ice VI is the same as that of ice VII. But diffraction pattern of ice VII' prepared from ice II was found to be slightly different from that of standard ice VII [66]. The infrared spectra of these forms were practically identical [67]. There is little reason at present to speak about ice VII' as a special form of ice, different from ice VII.

Crystallographic parameters of molecular crystals of ice modifications are given in table 3.

2.2.4. Non-molecular ice

Ice X. This is the only form of ice which does not contain water molecules. The existence of this modification was doubted for a long time, though more than 35 years ago Holzapfel supposed that at very high pressure a form of ice with symmetric hydrogen bonds can arise [69]. But even in 1999 Holzapfel still called ice X 'evasive' [36]. Classical ice X is isostructural to Cu₂O: oxygen atoms in both structures occupy the sites of a body-centred cubic lattice, protons (in ice X) and copper atoms (in Cu₂O) lie on the threefold axes and are equidistant from the two nearest oxygen atoms. Each oxygen atom is surrounded by four protons (copper atoms) located in vertices of a regular tetrahedron. It can be said that

the ice X structure is a three-dimensional network of strong symmetric hydrogen bonds. Here, perhaps, it is appropriate to recall that hydrogen bonds in liquid water and all ice modifications considered above are sometimes called weak. In condensed phases in which molecules are involved in weak hydrogen bonds O–H is only slightly longer and the H–O–H angle slightly greater than in the vapour. The distance between oxygen atoms of the hydrogen-bonded molecules is about 2.8 Å, that is close to the sum of van der Waals radii. The bond between the H₃O⁺ ion and the H₂O molecule is an example of a strong hydrogen bond. The O...O distance in this bond is about 2.4 Å and the proton is practically equidistant from the oxygen atoms. Two possibilities for realization of a symmetric hydrogen bond in ice at extremely high pressure were proposed: (1) there is one minimum of potential energy for the proton position along the O...O line [69] and (2) there are two minima of potential energy for the proton position and one maximum of the proton distribution function along this line [70]. In the second case ice can be proton disordered. The problem of existence of ice modifications in which these possibilities are realized has been the subject of wide speculation. Infrared spectroscopic studies gave strong evidence of the possibility that ice with strong symmetric hydrogen bonds can exist at very high pressure [71, 72]. Subsequent spectroscopic studies confirmed the existence of ice X [73, 74]. X-ray diffraction study also supports this [75]. These spectroscopic and x-ray experiments were done in diamond cells. The volume of the samples was too small for neutron diffraction experiments, the only way to determine unambiguously positions of protons (or, more precisely, of deuterons, because only in deuterated substances can hydrogen positions be determined by neutron diffraction). According to spectroscopic studies the ice VII \leftrightarrow ice X transformation in

D₂O samples occurs at a pressure some 10 GPa higher than in H₂O samples [74]. It is generally believed that at this pressure ice VII (or VIII) transforms into proton-disordered ice X and the proton-ordered form arises at higher (150–160 GPa) pressure [71, 76]. Interesting considerations about two forms of ice with symmetric hydrogen bonds can be found in [77].

2.3. More about transformations between ice modifications

A fairly simple and clear picture of transformations which occur in the ice frameworks as pressure (and hence density) increase could be drawn before the discovery of ice XII. At pressure below 200 MPa water molecules are surrounded by four nearest molecules placed in the vertices of practically ideal tetrahedra (ices Ih, Ic, XI). The increase of pressure leads to distortion of tetrahedra which results in the increase of ice density (ices II, III, IX). Further increase of density cannot be achieved only by distortion of the tetrahedra and frameworks with non-trivial topology arise (self-entangled in ices IV and V, self-clathrate in ice VI). At higher pressure again ice with ideal tetrahedral coordination arises: two ideal diamond frameworks inserted one into another. Discovery of ice XII made the situation more complicated. Topology of its framework is simple but it is denser than ices V and VI with not trivial topology.

Tetrahedrality index T can be used as the measure of distortion of the tetrahedra. T is calculated according to formula:

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

where l_i and l_j are edges of the tetrahedron with the oxygen atom of the molecule whose T is being calculated in the centre. The vertices of the tetrahedron are occupied by the oxygen atoms of the four nearest water molecules. $\langle l \rangle$ is the average length of the edges of this tetrahedron. The lower T is the more regular is the tetrahedron. For the ideal tetrahedron T equals zero. Four nearest oxygen atoms are chosen whether the corresponding molecules form a hydrogen bond with the central molecule or not. This circumstance is of no importance in the case of crystal structures of ice modifications (except VII and VIII) because water molecules in them always form hydrogen bonds with four nearest molecules and only with them. In the case of ices VII and VIII each molecule has eight nearest molecules equidistant from the central molecule. In this case we must take into consideration the presence of hydrogen bonds. If we do this, the tetrahedrality indices of the molecules in ices VII and VIII will be, as well as in ices Ih, Ic and XI, very close to zero. The values of tetrahedrality indices of molecules in other ice modifications are given in table 4.

The discovery of ice XII proved that a framework with simple topology can be constructed in which the tetrahedral surroundings of the molecules are distorted to a lesser extent than in topologically non-trivial ice VI. Density of ice XII is between densities of ices IV and VII and considerably greater than ice V density.

Now I shall give a short summary of conditions in which ice modifications are formed.

Table 4. Tetrahedrality indices of the molecules in high pressure ice modifications.

Modification	Tetrahedrality indices	
	Molecules of the first sort	Molecules of the second sort
II	0.0295	0.0289
III(IX)	0.0215	0.0167
IV	0.0246	0.0315
VI	0.0639	0.0483
XII	0.0013	0.0518

Ice Ih is undoubtedly the only form of ice which is stable at ambient and relatively low pressure. Once formed it does not transform into ice Ic or XI when cooled.

Ice Ic crystallizes from water vapour when deposited on a cold (~ 170 K) metal surface [20]. It can be obtained also by rapid cooling of emulsions containing water microdroplets [78], and by freezing of water in microporous materials [79, 80]. It is cubic ice Ic, to which quenched high pressure forms of crystalline and amorphous ices convert at ambient pressure when heated (see for details and references our review [30]) (quenched high density amorphous ice first converts into low density amorphous and then into cubic ice). Irrespective of the preparation method, heating of ice Ic leads to its irreversible transition into ice Ih. The temperature of this transition depends on the heating rate and prehistory of the sample. As a rule the transition takes place within the interval 140–230 K. It is interesting to note that crystallization of ice Ic in micropores can occur at a temperature a little higher than the upper limit of this transition.

Ice II. At pressure higher than 207 MPa ice III crystallizes from water. At $T \sim 238.5$ K ice III converts into ice II. Under He pressure ice crystallizes directly from liquid [81, 82]. This is explained by formation of a solid solution of He in ice II. The structure of this solution was determined in [81]. When all the cavities of the ice II framework are filled the composition of this solid solution reaches He(H₂O)₆. It is natural to call this solid solution helium clathrate [81]. Besides He, Ne and H₂ can solve in this ice modification [83, 84]. The possibility of filling of ice II cavities by Ar atoms is discussed in [85, 86]. Ice II and solid solutions of gases in it are examples of the existence of a thermodynamically stable empty clathrate framework. By the way, He and Ne can solve in ice Ih as well [87–89], but their solubility in this is considerably lower than in ice II, so they are not called clathrate hydrates.

Ice III. Starting with ice III, all the modifications which can be in equilibrium with liquid water (ices III, V, VI, VII and X) melt and crystallize without ‘anomalies’. The density of the liquid is less than the density of the crystal and the melting temperature increases with the rise of pressure. The field of ice III stability is very small. As already said ice III, when cooled very quickly, does not convert into ice II, retains its structure and acquires proton order.

Ice IV. This modification is metastable and sometimes forms from liquid at pressures between 0.2 and 1.0 GPa [90]. As often pointed out, it is easier to obtain ice IV from heavy water.

Some nucleating agents (e.g. certain amino acids) can facilitate formation of ice IV [91, 92]. It is said in [93] that ‘the effect of nucleating agents or of the pressure on the formation of ice IV is erratic’. The authors of [93] found a new way to obtain ice IV: by heating high density amorphous ice (produced by compression of ice Ih at 77 K) at a pressure of 0.81 GPa up to 183 K. During the process of this heating a mixture of ices IV and XII is formed. The lower the heating rate is the greater is the fraction of ice IV in the mixture.

Ice V is a stable form of ice and crystallizes from liquid water at pressure between 344 and 626 MPa. Its conversion to proton-ordered ice XIII when doped with HCl and cooled was already discussed.

Ice VI crystallizes from liquid water in the pressure interval 626–2200 MPa. Nothing extraordinary occurs when borders between ice VI and its neighbours in the phase diagram are crossed. The transition of ice VI to proton-disordered ice VII at low temperature has already been discussed above.

Ice VII crystallizes at pressures higher than 2.2 GPa. The line of liquid–ice VII ice equilibrium crosses the critical temperature (647 K) without any peculiarities. Above this temperature ice VII melts to supercritical fluid. The melting temperature of ice at very high pressure was studied in [94]. There is a discontinuity in this curve around 43 GPa and 1600 K. It is highly probable that this discontinuity corresponds to the ice VII \leftrightarrow ice X transition.

Conditions in which ices IX, X, XI, XIII and XIV are formed have been briefly discussed above.

Ice XII is metastable as ice IV. Ice XII was for the first time obtained by slow cooling of water in argon atmosphere at pressure 0.55 MPa [59]. Ice XII crystallizes along with argon clathrate hydrate with CSII structure. The stable ice modification at this temperature (160 K) and pressure is ice V. It is not clear yet why Ar causes ice XII crystallization. Formation of ice II instead of ice III in helium atmosphere is easy to understand: He atoms enter the cavities of the ice framework and stabilize its structure. But there are no cavities in the ice XII framework! We discuss these problems in more detail in [85], but give no answer. Ice XII can be formed not only in Ar atmosphere. Formation of ice XII in the process of ice Ih compression at temperatures 77–166 K was shown in [95, 96]. Later it was proven that high density amorphous ice is always an intermediate form in the ice Ih–ice XII transformation [97, 98]. Johary demonstrated that ice XII is indeed metastable in the field of stability of ices V and VI. The Gibbs energy of ice XII is 183 J mol^{−1} higher than that of ice V at 0.5 GPa and 180–475 J mol^{−1} higher than that of VI at 1.1 GPa and 100 K [99]. As already mentioned, a mixture of ices IV and XII is formed when high density amorphous ice is heated at high pressure. When the heating rate is faster than 15 K min^{−1} practically pure ice XII is formed [93]. So, there are two regions of ice XII metastability. The first lies in the ice V field of stability. Its borders are not known exactly. The borders of the second one were thoroughly studied in [100]. This region extends from 158 to 212 K and from 0.7 to 1.5 GPa, that is within the ice VI field of stability. It is interesting that

the two regions of metastability of ice XII are disconnected, that is it is impossible to pass from one to another without phase transitions.

2.4. Liquid layer on the surface of crystalline ice

Before proceeding to consideration of non-crystalline condensed phases of water I should like to touch on one remarkable property of crystalline water—the existence of a liquid layer on the ice surface at temperature much lower than the freezing point. This problem dates back to Faraday [101, 102]. A historical review of the problem can be found in [103]. This layer is commonly called quasiliquid. The formation of the (quasi)liquid layer on the surface of the crystal is not, as in the case of other water ‘anomalies’, a unique property of water (see, for instance, [104]), but the problem of the ice surface layer attracts much attention mainly because of its importance for understanding of a great number of natural phenomena and technological processes [105]. It is commonly believed that the liquid layer appears at a temperature of about 243 K [102]. According to atomic force microscopic measurements [106], the thickness of the quasiliquid layer at this temperature is 10–40 Å (the scatter of the results obtained by this method is very high). It may be said that atomic microscopic measurements overstate the values of the layer thickness, but at temperatures higher than 265 K the results obtained by this method agree sufficiently well with the results obtained by the glancing angle x-ray scattering [107], which is, to my mind, the most reliable method of estimation of the surface layer thickness. There are many methods of determination of the thickness of the surface layer. Most of them are enumerated and discussed in the excellent review by Li and Somorjai [102]. The results obtained by various methods are rather controversial. This is not surprising because they measure different properties and the properties of the ‘quasiliquid’ may change as the solid surface of the ice is approached. Little is known about the physical properties of this layer. The authors of [108] assumed for the interpretation of their atomic force microscopic results that the viscosity of the surface layer was the same as that of supercooled liquid at the same temperature. The obtained results were quite plausible. As I have already said I consider results obtained by glancing angle x-ray scattering to be the best estimation of the liquid layer thickness. This is about 40 Å at 264 K [107]. Thermodynamic theory, proposed in [108], gives results which are in good agreement with data of [107] and their extrapolation to lower temperature. The lowest values of the thickness obtained with the help of the atomic force microscope [106] also correspond to theoretical estimations of [108]. According to these estimations layer thickness is about 30 Å at 260 K, 20 Å at 252 K and 10 Å at 240 K. The layer disappears below 200 K. Instructive comparison of these results with those obtained in one of the earliest theoretical works [101] can be done. The work [101] was published when no reliable experimental data on liquid layer thickness were available (though 110 years after Faraday’s conjecture had been put forward). According to Fletcher the thickness of the liquid layer at a temperature a little below the melting point is ~ 100 Å, ~ 40 Å at 263 K; the layer disappears at ~ 240 K. So the main achievement of the 47

years elapsed since publication of [101] is the establishment of the fact that the liquid layer on the ice surface can exist at much lower temperatures than it was thought before. But as follows from the review paper which was published recently [102], this fact is not yet accepted by the scientific community.

3. Non-crystalline condensed phases of water

3.1. General remarks

The structure of non-crystalline phases has neither symmetry nor periodicity, therefore nothing but rather unexpressive radial distribution functions can be extracted from x-ray or neutron diffraction study of them. I have mentioned in section 1 that many physicists do believe that these functions are the only representations of the liquid (or amorphous body) structure. And I gave a reference to the paper by Martynov, in which, I think, this concept is expressed in the most brilliant way [12].

Many scientists tried to offer something more expressive and beautiful. The brightest of them was certainly Bernal [110–113]. Being a crystallographer, he constructed pictorial models of liquids and convincingly proclaimed that liquids do have structure, though principles of its organization and regularities inherent to it may be quite different than in the case of the crystals. Bernal wanted ‘some kind of theory of liquids that would be homologous to that of crystalline solids as being radically different in kind, and have a general quality of homogeneity’ [113]. Bernal’s ideas in a form intelligible for physicists are expounded in Ziman’s book [114]. In search of regularities in the structure of simple (consisting of spherically symmetrical particles) liquids Bernal studied heaps of steel and compressed Plasticine balls. He tried to create an object which consisted of the particles whose coordinates could be measured. Structure for a crystallographer is first of all a list of coordinates [115]. Lists of coordinates of symmetrically independent atoms and laws of their multiplication (which allow obtaining as large a model as one likes), unit cell parameters and the space group are published in the scientific journals and stored in the data banks. These lists are called crystal structures.

Radial distribution functions are a result of statistical treatment of an enormous number of such lists of coordinates. These functions are distributions of interatomic distances. A very important remark is appropriate here. The lists of coordinates which are behind distribution functions are instantaneous structures, while lists of coordinates resulting from the diffraction experiments refer to the time and space averaged structure. These questions are considered in more detail in my other publications [8–11]. If we cast a glance at an instantaneous structure of crystalline ices for example, it will be less elegant by far than ideal structures demonstrated in section 2 of this paper (figure 9). Instantaneous structure shown in figure 9 was obtained in the course of molecular dynamics simulation. After appearance of methods of computer simulation of matter on the atomic level of its organization instantaneous structures ceased to be ephemeral entities. But another problem arises. As just mentioned, the most fundamental regularities of crystal structures, including

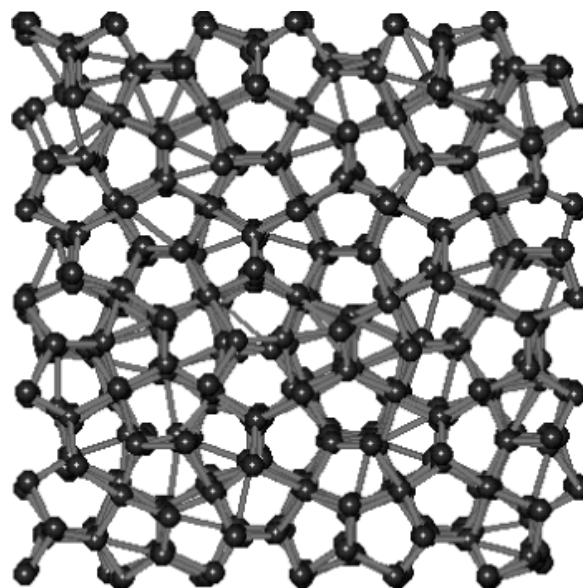


Figure 9. A snapshot of an instantaneous structure of ice XII. Oxygen atoms and hydrogen bonds are shown. $T = 186$ K.

such a general one as the periodicity, manifest themselves not in instantaneous, but in idealized, space and time averaged structures. These structures can be easily obtained by x-ray or neutron diffraction. Indirect information about instantaneous structure is contained in temperature factors or can be deduced from experimental methods. Bernal when constructing his models of liquids evidently also implied some idealized structures. The idea of vibrationally averaged structure of liquids was put forward not by a crystallographer, but by the theoretical physicist, a well known specialist in the physics of liquids, Fisher [116]. The Russian edition of this book was published in 1961. So Fisher began to think about it at approximately the same time as Bernal started constructing his models of the simple liquids. Eisenberg and Kauzmann proposed appropriate terminology [13]: I-structures for instantaneous structures and V-structures for vibrationally averaged ones. They proposed the term D-structure (diffuse averaged structure) as well, but as follows from their explanation it is nothing but a set of radial distribution functions, that is, not a structure at all from my point of view.

The result of the computer simulation is no more than a set of I-structures. There is no problem in obtaining the V-structure from it. Averaging of coordinates will suffice for the purpose. How it can be done is shown in [11] using ice III and amorphous ice of high density as examples. The time dependence of oxygen atom coordinates in liquid water is shown in figure 10. It is quite clear that averaging of these coordinates cannot give rise to any physically plausible structure. At the beginning of the 1980s the conception of inherent structures was suggested [117–119]. My understanding of this conception and its history can be found in [11]. Inherent structure is the structure of the configuration corresponding to the nearest potential energy minimum in the configurational (multidimensional) space.

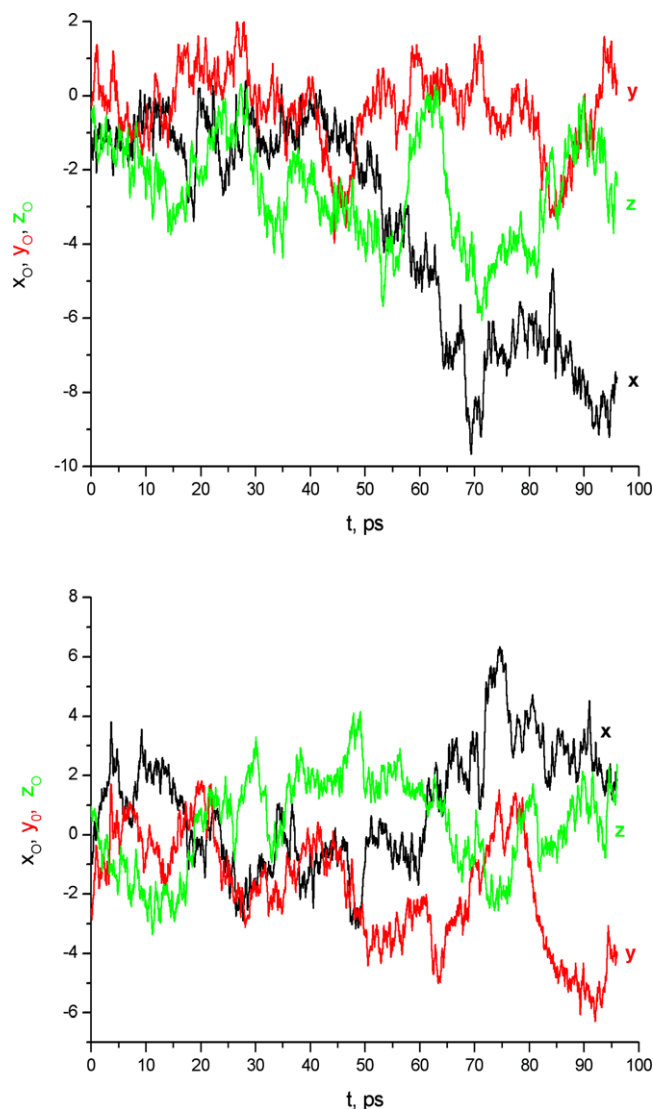


Figure 10. Dependence of x , y and z coordinates of water molecule oxygen atoms on time. Data for two arbitrary chosen molecules are shown. ($T = 297$ K, $d = 0.998$ g cm $^{-3}$.)

I suggested the term ‘Stillinger–Weber region’ for a region in configurational space (i.e. a set of I-structures) corresponding to a particular inherent structure [8]. The term was not accepted by the scientific community and this region is usually called the ‘inherent structure basin’. It is notable that in publications of Stillinger, Weber and their followers the expression ‘inherent structures in something’ is used (‘Inherent structures in water’ is the title of the paper [118]. Naberukhin, I, our colleagues and like-minded authors prefer to say ‘inherent structure of something’ (the title of the paper [120] is ‘Inherent structure of the molecular dynamics model of water’; the paper [121] is called ‘F-structures of hydrogen-bonded water clusters’). The term ‘F-structure’ (frozen structure) was proposed for a special case of inherent structures obtained by the Monte Carlo method [8]. Comparative analysis of various ways of obtaining inherent structures was done by Naberukhin *et al* [122].

3.2. Amorphous solid phases of water

An excellent and comprehensive review paper on amorphous ices was published recently [123]. Much interesting and useful information about properties of these phases is contained in the survey just published by Johary and Andersen [29]. In very good reviews on supercooled water [124, 125] much information and interesting considerations about amorphous ices also can be found. This is why I shall not write about them in detail and shall discuss only some problems relevant to the scope of the present paper. Amorphous polymorphism [126], sometimes called ‘polyamorphism’, is not a unique property of water. It is observed in other substances [127]. First of all, in structural analogues of water: Si, Ge, SiO $_2$, GeO $_2$. In the case of Si [128] and Ge [129] formation of high density amorphous phases is accompanied by a drastic change of the nature of interatomic interaction. As said above concerning corresponding transitions between crystalline phases, low density amorphous semiconducting Si and Ge transform into high density metallic phases [130]. Transitions between low and high density forms of SiO $_2$ and GeO $_2$ occur without serious changes of interactions between atoms [131–133]. The same can be said about transitions between solid amorphous phases of water. The individuality of water molecules and weak hydrogen bonds are retained. Nothing is known about the existence of amorphous phases with strong symmetric hydrogen bonds, analogous to ice X. After the pioneering work of Burton *et al* [20], for a long time the only way to produce amorphous ice was condensation of water vapour on a cold surface. Many interesting findings were made. They are summed up by Fletcher [134]. It is necessary to note that amorphous polymorphism of water was observed for the first time by Narten *et al* in 1976 [135], eight years ahead of the discovery of pressure-induced amorphization of ice Ih and of the formation of high density amorphous ice. The authors of [135] deposited water vapour on a copper surface at temperatures 10 and 77 K. The rate of deposition at 10 K was very slow, ~ 4 mg h $^{-1}$, so only after 2 weeks could a sample thick enough for x-ray diffraction study be obtained. X-ray diffraction patterns of the samples deposited at 77 and 10 K are different. The distribution function $g_{OO}(r)$ of the sample deposited at 10 K has an additional maximum at 3.3 Å. This peak is retained after heating of the sample up to 77 K but becomes a little broader. The density calculated from this distribution function is about 1.1 g cm $^{-3}$. The procedure of density estimation seems to be correct, for it gives 0.94 g cm $^{-3}$ for amorphous ice deposited at 77 K. The last value is in excellent agreement with the most precise and reliable values for vapour-deposited amorphous ice [136]. I give so many details of this work because its results not only are not discussed, but are not even mentioned in modern literature. It is not cited either in [29], or in [123]. In [137] reference to this paper is given among five others and nothing is said about what has been written in each of them. It is highly probable that the dense amorphous ice discovered by Narten *et al* [135] really exists, but no transition between low and high density forms was ever observed. The more natural way to obtain amorphous or vitreous ice is vitrification of liquid water in the course of its cooling. As mentioned in section 1,

many liquids in which molecules form a three-dimensional hydrogen-bonded network vitrify very easily. But water always crystallizes below the temperature of homogeneous nucleation. Johary *et al* managed to vitrify small droplets of water dispersed in the emulsion [137]. This vitrified water converts into cubic ice when heated, much as vapour-deposited amorphous ice does. The first transition from one form of amorphous ice into another was observed after amorphous ice of high density (HDA) was obtained by compression of ice Ih at 77 K [22]. The density of this high density amorphous ice at ~ 1.5 GPa is ~ 1.3 g cm $^{-3}$. No reverse transformation to ice Ih is observed when the pressure decreases. HDA expands elastically and its density reaches 1.17 g cm $^{-3}$ at ambient pressure. When heated, HDA transforms first into amorphous ice with density ~ 0.94 g cm $^{-3}$ (amorphous low density ice, LDA) and then to cubic ice Ic. Whether these two varieties of low density amorphous ice are the same is not clear so far (some arguments *pro et contra* can be found in [98]; for other references and discussion on the problem see [123, 124]). It is not so easy, as in the case of crystalline phases, to tell the difference between one form of amorphous substance and the other, if their densities and other properties are similar. For instance, most of the properties of ices Ih and Ic are identical, but one is optically anisotropic and the other is isotropic. Their diffraction patterns and hence their structures (lists of symmetrically independent coordinates, space groups and unit cells) are different. Amorphous substances are optically isotropic. Diffraction patterns and radial distribution functions of the substances whose particles have distorted tetrahedral surroundings are very similar and depend mainly on the density. So there is a need to carry out very careful and detailed study in order to prove that amorphous phases prepared in different ways and having close densities are identical.

The amorphous ice with density distinctly higher than that of LDA and HDA was obtained by isobaric heating of HDA at pressure a little higher than 0.1 GPa [138]. It can be stored for a long time at ambient pressure and temperature ~ 80 K. At these conditions its density is 1.25 g cm $^{-3}$. Results of neutron diffraction study of this phase are reported in [139]. This form of ice was called amorphous ice of very high density (VHDA). This modification seems to be formed sometimes in the course of ice Ih, LDA and HDA compression (see [123] and references therein). It is quite possible that authors of some publications in which formation of HDA was observed actually obtained VHDA (see [123] for examples). It is too early to sum up the results of studies of different forms of amorphous ice. Tulk *et al* [140] studying the HDA–LDA transition in the course of heating at ambient pressure observed several intermediate forms of amorphous ice, slightly different in their diffraction patterns. They cite results of calorimetric and spectroscopic studies which support their findings. Further information in favour of the existence of intermediate forms can be found in [123]. All amorphous substances are metastable by definition. Tulk and other authors advocate that there are, so to say, more and less metastable amorphous ices. According to [140] LDA and HDA are ‘more metastable’ phases which can exist in broad ranges of temperature and pressure while

intermediate forms exist in narrow intervals of thermodynamic parameters and some of them for a short time. Long passages in [123] are devoted to discussion of the question of whether HDA and VHDA are different, separate forms of amorphous ice, or are modifications of one form. It is also possible that HDA is a form intermediate between LDA and VHDA. No definitive answer is given. Results obtained by Koza *et al* support the idea that HDA is a form intermediate between LDA and VHDA [141]. They performed neutron diffraction and small-angle neutron scattering studies of amorphous ices and came to the conclusion that ‘the well-known high density amorphous structure HDA does not constitute any particular state of amorphous water network’. According to [141], LDA and VHDA are homogeneous amorphous phases, while HDA is heterogeneous (see also [142]. Computer simulations done by Martonak *et al* are also in favour of this point of view [143, 144]. Before proceeding to discussion of amorphous ice structure, let us give a compact summary of the transitions in which amorphous ices are involved. The amorphous phases are designated as they have been in the original publications or review papers. The word ‘ice’ before the Roman number of the crystalline modification is omitted.

Isothermal compression (77 K) Ih \rightarrow HDA (~ 1 GPa) [22] \rightarrow VII’ (4 GPa) [66].

Isothermal compression (77 K) Ic \rightarrow HDA (~ 0.8 GPa) [145].

Isothermal compression (77 K) LDA \rightarrow HDA (~ 0.6 GPa) [146] (the higher the temperature, the lower the pressure; at 135 K transformation occurs at $P \sim 0.2$ GPa and becomes reversible with hysteresis [123, 147]).

Heating at ambient pressure HDA \rightarrow LDA (~ 115 K) \rightarrow Ic (~ 150 K) \rightarrow Ih (~ 170 K) [133].

Heating of ambient pressure VIII \rightarrow LDA \rightarrow Ic \rightarrow Ih [68].

Isobaric heating 0.3 GPa HDA \rightarrow III [61].

Isobaric heating 0.4–0.7 GPa HDA \rightarrow IV + V + XII [61].

Heating at ambient pressure VHDA \rightarrow LDA (127 K) [139].

3.2.1. Structure of amorphous ices

3.2.1.1. Experimental data. The radial distribution function g_{OO} of LDA is typical for distorted tetrahedral networks [148]. Like the corresponding function for liquid water, it has three maxima: around 2.8, 4.5 and 6.7 Å. The first one corresponds to the distance between the nearest (hydrogen-bonded) molecules, the second one is the blurred edge of the tetrahedron whose vertices are occupied by four nearest molecules and the third corresponds to separation of the third neighbours in the network [10]. In comparison to liquid water, the first maximum of the LDA g_{OO} is naturally shifted towards shorter distances while the second and the third maxima are much better pronounced. The fourth broad maximum at about 8.5 Å can be noticed on the LDA g_{OO} function [148]. The second maximum of the HDA g_{OO} function is split into two peaks. The first of them is centred at about 4, the second one at about 4.4 Å. The third maximum on the HDA g_{OO} function

Table 5. Numbers of water molecules in the shells around the central molecule in the dense forms of amorphous ices.

The shell boundaries (Å)	Modification	
	HDA	VHDA
2.3–3.1	4.1	4.1
3.1–3.3	0.9	1.7
3.3–3.7	2.2	3.5
3.7–4.1	3.5	2.7

is shifted by about 0.3 Å to shorter distances in comparison with the LDA. The coordination number of water molecules (area under the first peak, the result of integration between 2.3 and 3.3 Å) is 3.9 for LDA and 5 for HDA [148]. The procedure of construction of spatial density functions (sdfs) showing the distribution of molecules around a central one was developed by Soper [149]. The procedure uses Monte Carlo simulation to obtain a set of configurations (I-structures) best satisfying the empirical distribution functions. So these sdfs are not results of diffraction experiment, but are obtained by computer simulation. As follows from the sdfs constructed for LDA and HDA, in both modifications the molecules are involved in four normal tetrahedrally directed hydrogen bonds. The fifth molecule does not form hydrogen bond with the central one [148]. Such close non-bonded first neighbours can be found in some high pressure ices ([148] and references therein). The g_{OO} function of VHDA shows major changes from that of HDA [139]. The broad split second peak is shifted inwards, forming a shoulder on the first peak. The first peak of the VHDA itself is a little lower than that of HDA. The area under this peak (integration to the first minimum of the g_{OO} function, which is 3.1 Å for VHDA) corresponds to coordination number 4 for both HDA and VHDA. Here the numbers of water molecules in the shells surrounding the central molecule, determined by integration of r_{OO} functions, are given for two forms of dense amorphous ice [139] (table 5).

Analysis of g_{OO} functions can suggest that, on moving from HDA to VHDA, molecules are pushed inwards from the 3.7–4.1 Å interval to the 3.3–3.7 Å interval. As for g_{OH} and g_{HH} radial distribution functions, they are rather similar for all three amorphous ices [139, 148] and their peaks correspond to interatomic distances in a pair of hydrogen-bonded molecules. So in all three forms of amorphous ice studied in [139] and [148], water molecules form topologically simple three-dimensional distorted tetrahedral networks. In [150] the similarity of vibrational spectra (obtained by inelastic neutron scattering) of HDA ice and crystalline ice VI was noted. This similarity does not mean that their structures are alike. The topology of the hydrogen-bonded network in ice VI is not simple (see section 2.2.3).

3.2.1.2. Structure of amorphous ices according to results of computer simulation. Different ways of obtaining of amorphous ices were reproduced by methods of computer simulation. In [151], deposition of water vapour on a cold surface was simulated. In [143, 144], model amorphous ices were prepared by simulation of ice Ih compression. Isochoric cooling of liquid water was modelled in [152]. In [153] different ways

of preparation of amorphous solid water were modelled and compared: isothermal compression/decompression, isochoric cooling/heating, isobaric cooling/heating. Most of the works on computer simulation of amorphous ices are discussed and analysed in detail in [123]. Radial distribution functions as a rule reproduce satisfactory those obtained from x-ray or neutron diffraction studies. It is quite obvious already that the main aim of computer simulation is not to reproduce experimental data, but to obtain information which cannot be obtained by other methods (at least at present). Reproduction of experimental data is only the test of correctness of calculation of interatomic interactions and of simulation algorithms. The situation with reliability of computer results is very good. Not only radial distribution functions, but thermodynamic parameters of transitions between amorphous ices, were reproduced [123]. As to the properties which could not be measured, not so much information about amorphous ices was obtained. While discussing the structure of crystalline ices we mentioned hydrogen-bonded rings as important structural elements. It is impossible to determine experimentally how many different rings there are in the frameworks of amorphous ices. It is easy to do it analysing results of computer simulation. It was shown in [144] that in model amorphous ice at ambient pressure and 80 K six-membered rings predominate. Then follow (in order of decrease of their number in the framework) seven-, five- and eight-membered rings. The number of nine- and ten-membered rings at low pressure is insignificant. The number of six-membered rings decreases as pressure increases. The numbers of eight-, nine- and ten-membered rings sharply increase with pressure up to ~1 GPa. The numbers of five- and seven-membered rings depend slightly on pressure. The most dramatic change of ring statistics occurs when pressure increases from 0.2 to 0.4 GPa. This statistics changes slightly when pressure increases from 1 to 2.2 GPa. At 2.2 GPa numbers of n -membered rings decrease in the order: $8 > 9 > 7 > 10 > 6 \approx 5$. The distribution of the elongation parameter ε of rings was also calculated. Parameter ε is defined as:

$$\varepsilon = (I_2 - I_1)/I_3$$

where I_1 , I_2 and I_3 are eigenvalues of the ring inertia tensor sorted by increasing magnitude.

If ε is zero, the ring is circular or spherical. At the pressure below 0.225 GPa ε values of five- and six-membered rings are small and their distribution is narrow. At the pressures higher than 0.6 GPa ε values for these rings increase and their distribution becomes broad. In the case of seven-membered rings small ε values predominate at ambient pressures only. The distribution of ε values has a maximum at about 0.1 when the pressure is zero. At $p = 0.15$ GPa this maximum is already at 0.45. The distribution of ε values for seven-membered rings does not change notably when pressure increases from 0.15 to 4.4 GPa (density at the latter pressure is 1.6 g cm⁻³!). Interesting information can also be obtained from ring-restricted radial distribution functions (n -rRDF). These functions are defined as the probability of finding two atoms at a distance r within the n -membered ring. Data for $n = 6$ and 9 are given in [144]. The first peak of these functions

changes its form insignificantly when pressure increases to 4.4 GPa. The shift of its position is as small as 0.04 Å. As to the second peak, whose maximum is around 4.5 Å, its form in the case of 6-rRDF is retained up to $p = 0.225$ GPa. Further elevation of pressure (data for 0.6 GPa and higher pressure are given in [144]) gives rise to the broadening of this peak. In the 0.6–1.5 GPa pressure interval the 6-rRDF curve is almost flat between 3.4 and 5 Å. On the 6-rRDF curve calculated for 4.2 GPa a shoulder around 3.2 Å typical for VHDA $r_{OO}(r)$ can be seen clearly. The form of 9-rRDF at $r > 3$ Å starts to change at $p = 0.15$ GPa and changes constantly while the pressure increases. At 4.2 GPa the 6-rRDF and 9-rRDF curves are very similar. So structural peculiarities of model amorphous ices change steadily with the increase of pressure. But the main features of six-membered rings (their number, form and interatomic distances in them) do change when the pressure is low enough and LDA ice is (meta)stable. These results need further comprehension. Much more information can be extracted from the results of computer simulation. When speaking of computer simulation, as a rule molecular dynamics and Monte Carlo computation are implied. Anyhow the work in which VHDA ice structure was modelled by positional disordering of ices IV, VI and XII [154] can also be assigned to computer simulation. I do not think that it is a good idea to construct a non-crystalline solid from the crystalline phases especially because the topology of the VHDA network is very unlikely to be nontrivial, in contrast to the networks of ices IV and VI.

3.2.1.3. Structural heterogeneity of amorphous ices (computer simulation). In molecular crystals chemically identical molecules can occupy several crystallographically different positions. In each ice modification included in table 3 there are two crystallographically different sorts of molecules. The local environment of the molecule can be characterized by different parameters. The tetrahedrality index (T) for instance shows a degree of deviation of the nearest surroundings of the molecule from the ideal tetrahedral one (see table 4 in section 2.3). The volume of the Voronoi polyhedron (VVP) shows local density around a particular molecule. Figuratively speaking, the inverse of the VVP is the density of a single molecule [10]. Thus, the VVP values of the two sorts of molecules in ice IV are 24.23 and 21.15 Å³. Of course discrete values of such parameters as T and VVP refer to idealized (V-)structures only. In the course of computer simulation of the crystals a set of I-structures can be obtained (see section 3.1). If we calculate T or VVP values for the I-structures we shall obtain their continuous distribution. Values of the parameters for the molecules belonging to two crystallographically different types can overlap in the I-structures. Nevertheless, molecules from different crystallographic classes will retain their distinction in the dynamical properties, such as amplitudes and frequencies of their vibrations. This was demonstrated for ices II, IX [155, 156], IV and XII [157]. In amorphous ices molecules can be divided into classes according to the values of such parameters as T or VVP. Thus, for instance, 25% of the molecules with the lowest values of T or VVP can be included in one class and 25% of the molecules with the

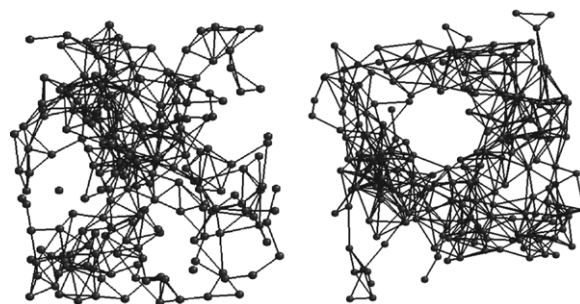


Figure 11. HDA ice (frozen compressed liquid water, density 1.17 g cm⁻³). 576 molecules in the cubic periodic cell. Density 1.17 g cm⁻³. Molecular dynamics simulation. $T = 102$ K. Instantaneous structure. Space distribution of molecules with small (<24.5 Å³, 212 molecules, 37% of total, left) and large (>26 Å³, 217 molecules, 38% of total, right). Both sorts of molecules form infinite ramifying clusters [160].

highest values of these parameters will be included in the other class. As correlation between T and VVP is rather poor [158, 159], classes in which molecules were included according to values of T would not coincide with the classes in which molecules were included according to values of VVP. The space distribution of molecules with large and small VVP values for the HDA model obtained by cooling of compressed water is shown in figure 11. Molecules with high or low values of VVP group together, forming infinite ramifying clusters, piercing the volume of the system [160]. The same can be said about molecules with high and low T values. Simulation of model LDA (cooled water with density 0.94 g cm⁻³) revealed the same peculiarity [161]. Dynamical properties (amplitude and frequency of vibrations) were found to be different for the classes of molecules with high and low values of T or VVP (figure 12) [160, 161]. This difference is analogous to the difference of dynamical characteristics of the crystallographically different molecules in crystalline ices. As VVP and T values of the molecules fluctuate during the simulation even when the temperature of the system is fairly low, it is more correct to study structural heterogeneity on the level of inherent structures. F-structures of water with density 0.94, 1.17 and 1.25 g cm⁻³ were prepared by the Monte Carlo method. Before starting the Monte Carlo procedure, a molecular dynamics simulation 10 ps long at 100 K has been performed for each density. The independent periodic cell contained 3456 molecules. Obtained configurations can be regarded as F-structures of amorphous ices prepared by isochoric cooling of stretched or compressed water. The F-structures are shown in figure 13. In each configuration all the molecules are divided into two equal classes, with small and large VVP values (red and blue balls). It is seen that molecules of one colour tend to get together ('birds of a feather flock together'). In [10, 162] a quantitative criterion of heterogeneity revealed in such a way was suggested. Suppose we have some system of points of two kinds. The number of points of one kind is the same as that of the other kind. Each point has four nearest neighbours. If points are distributed in space randomly, the probability to find four points of the same kind near a particular point will be 6.25%. The probability to find three

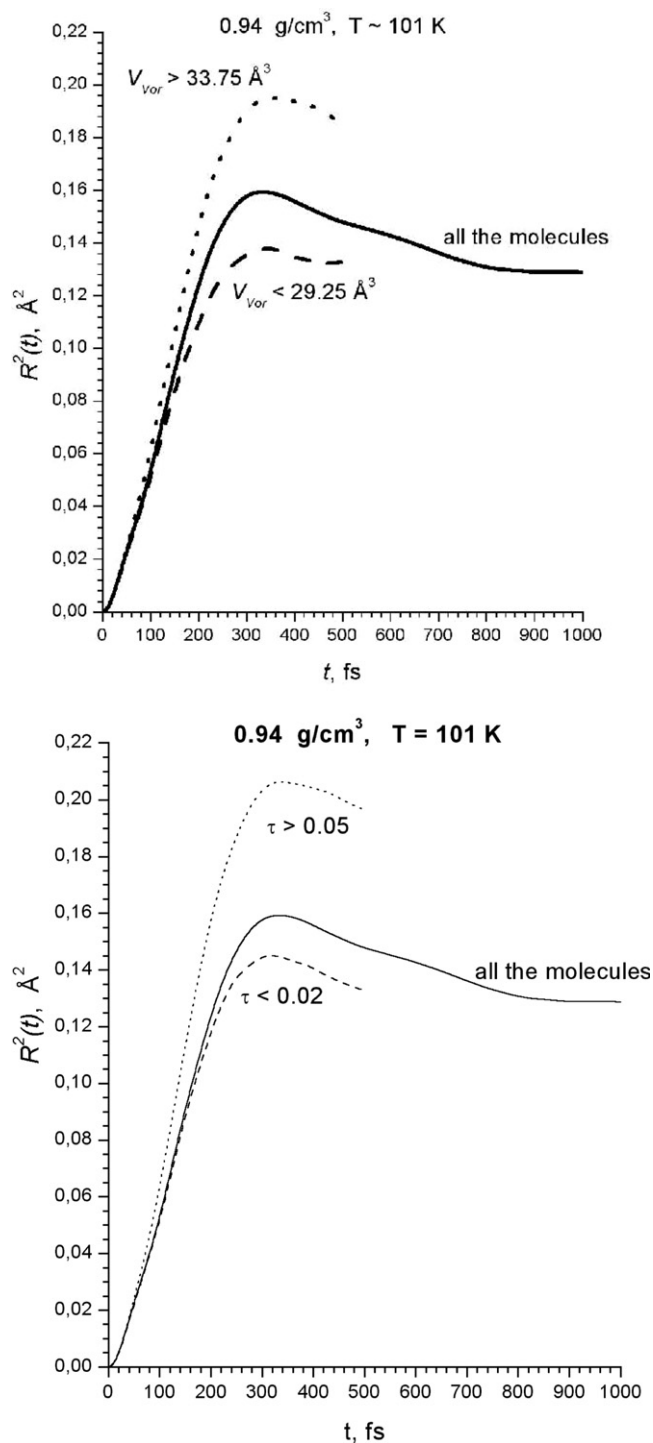


Figure 12. Time dependence of mean square displacement of centres of mass of water molecules ($R^2(t)$) with different values of parameters describing their local surrounding: Voronoi polyhedron volumes (V_{Vor} , top) and tetrahedrality indices (τ , bottom). Data for LDA ice model [160].

points of the same and one of the other kind will be 25% and there is 37.5% probability to find two points of one and two of the other kind. The deviation of actual probability from the probabilities calculated for random distribution can be a measure of the degree of heterogeneity of the structure. Here are results of calculations for the F-structure shown in

figure 13 (table 6). The four nearest neighbours were found for each molecule with the help of the program for calculation of tetrahedrality indices. Molecules with small values of VVP are called ‘small’, those with large VVP values are called ‘large’. It is seen that the molecules prefer to be surrounded by molecules of the sort to which they belong themselves. It is trivial that molecules belonging to each of two equal classes form a percolating cluster [10]. These two clusters penetrate each other. It is not so trivial that two mutually penetrating clusters do not break when the number of molecules in the clusters decreases because of the use of stricter selection criteria. Experience suggests that percolation persists when about half of the molecules are left in each cluster. One-third of molecules with lowest and one-third of molecules with highest VVP values were selected to be shown in figures 14 and 15. The molecules connected by hydrogen bonds are shown in these figures. The molecules were assumed to be hydrogen-bonded if distance between oxygen atoms is less than 3.3 Å for F-structure with density 0.94 g cm⁻³ and less than 3.1 Å for F-structure with density 1.25. These criteria correspond to the first minima of the $g_{\text{OO}}(r)$ radial distribution functions of LDA [148] and VHDA [139] amorphous ices respectively. Not all 1152 selected molecules are incorporated in the hydrogen-bonded cluster. The clusters formed by molecules with lowest VVP values seem to be more compact and contain more molecules.

3.2.2. Concluding remarks on the solid non-crystalline phases of water. There is no doubt that several kinds of amorphous ice exist. It is impossible to say now how many of them. All of them are metastable. The stable phases at temperatures and pressures at which amorphous ice have been obtained are crystalline ices, but metastable phases can be more or less (meta)stable with respect to one or another stable or metastable phases. The fact that isobaric heating of HDA ice gives rise to denser VHDA modification suggests that the latter is more stable than the former at this pressure. HDA ice converts into LDA ice when heated at ambient pressure. This may mean that LDA is more stable at low pressure. Impressive evidence that LDA and VHDA are the most (meta)stable forms of amorphous ice is given in experimental works [141, 142]. Computer simulation also supports this assertion [143, 144]. Subotin and Belosludov [163] calculated thermodynamic properties and vibrational spectra of model LDA, HDA and VHDA ices. The chemical potential of VHDA is lower than that of HDA at all temperatures and pressures for which calculations have been performed. The results of recent publications are controversial and it is still impossible to say how many discrete forms of amorphous ice exist and whether there is a continuum of high density forms of amorphous solid water [143, 164].

3.3. Liquid water

3.3.1. Historical background. A brief historical outline of the development of our knowledge about all condensed states of water was given in section 1. We shall specify now how the views on the arrangement of molecules in liquid water changed during a period of more than 100 years. A more

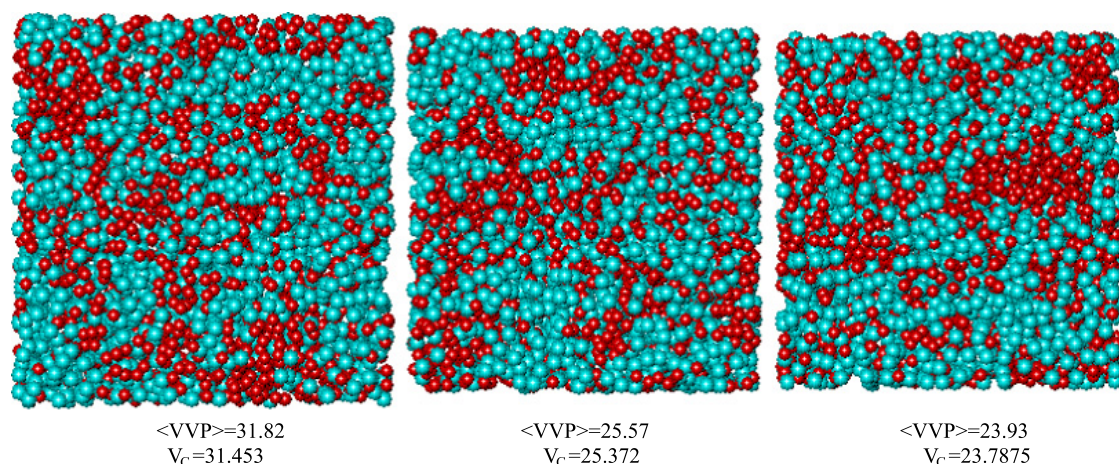


Figure 13. F-structures of water with density 0.94 (left), 1.17 (centre) and 1.25 g cm⁻³ (right). 3456 molecules in cubic periodic cell. In each configuration molecules are divided into two classes of 1728 molecules each. For each configuration the critical value of VVP (V_C) was determined. In the first class molecules with small values of VVP are included ($VVP < V_C$, small red (dark in the printed edition) balls). The second class contains molecules with large VVP values ($VVP > V_C$, larger blue (light in the printed edition) balls). Average VVP values and V_C are indicated.

Table 6. Surroundings of molecules in F-structures of model amorphous ices.

Surroundings of the ‘small’ molecules			Surroundings of the ‘large’ molecules			Random
Four nearest neighbours			Four nearest neighbours			
‘Small’	‘Large’	Probability (%)	‘Small’	‘Large’	Probability (%)	
Density = 0.94 g cm ⁻³ , ⟨VVP⟩ = 31.82 Å ³ , V _C = 31.453 Å ³						
0	4	2.78	0	4	12.73	6.25
1	3	14.41	1	3	34.55	25
2	2	30.73	2	2	30.32	37.5
3	1	32.93	3	1	16.78	25
4	0	19.15	4	0	5.61	6.25
Density = 1.17 g cm ⁻³ , ⟨VVP⟩ = 25.57 Å ³ , V _C = 25.372 Å ³						
0	4	2.84	0	4	12.5	6.25
1	3	14.18	1	3	30.96	25
2	2	32.29	2	2	33.33	37.5
3	1	33.33	3	1	19.10	25
4	0	17.36	4	0	4.11	6.25
Density = 1.25 g cm ⁻³ , ⟨VVP⟩ = 43.57 Å ³ , V _C = 23.788 Å ³						
0	4	3.30	0	4	13.25	6.25
1	3	15.97	1	3	30.73	25
2	2	30.84	2	2	32.35	37.5
3	1	33.04	3	1	18.92	25
4	0	16.84	4	0	4.74	6.25

detailed presentation of my interpretation of this history is given in [10]. In a briefer form it can be found in [158, 159]. I have heard many times the expression 'water is a mirror of science'. It means that development of our notion of water reflects the development of science itself. New ideas, new experimental methods, new approaches were first of all applied to water. In the time of Röntgen nothing was known of how molecules can be arranged. But most scientists believed that molecules did exist. So Röntgen and his followers considered water as a mixture of molecular complexes (later they were called 'hydrols'). Some of these complexes are less dense and ice-like; the others were denser proper water complexes. Change of the fractions of these complexes with temperature

and pressure could explain the non-monotonic dependence of some water properties on these parameters. Determination of the structure of crystalline ice put an end to speculation about ice-like complexes. There are no complexes in ice; there is a three-dimensional network. The idea that such a network exists in liquid water as well was put forward by Bernal and Fowler [19] (see also [165]). This idea was not immediately recognized by the scientific community, but some contemporaries accept it. 'The ocean is one single molecule', Langmuir used to say. It is necessary to note that Bernal and Fowler's concept of water structure contains elements of the two-state model. They reasoned that at temperature close to the melting point this network is a mixture of two structures:

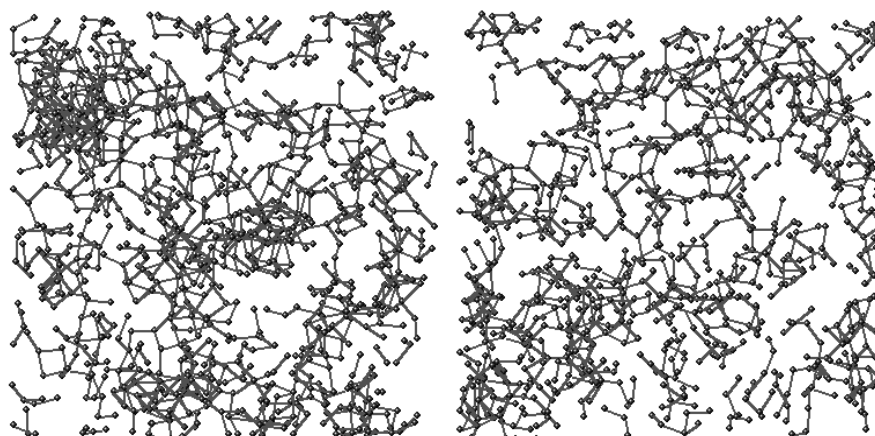


Figure 14. F-structure of model LDA ice. Left—molecules with $VVP < 30.118 \text{ \AA}^3$. There are 1152 such molecules. 1046 of them have at least one neighbour with $r_{OO} < 3.3 \text{ \AA}$ ('non-solitary' molecules); they are shown in the figure and are connected by bonds. Right—the same for molecules with $VVP > 32.852 \text{ \AA}$. 950 'non-solitary' molecules from 1152 are shown. The total number of molecules is 3456. The density is 0.94 g cm^{-3} .

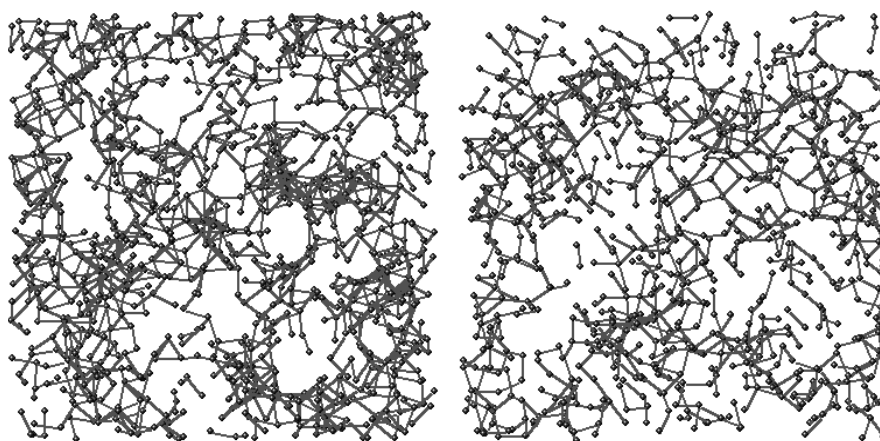


Figure 15. F-structure of model VHDA ice. Left—molecules with $VVP < 23.036 \text{ \AA}^3$. There are 1152 such molecules. 1152 of them have at least one neighbour with $r_{OO} < 3.1 \text{ \AA}$ ('non-solitary' molecules); they are shown in the figure and are connected by bonds. Right—the same for molecules with $VVP > 24.584 \text{ \AA}$. 918 'non-solitary' molecules from 1152 are shown. The total number of molecules is 3456. The density is 1.25 g cm^{-3} .

denser quartz-like and less dense tridimite-like (or ice-like). So this was the concretization of Röntgen's idea of water as a mixture of ice-like and water-like particles. The next version of the network model deprived of allusions to particular crystal structures was proposed by Pople in 1951 [166]. Among other things, he calculated $g_{OO}(r)$ on the assumption that hydrogen bonds are bent. According to Pople, hydrogen bond bending was also the reason for the greater density of water in comparison with ice. Bernal returned to the problem of liquid water in 1964 [167] after publication of his famous works on the structure of simple liquids. He applied the notion of a random tetrahedral network to water. Interesting details of Bernal's ideas of that time can be found in the paper by his disciple Finney [165]. In this paper self-critical statements by Bernal about his early ideas about water are given. Speaking about his attempt 'to picture water structure as that of a mixture of the analogous four-coordinated structures of . . . quartz and tridimite', he continues: 'this was ultimately to prove rather a

delusive approach, postulating a greater degree of order . . . in the liquid than actually exists there'. The conception of random tetrahedral network was developed quantitatively by Sceats and Rice [168–170]. They calculated many properties of water including thermodynamic ones. This was the mainstream direction of the development of models of water structure. Two other groups of models were developed and discussed in the 1950s and 1960s. The first model belonging to one of these groups was put forward by Samoilov in 1946 [171] (see also [172]; concerning him and his work see [173]). According to Samoilov's model, water retains an ice-like network; cavities in this network are partially filled by water molecules. The network itself is perturbed by thermal motion. According to this model the ice melting must be accompanied by falling of the molecules in the cavities; this is why density increases. Unlike Samoilov, Pauling supposed that the network is not ice-like, but gas-hydrate-like [174]. These models can be called clathrate because filling of the cavities is their main feature.

Sometimes they are called interstitial. The models are very elegant but this direction in the science of water is undoubtedly dead end. The second group of models is a direct development of Röntgen's two-state idea. They suggest that water is a microheterogeneous system consisting of two microphases: fragments of hydrogen-bonded tetrahedral framework and the other in which molecules are not involved in hydrogen bonds. The most popular among these models was that proposed by Némety and Scheraga [175]. The picture showing hydrogen-bonded water clusters floating in a 'sea' of non-bonded molecules swept over reviews and monographs. Under the pressure of experimental data conversion of these groups of models occurred. Both microphases of classical two-state models came to be regarded as containing hydrogen bonds; the possibility of formation of hydrogen bonds between cavity and framework molecules began to be admitted by apologists of the clathrate models. So the picture of water as a continuous three-dimensional network predominated on the eve of the computer simulation era. The impossibility of the models of Némety and Scheraga type was ultimately demonstrated when methods of percolation theory were applied to water [21]. The three-dimensional network was accepted practically by all the scientists involved in the study of water. It was still unclear to what extent the network was heterogeneous and in what number of hydrogen bonds the molecules were involved. Classical random network models imply that the network is homogeneous. The percolation threshold for three-dimensional networks is about 1.6–1.7. This is the minimal number of hydrogen bonds per molecule to allow them to form an infinite network. Such models of water as 'water is ice Ih perturbed by thermal motion' [172], 'water is a mixture of distorted ices Ih and III' [176] cannot be considered seriously. The energies of the frameworks of all ice modifications, of clathrate hydrates and of any other conceivable tetrahedral networks are very close to each other. Statistical physics teaches us that the probability to meet a particular configuration in the ensemble is proportional to the Boltzmann factor $e^{-E/kt}$. So water must be a mixture of innumerable configurations. The most direct method to study them is to generate them with the help of computer simulation. Water was simulated for the first time in 1969 [14]. Many thousands of simulations have been performed since then. More and more powerful computers, more and more perfect algorithms, have been coming into use during the last almost 40 years. Simultaneously, many new experimental facts were discovered. New experimental methods appeared and old ones were improved. Many publications are dedicated to water. It is absolutely impossible to consider all of them. The last comprehensive summary of the knowledge about water and aqueous systems was done in the 1970s–1980s years [25, 26]. A more modern monograph can be recommended [177]. Special issues of some journals dedicated to water have been published (for instance [178, 179]). A very good review on water was given by Finney [180]. I shall try to depict the general picture of the modern state of the art in the field of structure and properties of liquid water. It differs greatly in its scope and manner of presentation of material from my recently published review paper [10]. Let us begin from the structure.

3.3.2. Structure of liquid water. As practically no one doubts that a three-dimensional network of hydrogen-bonded molecules exists in liquid water, the question of how this network is organized becomes the central one in the problem of the structure of liquid water.

3.3.2.1. In how many hydrogen bonds are water molecules involved? Experimental evidence. There is no direct experimental method which can give an unambiguous answer to the question. The most reliable information can be obtained from vibration (IR and Raman) spectra in the region of stretching vibrations of the O–H bond near 3550 cm^{-1} . The most reasonable, to my mind, interpretation of this band is based on the fluctuation concept of hydrogen bonding [181]. This conception was developed by Efimov and Naberukhin (the latest publications are [182–184]; references to the earlier ones are given in them). According to this conception the form of the stretching band is interpreted in terms of an energy distribution of hydrogen bonds in which all the protons are involved. The contour of the Raman spectrum in the range of stretching vibrations has two broad maxima. Forty years ago the second maximum was attributed to broken bonds, but later strong proofs were given in favour of the viewpoint that corresponding vibrations refer to the protons that are also involved in hydrogen bonds. The result of the first x-ray absorption spectroscopy (XAS) studies of water [185, 186] spread confusion in the minds of those who were interested in hydrogen bonds in water. In [186] non-resonant x-ray Raman scattering (XRS) of water was also studied. In XAS experiments with water, x-ray absorption at the boundary of the K-band was recorded. The results were shocking. It is stated in [185] that water molecules are involved in 2.5–2.8 hydrogen bonds each (on average). According to [186] 15% of water molecules are donors of two, 80% of one hydrogen bond; protons of 5% of molecules are not in hydrogen bonding at all. The contradiction of these results with other experiments and computer simulations is not yet ultimately explained. But the title of one of the latest papers on the subject is encouraging: 'Standard model for liquid water withstands x-ray probe' (arXiv: [cond-mat/0512416v1](https://arxiv.org/abs/cond-mat/0512416v1)). It seems that this paper was published under the more neutral title 'X-ray absorption spectra for liquid water from first principles calculations' [187].

3.3.2.2. Hydrogen bonds in computer simulated liquid water. The result of computer simulation is a set of lists of atomic coordinates. These lists can be treated in the same manner as crystal structures. As a rule there no problem to tell which water molecule forms hydrogen bonds with another and which does not. The crystallographer does not use any criteria to find hydrogen bonds in the crystal structure but relies upon his intuition and experience. Ambiguity arises only when a proton is involved in more than one hydrogen bond [188, 189] (so-called bi or trifurcated hydrogen bond). As crystal structures are inherent (V-)structures it is natural to compare them with inherent structures of liquid water. The two-dimensional distribution of O...O distance (R_{OO})–pair interaction energy (E_{WW}) for an inherent (F-)structure of water

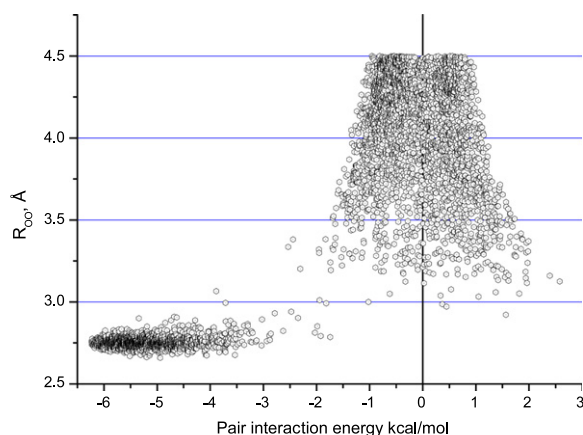


Figure 16. Projection of two-dimensional distribution R_{OO} –pair interaction energy for an F-structure of water. Each dot corresponds to one pair of molecules. The region corresponding to hydrogen bonds has clear-cut boundaries. There are few dubious pairs of molecules.

is shown in figure 16. The hydrogen-bonded pairs occupy the region with clear-cut boundaries. Few pairs fall between the regions of hydrogen-bonded and non-bonded pairs. Analysis of the geometry of these pairs showed that most of these pairs can be regarded as connected by asymmetric bifurcated bonds. Thus the situation is similar to that in the crystals. It was as long ago as in 1981 that Naberukhin wrote ‘the hydrogen bond in liquid water can be determined only at the level of V-structures’ [115]. This prophetic thought was formulated before the inherent structure concept was put forward. But in many cases it is necessary to look for hydrogen bonds in the I-structures which are generated in the course of computer simulation. To this end hydrogen-bond criteria are used.

3.3.2.2a. Hydrogen-bond criteria. Since the beginning of computer simulation of water two kinds of hydrogen-bond criteria have been used: geometric and energetic. When we use geometric criteria, we imply that two water molecules are involved in an H bond if certain geometric parameters, which describe their mutual position, fall in a fixed range. As a rule, limits on the simplest parameters such as the $O \cdots O$ distance R_{OO}^{\max} , the $O \cdots H$ distance R_{OH}^{\max} , and/or the $O-H \cdots O$ angle α_{OHO}^{\min} are imposed [190]. Sometimes the $H-O \cdots O$ angle is used to characterize hydrogen-bond bending. According to the energetic criterion, each pair of molecules with pair interaction energy lower than some chosen value E_{WW}^{\max} is considered to be hydrogen-bonded. Sometimes a combination of geometric and energetic criteria is used (for instance in [191]). A detailed discussion of the problem of hydrogen-bond criteria can be found in [10]. Two papers have recently appeared in which the problem of hydrogen-bond criteria is thoroughly considered [192, 193]. In [192] results of molecular dynamics simulation of water models in which intermolecular interactions were calculated with the help of four different potential functions were used for elaboration of the criteria. All four models were simulated at the temperature of maximum density (TMD; for all the models this is lower than the

experimental one) and at 40 K below the TMD. It is pointed out in this paper that there are gaps in the distribution functions between hydrogen-bonded pairs of molecules and non-bonded ones in the inherent structures (compare figure 16). Matsumoto comes practically to the same conclusion that was formulated by Naberukhin more than 25 years ago: hydrogen bonds can be unambiguously determined only in the inherent structures. The network topology of the inherent structure is chosen as in [192]; the network topology of instantaneous structures is regarded as that of the inherent structures to which thermal noise is added. For the search of hydrogen bonds in the instantaneous structures five criteria were considered for each model and temperature (in our notation): E_{WW}^{\max} , R_{OH}^{\max} , $E_{WW}^{\max} + R_{OO}^{\max}$, $E_{WW}^{\max} + \cos \alpha_{HOO}^{\max}$ and $R_{OH}^{\max} + \cos \alpha_{HOO}^{\max}$. Bayesian decision theory was used to determine optimal values of the criteria. Matsumoto comes to the conclusion that geometric criteria give better results than energetic ones. Numbers of hydrogen bonds per molecule are not given in [192] explicitly. Network topology is characterized by ring size distribution. Six-membered rings predominate in all the models studied. Five- and seven-membered rings are also abundant. The question of ring distribution will be discussed in more detail below. It is proposed in [193] to use values of hydrogen bond parameters (pair interaction energy, r_{OO} and r_{OH} distances) corresponding to minima of distribution functions as hydrogen-bond criteria. Such an approach is natural and, of course, not a new one. For instance, it was used to determine hydrogen-bond criteria in [190]; rank distribution functions of r_{OO} , r_{OH} and E_{WW} , not ordinary ones, were analysed in that work. The authors of [193] analyse results of application of different criteria and their combinations. According to [193], $R_{OO}^{\max} = 3.3 \text{ Å}$ (the same as in [190] though different interaction models were used in these works). If this criterion is used alone, the average number of hydrogen bonds in which a water molecule (SPC/E interaction model, 300 K) is involved is 4.3. The authors think that this is too many. 3.7 hydrogen bonds per molecule, obtained with $R_{OH}^{\max} = 2.41 \text{ Å}$, they consider more reasonable. Use of $E_{WW}^{\max} = -12.9 \text{ kJ mol}^{-1}$ gives 3.2 bonds per molecule. Two-dimensional distance–angle distributions were also obtained in [193]. The potential of mean force (PMF),

$$W(R, \alpha) = kT \ln g(R, \alpha) \quad (\text{where } R \text{ distance } (r_{OO} \text{ or } r_{OH}) \text{ and } \alpha \text{ is some angle}),$$

was calculated and plotted. Some maximal value of PMF was chosen as the hydrogen-bond criterion for a given pair of parameters. Such hydrogen-bond definitions lead to an estimate of the number of hydrogen bonds per molecule lying between 3.2 and 3.4. An attempt was also made [193] to take into account the change of the electronic structure of water molecules as a result of hydrogen bond formation. To this end pairs of water molecules were selected at random. The electronic occupancy (N) of the σ_{OH}^* antibonding orbital of the electron acceptor molecule was calculated in the framework of the natural bond orbital approach [194]. The distribution of the occupancies is bimodal. The first narrow peak at small N values corresponds to weakly interacting dimers; the second broad one corresponds to hydrogen bonds. The distribution has

a minimum at $N = 0.0085$. It is an ‘electronic’ hydrogen-bond criterion; it takes into account the change of the water molecule electronic structure due to formation of a hydrogen bond. I want to recall that the most direct experimental manifestation of the hydrogen bond is the shift of the stretching vibrational band, which is a result of the change of the electronic structure.

An interesting discussion of the problem of hydrogen definitions in computer simulated water can be found in [193]. So much attention is given to this paper because it is the last publication on the topic. The problem is considered in detail; references to 131 publications are given.

There is an interesting approach to the hydrogen-bond definition in the instantaneous structures which has not been touched in [193]. It was put forward by Bergman [195]. The average distribution of the probability of occurrence of oxygen atoms of water molecules around the chosen one is constructed. To obtain such a distribution it is necessary, of course, to perform a preliminary computer simulation. Such distributions were obtained many times for characterization of the local structure of non-crystalline water (see, for instance, [196–199]). These distributions have already been mentioned above in the discussion of the structure of amorphous ices (section 3.2.1.1 and [139, 148, 149]). There are three regions with high probability of occurrence of adjacent molecules coordinated to a particular molecule. Two regions are near each hydrogen atom (their centres lie at distances of approximately 1.8 Å from the H atoms on the continuation of the O–H bond). The third, crescent-formed, region is around the oxygen atom on the side opposite to the hydrogen atoms. Bergman suggested quite reasonably that molecules whose oxygen atoms are found in these areas should be considered to be hydrogen-bonded to the chosen molecule. Thus first it is necessary to calculate the probability densities of the oxygen atoms around the water molecules. Then one must outline regions in space around the water molecules in which the molecules will be regarded as hydrogen-bonded with the given one. To this end it is necessary to choose some level of probability. Bergmann calls such a procedure ‘effective hydrogen bond definition’. The procedure implicitly takes into account the scatter of r_{OO} and r_{OH} distances and the nonlinearity of the hydrogen bonds. If, in the case of traditional hydrogen-bond criteria, choices of R_{OO}^{\max} , R_{OH}^{\max} , α_{HO}^{\min} and E_{WW}^{\max} are to some extent ambiguous, the ambiguity of Bergmann’s procedure dwells in the limit probability level.

3.3.2.2b. The dynamic hydrogen-bond criterion was put forward in [200]. It was further developed in [190, 201] (see also [10]). Let us have a look at figure 17(a). The dependence of r_{OO} distance on time for two water molecules is shown. There are four episodes when hydrogen between these two molecules existed in the time interval between 20 and 55 ps of molecular dynamics computer simulation: the first very short one around 22 ps, the second a longer one between 24.5 and 30 ps, the third between 34 and 36 ps and the longest one between 39 and 48 ps. For most of the time during these episodes the r_{OO} distance was shorter than 3.0 Å. Several times it exceeded 3.3 Å (the R_{OO}^{\max} value usually used in our works). Several times it was less than 3.3 Å for a short time;

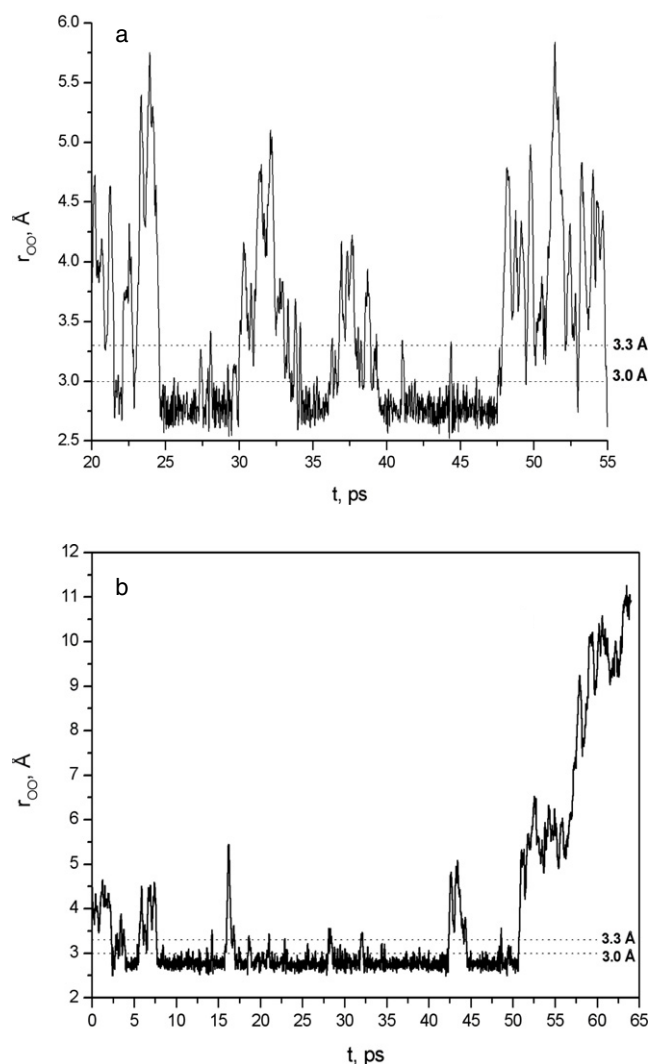


Figure 17. Dependence of r_{OO} distance on time. Fragments of molecular dynamics trajectories. 3456 molecules in the cubic periodic cell. (a) Explanations in the text: $T = 298$ K, $d = 0.998$ g cm $^{-3}$. (b) The hydrogen bond existed for almost 50 ps with some short intervals when r_{OO} was greater than 3.3 Å. The episodes after 5 and 42 ps are undoubtedly disruptions of the bond. The episode at about 16 ps according to all reasonable dynamic criteria should be regarded as disruption, but it looks like a big hydrogen-bond fluctuation. ($T = 297$ K, $d = 0.998$ g cm $^{-3}$.)

sometimes it was even less than 3.0 Å for a very short period of time. All these brief episodes during which the r_{OO} distance was short enough cannot, of course, be regarded as hydrogen bond formation. The same can be said about the episodes when the r_{OO} value for a short time exceeded the upper limits which we prescribe to hydrogen bonds. Hydrogen bonds were not disrupted during them. Another example of $r_{OO}(t)$ dependence is shown in figure 17(b). In this case the bond existed for almost 50 ps with some short breaks.

This approach belongs to the same circle of ideas as inherent structures: it is impossible to say whether particular molecules form a hydrogen bond between them using information about a particular I-structure only. According to the inherent structure conception it is necessary to minimize

the potential energy of a particular I-structure in order to judge which molecules are involved in hydrogen bonding. According to the dynamic hydrogen-bond criterion we must know the past and future of a particular configuration (I-structure) obtained in the course of molecular dynamics simulation. When applying this criterion we come across so to speak a double ambiguity. One is connected with the uncertainty of geometric and energetic criteria ($E_{\text{WW}}(t)$ was followed in [200]; the dependence of any hydrogen bond parameter on time can be studied for elaboration of the dynamic criterion). The other ambiguity is the choice of the period of time during which the bond was regarded not to be formed or not to be broken. It is natural to accept that a hydrogen bond is not formed or disrupted if the period during which the hydrogen-bond parameter was less or greater than limiting values was shorter than the period of r_{OO} (or r_{OH}) oscillations. As seen in figure 17, the higher the peak of the r_{OO} oscillation the greater the distance between nearest minima r_{OO} . So solution of the problem suggested by Tytik [202] perhaps is not the ultimate one. Tytik analysed the rank distribution of the lifetimes of hydrogen bonds and of ‘not-lifetimes’ (periods during which the hydrogen atom was not involved in hydrogen bonding) obtained without taking into account the dynamic criterion. He came to the conclusion that the threshold value is 0.08 ps. This time interval is slightly shorter than the average r_{OO} oscillation period [10].

3.3.2.3. In what way are molecules surrounded in liquid water?

Experimental data and general speculative considerations still give rather poor information about subtle peculiarities of surroundings of water molecules in the liquid. If we do not take into account extreme interpretations of XAS and XRS experiments [185, 186], the picture of water structure that follows from the experimental data is that water is a random distorted three-dimensional network in which all the molecules on average participate in four hydrogen bonds. Attempts to estimate fractions of water molecules forming two, three and four bonds have been made many times since the beginning of the 1950s, but they cannot be seriously discussed at present. Many dozens of estimations of these fractions are given in publications based on results of computer simulations of liquid water, from the earliest ones in which imperfect interaction models and hydrogen bond criteria were used. For a review see [203]. I shall not discuss the results of these studies, which are rather controversial. But in all of them along with two-, three- and four- (the most abundant) species five-coordinated molecules were found. In some publications water molecules which are not involved in four hydrogen bonds are treated as defects of the network (see for instance [204] and references therein). But I prefer to think that they are natural elements of the network. From all that vast stock of early works on simulation of liquid water I want to attract the reader’s attention to the fact that the distributions of potential energies of molecules involved in particular numbers of hydrogen bonds are very broad. Distributions of potential energies of molecules forming three, four and five hydrogen bonds overlap and there are many molecules with four hydrogen bonds whose potential energy is higher than that of the molecules with three

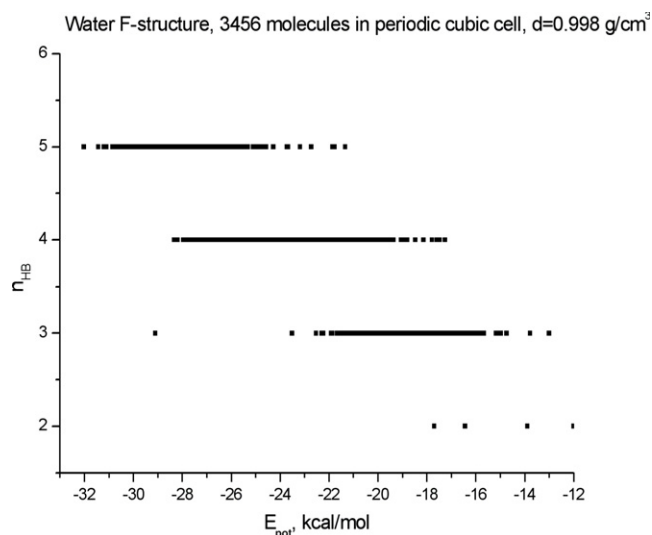


Figure 18. Overlapping of potential energy distributions of molecules involved in different numbers of hydrogen bonds (F-structure). Each dot corresponds to one molecule. Hydrogen bond criterion: $R_{\text{OO}}^{\text{max}} = 3.2 \text{ \AA}$, $R_{\text{OH}}^{\text{max}} = 2.4$. The average number of hydrogen bonds per molecule is 4.04. 0.17% of molecules are involved in two, 13.31% in three, 76.53% in four, 10.16% in five hydrogen bonds. 0.42% of molecules participate in bifurcated bonds.

bonds [205]. Overlapping of potential energy distributions with different numbers of hydrogen bonds is retained in the inherent structure (figure 18). So there are no discrete energy levels on which molecules with particular numbers of hydrogen bonds reside, as supposed in some early theoretical models of water (for instance [175]).

A more informative characteristic of the local surroundings of the water molecule than the total number of hydrogen bonds is the type of coordination [206, 207]. A symbol $a_n d_m$ can be assigned to each molecule; n is the number of hydrogen bonds in which a molecule participates as an acceptor and m as a donor of protons. Molecules belonging to types of coordination $a_3 d_1$, $a_1 d_3$ and $a_2 d_2$ participate in four hydrogen bonds. Molecules whose types of coordination are $a_2 d_3$ or $a_3 d_2$ form five bonds. The type of coordination of all the molecules in all ice crystalline ice modifications (except ice X) is $a_2 d_2$. Data of coordination type distribution for I-structures at ambient temperature are given in table 7. They are essentially the same as obtained for the model containing 768 molecules [10].

Note. The average values for 5 I- and 10 F-structures are given. 3456 molecules in each configuration. Hydrogen-bond criterion for I-structures: $R_{\text{OO}}^{\text{max}} = 3.3 \text{ \AA}$, $R_{\text{OH}}^{\text{max}} = 2.6 \text{ \AA}$; only those types of coordination are given whose probability is greater than 1%. Data are taken from [162]. F-structures were prepared by the Monte Carlo method specially for this paper. Types of coordination other than given in the last column of the table occur extremely rarely in the F-structures.

About half of the molecules have classical $a_2 d_2$ coordination type at ambient conditions. In the F-structures the fraction of molecules with this type of coordination considerably increases and reaches three-quarters (the last

Table 7. Types of coordination for the water model with density 0.998 g cm^{-3} .

Number of bonds in which the molecule is H-bond acceptor (n)	Number of bonds in which the molecule is H-bond donor (m)	Type of coordination $a_n d_m$	Total number of bonds	Probability (%)	
				I-structures 297 K	F-structures
1	1	$a_1 d_1$	2	2.32	0.25
2	1	$a_2 d_1$	3	6.79	2.30
3	1	$a_3 d_1$	4	1.26	0.14
1	2	$a_1 d_2$	3	12.6	12.23
2	2	$a_2 d_2$	4	50.25	75.07
3	2	$a_3 d_2$	5	13.60	9.86
1	3	$a_1 d_3$	4	1.94	—
2	3	$a_2 d_3$	5	7.15	0.15
3	3	$a_3 d_3$	6	1.93	—

column in table 7). The probability of $a_1 d_2$ coordination type is practically the same in I- and F-structures. The probability to find bifurcated bonds in the F-structures is much lower than in I-structures, but four to six molecules involved in such a bond are certainly present in each F-structure (3456 molecules). Bergman in [195] discusses types of coordination in a less pictorial, veiled form than is done in our works. For a long time it was thought that such a subtle peculiarity of water structure as the type of coordination distribution could be studied only in computer models. The emergence of the XAF method [185–187] instilled hope that it may be possible to do experimentally. Let us wait for the elimination of contradictions between the results obtained by this and more traditional methods.

3.3.2.4. Topology and structure of the hydrogen-bonded network. The most popular way to characterize network topology is to count hydrogen-bonded rings. This can be done for computer generated models. The results depend on the intermolecular interaction potential used, on hydrogen-bond criteria and on the ring search algorithm used. Sometimes only the rings containing the smallest number of molecules in which a particular molecule participates are taken into account. If we take into account all the rings, their number per molecule must increase monotonically with the number of molecules in them [195, 208]. Bergman prefers to say ‘loops’ instead of ‘rings’. He distinguishes ‘clean’ and ‘dirty’ loops. Clean loops in his terminology are loops whose molecules are not additionally connected by external (with respect to this loop) chains which are shorter than the fragment of the loop connecting these molecules. Bergman gives the following numbers of clean loops in which water molecules participate (table 8).

The loops were looked for in the I-structures obtained during molecular dynamics simulation within the *NVT* ensemble (256 molecules in the periodic cubic cell, $T = 300 \text{ K}$, SPC/E potential). Bergman gives a more detailed classification of loops by taking into account the directions of the hydrogen bonds. Actually, he gives quantitative characterization of the ‘dromicity’ concept put forward by Saenger [209] (homodrome, heterodrome and antidrome rings). Bergman considers not only loops with different directions of the bonds but chains as well. The importance of the direction of hydrogen bonds for the network is not clear

Table 8. The number of clean loops in the computer model of water [195].

Number of edges in the loop	Number of clean loops per molecule
3	0.0011
4	0.0055
5	0.156
6	0.192
7	0.189
8	0.157
9	0.144
10	0.115

yet. It is almost obvious that isolated homodrome four-, five- and six-membered rings are more stable than heterodrome and antidrome [210]. Very interesting results were obtained by Kirov [211, 212]. He discovered, in particular, that a change of the direction of all hydrogen bonds in a cluster may lead to a change of its energy [211]. Is this finding important to our understanding of the structure of three-dimensional water network? There is no answer at present. Few works have been dedicated to the search for the regularities in the structure of the hydrogen-bonded water network beyond the first coordination sphere. It is precisely these regularities which can help us to understand principles of organization of the network in much larger volumes, or to understand the *total* structure of water (according to Zorky [213]). Study of the ring statistics is only the first and not very interesting step on the road to this understanding. The next step was done by Bushuev *et al* [208]. They calculated distribution functions of distances between the centres of rings (g_{55} , g_{66} , g_{56} etc functions; i.e. distribution of distances between centres of five- and six-membered rings, as well as between the centres of five- and six-membered rings, and so on). Analyses of these functions allowed Bushuev *et al* to derive the structure of the typical fragments of the hydrogen-bonded network containing close-lying rings. Among these fragments such configurations as the adamantane-like cavity of the ice Ic framework (four fused six-membered rings in the chair conformation), the ice Ih cavity (five fused six-membered rings, two in the chair and three in the boat conformation) and a fragment of clathrate structure (two edge-sharing pentagons or edge-sharing pentagon and hexagon) can be mentioned. However, most fragments identified by using these distribution functions do not resemble fragments of any

crystal structure. Bushuev *et al* [208] also studied the form of clusters into which the network decomposes slightly below the percolation threshold (the energetic criterion was used, so these clusters contained molecules connected by the stronger hydrogen bonds). These clusters mainly look like poorly branched chains with small numbers of closed rings.

3.3.2.5. Structural heterogeneity of liquid water. As pointed out in section 3.3.1, central to most of the intuitive speculative models of water put forward from the end of the 19th century up to the 1970s was the idea of structural heterogeneity of liquid water. It was only random network models emphasizing hydrogen bond bending that were not based on this idea. Models which imply structural heterogeneity explain easily and naturally the non-monotonic dependence of many properties of water on temperature and pressure. Of course such dependences may be due to the intrinsic properties of the network (such as the non-monotonic temperature dependence of ice Ih density, see section 1 and [6]). But the image of water as a structurally non-homogeneous liquid was much more attractive for the scientific community. Elements of structural inhomogeneity of water were reported in the early simulations of water stimulated by the application of percolation theory to liquid water [214, 215]. In particular, subsystems of water molecules connected by strong and weak hydrogen bonds were isolated in the configurations obtained by molecular dynamics simulation. Inhomogeneity of local density was also found (the title of [215] is ‘Low density “patches” in hydrogen bond networks of liquid water: evidence from molecular dynamics computer simulation’). Bushuev *et al* [208] constructed $g_{OO}(r)$ radial distribution functions for molecules with very low (-117 kJ mol^{-1} ; -98 kJ mol^{-1} on average) and very high (above -75 kJ mol^{-1}) energy. Analysis of these functions showed that low-energy and high-energy molecules group together. But it is impossible to determine the form of the regions where the molecules with low or high values of potential energy are grouped. ‘Inhomogeneity’ is a widespread word in modern publications devoted to water. ‘Static and dynamic inhomogeneities in water’ is the title of a very interesting paper by Stanley *et al* [216]. The paper carries many original and bright ideas; the list of references is long and comprehensive. However, few details about specific features of these inhomogeneities can be found in the paper.

In our works, structural inhomogeneity of the network of computer simulated water was revealed as a non-uniform space arrangement of molecules whose local environment characteristics lie within certain limits. This approach was already discussed in section 3.2.1.3, where it was applied to the structure of amorphous ices. In table 9 data on surroundings of molecules in liquid water at ambient conditions are given [162]. Molecules are classified not only with respect to VVP values but also with respect to tetrahedrity and potential energy. It is seen that the tendency of molecules to surround themselves with molecules with similar VVP values as expressed for liquid water is no less pronounced than in the case of F-structures of amorphous ices (table 6). This tendency is the strongest for ‘small’ molecules. Surroundings of ‘weak’ molecules practically coincide with random ones. For all

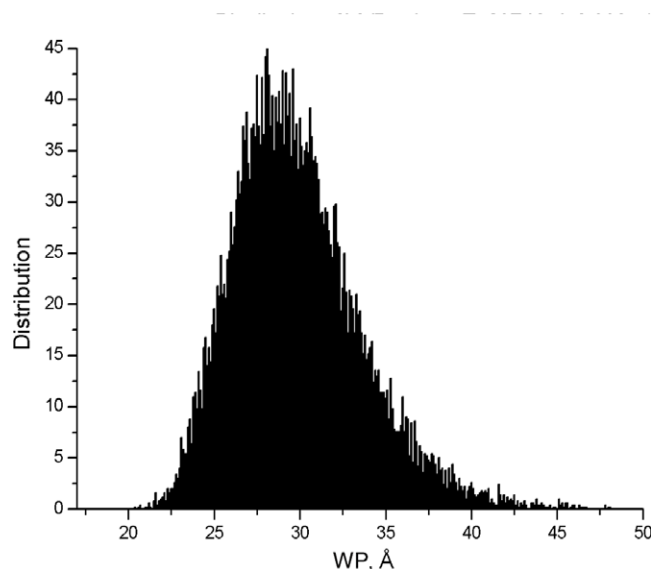


Figure 19. Distribution of Voronoi polyhedron volumes at ambient temperature and pressure. Average for five I-structures (the same as were used to obtain data given in table 7). ($T = 297 \text{ K}$, $d = 0.998 \text{ g cm}^{-3}$.)

three parameters molecules with low values tend to ‘flock together’ more readily than molecules with high values of the parameters. If we choose some small fraction of molecules with lowest and highest values of the parameters describing their local surroundings, they will form ramifying three-dimensional clusters [157, 158]. I do not give corresponding pictures because they look just the same as figures 14 and 15. The reader can find such pictures for liquid water in my paper [10].

3.3.2.6. Revival of the two-state or mixture models of liquid water. Discovery of the polymorphism of amorphous ices revived the concepts of water as a mixture of two states. Now LDA and HDA non-crystalline phases of ice were considered as prototypes of less and more dense microphases of water. Here are some quotations and references. ‘Water is considered to be a regular solution of two components, whose local configurations correspond to short-range order of the LDA and HDA modifications of the amorphous ices’ [217]. ‘Analyses based on order parameters of structural fluctuations show that liquid water is a composite of high density amorphous (HDA)-like regions and low density amorphous (LDA)-like regions’ [218]. ‘The purpose of the present paper is to try to get the venerable mixture model for liquid water back onto its feet’ [219]. After discovery of VHDA this modification became a more likely candidate for a denser state of water (see, e.g. [153]). In fact, as will be shown below, (section 3.3.3.2), a primitive two-state model cannot explain the non-monotonic dependence of the diffusion coefficient on the density. The distribution of Voronoi polyhedron volumes (local density) in I-structures obtained in our simulations is unimodal (figure 19). Inhomogeneity with respect to local density revealed in our simulations is much more subtle and interesting than is implied in primitive two-state models.

Table 9. Surroundings of water molecules at ambient temperature and pressure. (Average data for five I-structures (3456 molecules in a cubic periodic box) are given. All the molecules in each configuration were subdivided into two equal classes with low and high values of Voronoi polyhedron volume (VVP), tetrahedrity index (T) or potential energy (E_{pot}). The molecules with low values of these parameters are called small, good and strong respectively. The molecules with high values of the parameter are called large, bad and weak.)

Voronoi polyhedron volume						Tetrahedrity					
Surroundings of small molecules			Surroundings of large molecules			Surroundings of good molecules			Surroundings of bad molecules		
Among four nearest neighbours			Among four nearest neighbours			Among four nearest neighbours			Among four nearest neighbours		
Small	Large	(%)	Small	Large	(%)	Good	Bad	(%)	Good	Bad	(%)
0	4	3.29	0	4	10.73	0	4	3.97	0	4	9.08
1	3	15.24	1	3	26.93	1	3	18.96	1	3	28.10
2	2	29.91	2	2	33.17	2	2	35.23	2	2	35.14
3	1	33.90	3	1	22.70	3	1	31.08	3	1	21.70
4	0	17.96	4	0	6.47	4	0	10.83	4	0	5.70

Potential energy						Random distribution (%)
Surroundings of strong molecules			Surroundings of weak molecules			
Among four nearest neighbours			Among four nearest neighbours			
Strong	Weak	(%)	Strong	Weak	(%)	
0	4	3.42	0	4	5.27	6.25
1	3	19.40	1	3	23.70	25.0
2	2	36.36	2	2	38.34	37.5
3	1	31.18	3	1	26.00	25.0
4	0	9.64	4	0	6.66	6.25

3.3.3. Dynamical properties of liquid water

3.3.3.1. How long do hydrogen bonds live? How are they being broken?

3.3.3.1a. Experimental evidence. For a long time experiment could not give a direct answer to these questions. It was generally believed that hydrogen-bond lifetimes were of the same order of magnitude as the dielectric relaxation time (for the latest review see [220]), the NMR correlation time (one-third of the former, see e.g. [221]) and the residence time, calculated from quasielastic neutron scattering [222]. All these times are of the order of several picoseconds at ambient temperature. As to the mechanism of changing of hydrogen-bond partners, only two of them are possible: (1) the O–H···O bond breaks, the proton for some time is not involved in any bond, then the hydrogen bond with the oxygen atom of another water molecule is formed; (2) the hydrogen atom participates for some time in a bifurcated bond and then it ‘chooses’ one of the partners. If it returns to the previous oxygen atom it means that the bond was not broken. If the hydrogen atom forms a bond with the other oxygen atom, a new bond forms. How long does the hydrogen atom participate in no bond? How long does the bifurcated configuration exist? Until not long ago the answer to these questions could be obtained from computer simulation only. Methods of ultrafast spectroscopy are being developed now [223–227]. They can deprive computer simulation of the monopoly in providing detailed information on the subtle characteristics of the behaviour of molecules. The title of paper [226] is ‘Hydrogen bonds in liquid water are broken only fleetingly’. It is shown there that the hydrogen atom of the broken hydrogen

bond needs no more than 200 fs to find a new oxygen. Some other interesting findings were made with the help of ultrafast vibrational spectroscopy, but it is too early yet to sum up its achievements in the field of hydrogen-bond dynamics.

3.3.3.1b. Computer simulation. The advantage of computer simulation is that it allows obtaining not only average values for lifetimes or of ‘not-lifetimes’ of hydrogen bonds, but the distribution of these times as well. In most publications, beginning with the classical work by Rapaport [228], the dynamic criterion was not used. Each short spike of r_{OO} , r_{OH} or E_{WW} was regarded as hydrogen-bond disruption or a very short-living hydrogen bond. As a consequence too small average values of hydrogen-bond lifetimes were obtained. A distinguishing feature of hydrogen-bond lifetime distribution is that it is very broad [159, 190, 201, 202]. It is broad even when we do take the dynamic criterion into account. In these papers hydrogen-bond lifetimes were obtained from the results of molecular dynamics simulation of water microdroplets containing several hundreds of molecules. The longest lifetimes observed were about 30 ps. The average value is about 2 ps for microdroplets. As the molecules move more intensively near the surface, the average value for bulk water must be greater. The distribution of lifetimes of coordination types $a_n d_m$ in the microdroplet was also studied [159]. It is quite natural that the longest lifetimes were found for the most abundant coordination type $a_2 d_2$. The average lifetime for this coordination type is approximately one-quarter that of the hydrogen bond and equals 0.7 ps; the longest observed lifetime is 7.4 ps. Lifetimes of a rather rare coordination type with one bifurcated bond, $a_2 d_3$, are much shorter (0.19 and 0.62 ps respectively). The distribution of hydrogen-bond

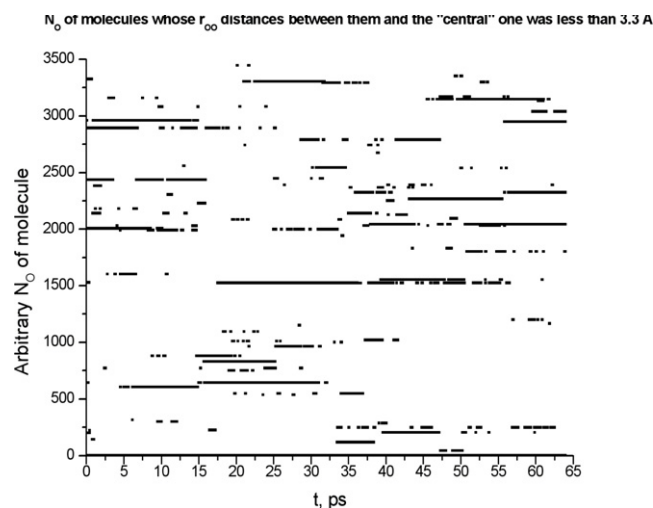


Figure 20. 'Biographical map' of a molecule. Each event when the r_{OO} distance between a chosen molecule (called 'central') and another molecule has been shorter than 3.3 Å corresponds to a dot. Arbitrary numbers assigned to the molecules are shown on the y-axis.

lifetimes in bulk water has not been studied in such detail. It is fairly broad too. A pictorial indication of it can be given by figure 20. Some additional information about hydrogen-bond lifetimes in bulk liquid water will be given in the next section. Both conceivable mechanisms of changing hydrogen-bond partners mentioned in the previous section were observed in computer simulated water (see for instance [190]). I do not know of works where the probability of each of these mechanisms has been estimated. It is necessary to note that there can be a situation when the hydrogen bond between two particular molecules is preserved, but other protons become involved in the bond between the same molecules [190].

3.3.3.2. Dynamic inhomogeneity of water. There are several kinds of dynamic inhomogeneity. The most trivial one lies in the fact that dynamic properties of the molecules with different surroundings are different. This was demonstrated for the crystalline ices [55, 155–157] and for amorphous ice [160, 161] (see figure 12). It is quite natural that the amplitude of oscillations of molecules with greater values of VVP (less local density around them) is greater than that of molecules with smaller values of VVP (more dense local surroundings). It seems to be quite natural as well that the slope of the temporal dependence of the mean square displacement $\langle r^2 \rangle(t)$ (proportional to the diffusion coefficient) of the molecules in the denser regions of the water network (with smaller VVP values) is smaller than that of the molecules in the looser regions (with large VVP volumes) [158, 159] (see figure 21). It is not easy to determine diffusion coefficients of molecules from the low and high density regions (by means of computer simulation), because the molecules do not maintain their VVP values for a long time. The mean square displacement function $\langle r^2 \rangle(t)$ reaches the diffusion regime ($\langle r^2 \rangle(t) = 6Dt$, D is the diffusion coefficient) at $t > 1$ ps [10]. We managed to follow $\langle r^2 \rangle(t)$ for the molecules with high and

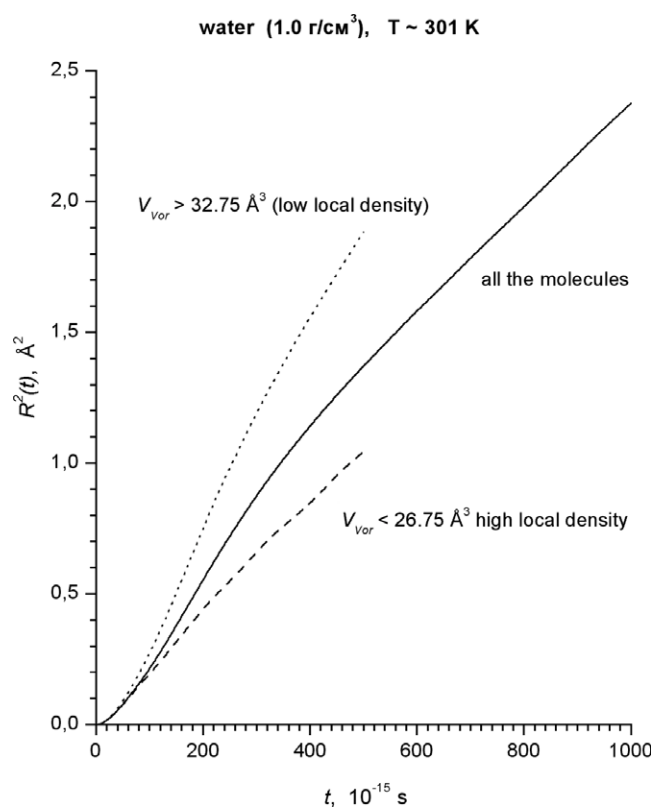


Figure 21. Time dependence of centre of mass mean square displacement for molecules with high and low values of the Voronoi polyhedron volumes (V_{vor}). Liquid water at ambient conditions.

low VVP values only for about 0.5 ps (figure 21). But there is no doubt that, according to computer simulation, the diffusion coefficient of molecules in the regions with high local density is smaller than that of the molecules with low local density.

Meanwhile, one of the best known and bright 'anomalies' of water is the increase of diffusion coefficient with increase of density (this 'anomaly' is observed at $T < 310$ K; D reaches a maximum at a pressure of about 200 MPa, which corresponds to a density ~ 1.08 g cm $^{-3}$ at ambient temperature [211, 229]). This has been reproduced many times by computer simulation (see for instance [230]). In our works a non-monotonic dependence of D (calculated for all molecules) on pressure was also found [10] (see figure 22). Trivial dependence of diffusion coefficient on local density leads to a non-trivial situation. A paradox arises: if we compress the whole system, the diffusion coefficient increases, but the diffusion coefficient in the regions with high local density is lower than in the regions with low local density and in the system as a whole. This means that this 'anomaly' cannot be explained by a primitive two-state model, which implies that water is a composite of high density regions and low density regions [218] (see section 3.3.2.5). The explanation of this paradox may lie in the intrinsic properties of hydrogen-bonded tetrahedral networks. The melting temperature of ice Ih decreases as the pressure (and density of both crystalline and liquid phases) increases. This is the trivial consequence of the fact that the volume of water decreases after melting. At about 200 MPa, when ice III becomes the stable phase, the melting temperature reaches

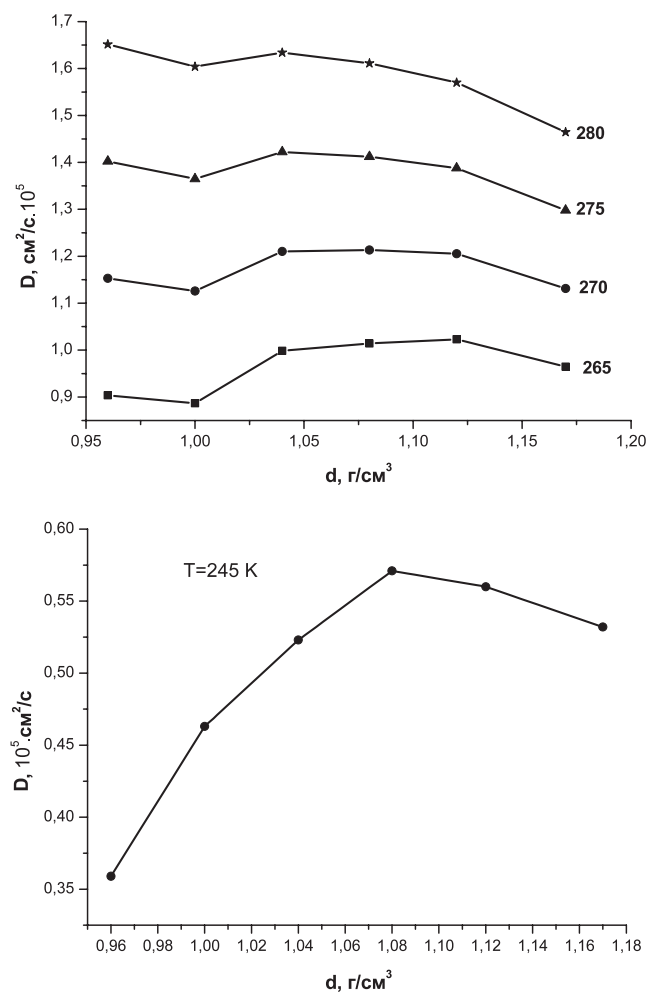


Figure 22. Density dependence of water diffusion coefficient obtained by computer simulation [10]. The system contained 576 molecules in the cubic simulation cell. Top: temperatures close to the melting point; they are indicated near the curves. Bottom: deeply supercooled water.

its minimum. Ice III and all denser phases of ice melt quite normally: the density decreases during melting; the melting temperature increases with growth of pressure. But not only the pressure dependence of the melting temperature changes at about 200 MPa. So does the pressure dependence of the temperature of homogeneous nucleation (T_H) (figure 23) as well. It also has a minimum at about 200 MPa. Between these two temperatures supercooled liquid water can exist. I think that the key to the explanation of the unusual dependence of the diffusion coefficient on pressure (and on density) lies in the pressure dependences of T_m and T_H . We can assume that the diffusion coefficient depends not so much on the absolute value of temperature as on the difference $T - T_m$ (or $T - T_H$). No wonder that the diffusion coefficient should reach a maximum (and the viscosity should reach a minimum) at a pressure $\sim 200 \text{ MPa}$, when T_m and T_H are minimal.

Dynamic heterogeneity of this kind is also manifested when molecules are classified according to tetrahedrality indices [158, 231]. The diffusion coefficient of ‘bad’ (with high values of T) molecules is greater than that of ‘good’ (with

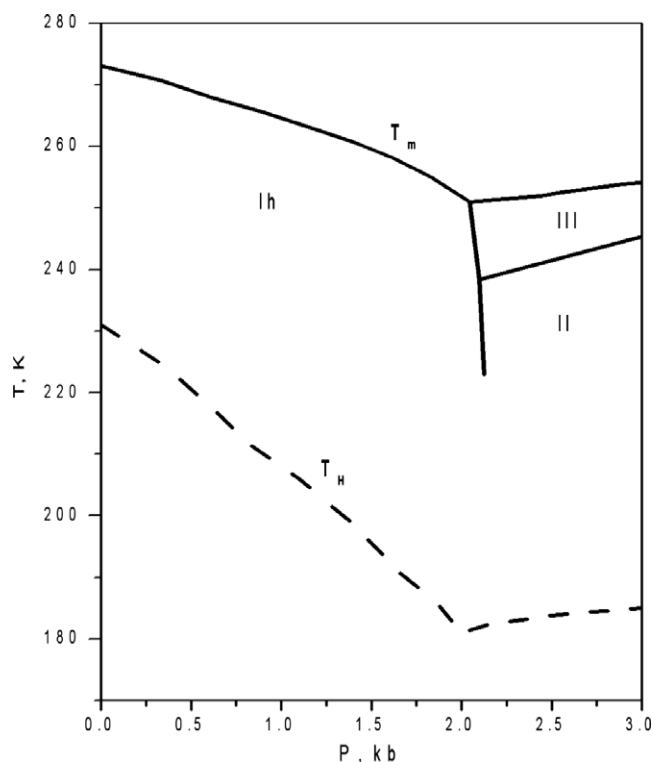


Figure 23. Schematic phase diagram of water at relatively low pressures. T_m (solid line) is the melting temperature of ices (their standard names are shown in the regions of their stability). T_H (dashed line) is the homogeneous nucleation temperature.

low values of T) molecules. This looks quite normal from the point of view of mixed molecules, because in dense systems the ideal tetrahedral environment of the molecules should be more distorted than in systems with low density. But it does not explain the volume paradox.

Another less trivial dynamic heterogeneity of liquid water is the result of the broad distribution of the hydrogen-bond lifetimes. A certain number of long-living bonds exist. This means that associates incorporating two or more molecules exist in liquid water and move as a unified complex for rather a long time [190]. Such associates could not be revealed by the analysis of the separate instantaneous structures. It is necessary to colour the hydrogen-bonded network with respect to lifetimes of hydrogen bonds. To this end molecular dynamics 50 ps long was obtained (34 546 molecules, 298 K, 0.998 g cm^{-3}) [232]. Coordinates of the molecules in the configurations separated by 1 ps were recorded. Lists of hydrogen bonds (geometric criterion, $r_{\text{OO}}^{\text{max}} = 3.3 \text{ \AA}$) were compiled for each configuration. The configuration obtained at 25 ps was chosen as a reference one and its list of hydrogen bonds was compared with hydrogen bond lists of all the other configurations. This is a rather rough procedure for estimation of hydrogen bond lifetimes but it may be quite adequate for revealing associates of molecules connected by long-living bonds. If we colour in the reference configuration the bonds with lifetimes longer than 7 ps they will form an infinite ramifying cluster, resembling clusters formed by molecules with high or low values of VVP. Of course not all the bonds

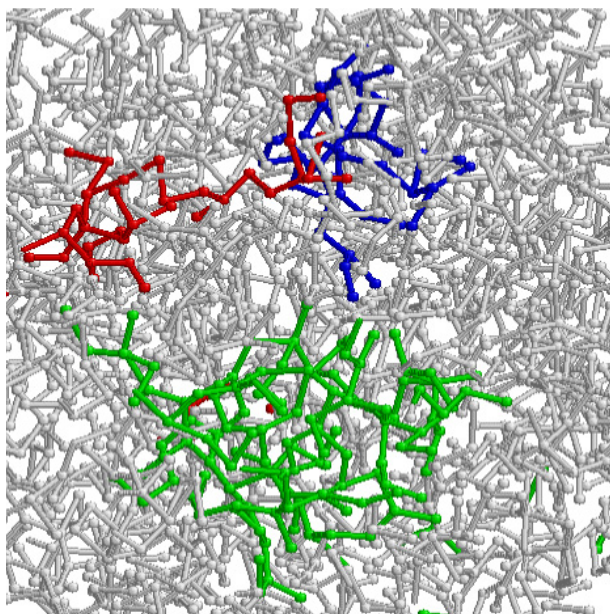


Figure 24. Clusters formed by molecules participating at least in one hydrogen bond whose lifetime is longer than 8 ps (grey colour). Three of them are coloured in red (medium grey in the printed edition), blue (dark grey in the printed edition) and green (black in the printed edition). $T = 298$ K, 3456 molecules in the simulation periodic cell.

living longer than 7 ps belong to this cluster. The bonds living longer than 8 ps do not form an infinite cluster, but clusters containing several hundreds of molecules can be found (figure 24). This means that the percolation threshold with respect to hydrogen-bond lifetimes (determined in such a rough way) lies between 7 and 8 ps in the case of this particular molecular dynamics trajectory. The average value of the percolation threshold is 7.96 ps at room temperature. About 20% of bonds have lifetimes longer than 7 ps. It should be stressed that molecules participating in long-living bonds do not form compact complexes but rather loose branching clusters. There are many molecules which do not participate in long-living bonds and frequently exchange their neighbours inside these clusters. Bonds with lifetimes longer than 20 ps are united into small clusters containing one bond (two molecules), two bonds (three molecules) and very rarely three bonds (four molecules) (figure 25). This is a vivid illustration of collective diffusion. Molecules connected by long-living hydrogen bonds can move only concertedly. If we colour the network randomly, taking into account the probability to find a bond with a particular lifetime, we shall obtain practically the same percolation threshold and distributions of cluster sizes as obtained from analysis of actual configurations. This means that there is no special tendency to group bonds with particular lifetimes together. So this kind of dynamic heterogeneity turned out to be trivial. Of course, this problem needs more thorough investigation.

3.3.3.3. How do water molecules move in the liquid?

3.3.3.3a Diffusional motion. The most popular picture of molecular motions in liquid was proposed by Frenkel



Figure 25. Clusters formed by molecules participating at least in one hydrogen bond whose lifetime is longer than 20 ps. $T = 298$ K, 3456 molecules in the simulation periodic cell.

in the 1930s (see his famous book [233]). This picture implies that a molecule oscillates for some time around a temporary position and then jumps to the another position. Frenkel admitted that this temporary position can move as well. Quasielastic neutron scattering (QENS) [222] presented possibility to obtain information about molecular motions from the experiment. The first QENS experiments with water appeared at the end of the 1950s and were interpreted within the framework of Frenkel's picture. Singwi and Sjolander put forward the model according to which temporary positions of molecules do not move between the jumps [235]. The form of the QENS peak can be described by a formula with two parameters: residence time τ_0 during which molecules oscillate and diffusion coefficient D . Oskotskii took into account the possibility of drift of average positions of molecules between the jumps [236]. The form of the QENS peak according to Oskotskii can be described by a formula in which in comparison with Singwi and Sjolander's formula there is an additional term containing diffusion coefficient D_0 describing the drift of temporary positions of molecules. Oskotskii obtained the following parameters of the model: $D = 2.66 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\tau_0 = 1.7 \text{ ps}$, $D_0 = 0.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The length of the jump is 1.6 Å. According to later QENS experiments treated using Oskotskii's model these parameters are $D = 2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\tau_0 = 3.1 \text{ ps}$, $D_0 = 0.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [236]. All these data were obtained for room temperature. So the residence time is close to the correlation time obtained from NMR experiments and to the average hydrogen-bond lifetime found by molecular dynamics simulation. Extensive QENS study of water in a broad interval of temperature including far below the freezing point was undertaken by Teixeira *et al* [237]. Further details of development of the methods of interpretation of QENS experiments and studies of water by this method can be found

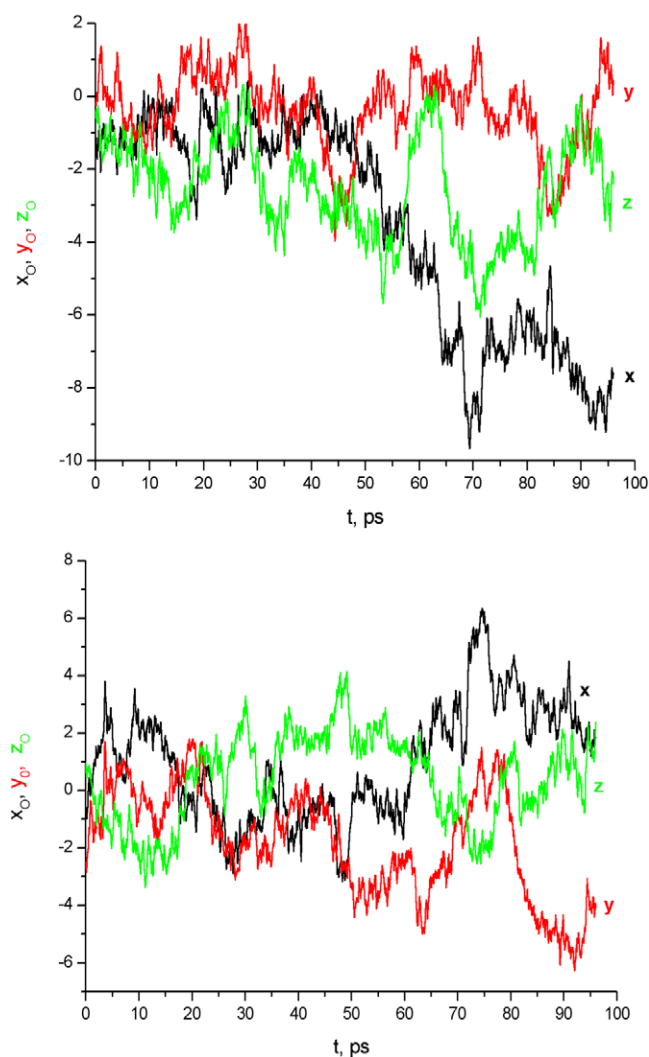


Figure 26. Trajectories of two water molecules. Dependence of x , y and z coordinates of oxygen atoms on time. Coordinates were recorded during 96 ps of virtual time. ($T = 297$ K, $d = 0.998$ g cm $^{-3}$.)

in an excellent book by Bée [222]. It is the general belief that the wait-and-jump picture which follows from the QENS experiment corresponds to actual motions of molecules in the liquid. Nothing of the kind is observed in computer simulation. If we cast a glance at the trajectories of individual molecules we shall not see frequent fast jumps (figure 26). It seems that a molecule made a sequence of jumps along the x -axis between 52 and 74 ps. In fact each of these jumps lasted more than 1 ps and they were 2–3 Å long. We call such events in the life of molecules ‘slow jumps’. They are rather rare events. These slow jumps are not obligatorily accompanied by disruption of hydrogen bonds. Sometimes two molecules jump together [232] (see figure 27). Sometimes the molecules hang about in the same place, sometimes they drift constantly and sometimes they make slow jumps. Projections of the trajectories on the plane resemble random wandering (figure 28). It is seen on the top picture of figure 28 that there are three preferable regions in which the molecules stay for a fairly long time. But in the case of other molecules such

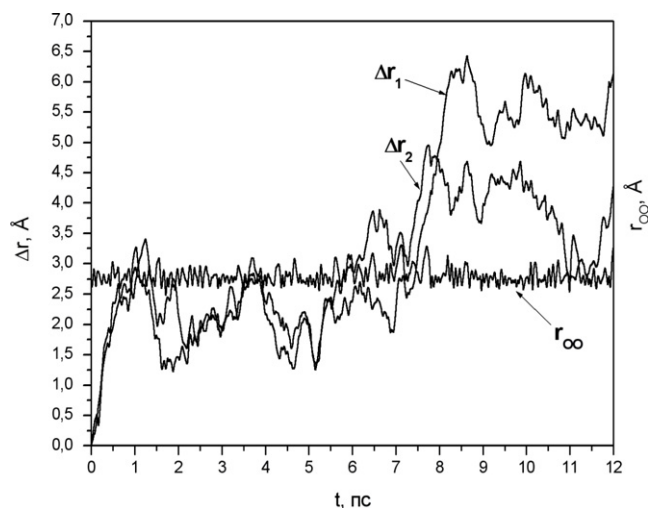


Figure 27. Concerted motion of two water molecules connected by a hydrogen bond. Between 6 and 7 ps they jumped together but the bond was not broken. Left y-axis, oxygen atom displacement from the initial position; right y-axis, r_{OO} distance.

regions cannot be isolated (figure 28, bottom). Few attempts to reconcile QENS experiments with the results of computer simulations have been made. There is some progress, but the reconciliation is not yet achieved [238, 239].

3.3.3.3b. Translational vibrations. All diffusion motions discussed in the previous section go on against the background of translational vibrations. The vibrations seen in figure 26 have average frequency about 60 cm $^{-1}$ (~ 7 meV; the period is ~ 0.6 ps). The second frequency is better seen in figure 17, where the dependence of r_{OO} on time is plotted. $\tau_0 = 3.1$ ps. Its frequency is about 200 cm $^{-1}$ (~ 25 meV; the period is ~ 170 fs). These frequencies can be obtained experimentally in the most direct way from measurements of inelastic neutron scattering, but of course they can be revealed by infrared and Raman spectroscopy. Vibrational spectra can be easily obtained from the results of computer simulation. It is enough to calculate the corresponding velocity autocorrelation function; the density of vibrational states is nothing but the Fourier transformation of this function. Frequencies of these vibrations almost do not depend on temperature, while the dependence of their amplitudes on temperature is very great. There nothing peculiar or interesting in these vibrations. I am speaking about them only because they, along with librational vibrations, are the only reasons for the difference between instantaneous and inherent structures about which so much was said in this paper.

3.3.3.3c. Rotational motions. Rotational motions of water molecules can be easily observed in computer simulations. It is necessary to shift the origin of the coordinates to the centre of the oxygen atom and to follow hydrogen positions (figure 29). The character of rotational motions resembles that of diffusional motion. Molecules oscillate all the time. They can maintain their average orientation for a long time or change it gradually. From time to time they make fast

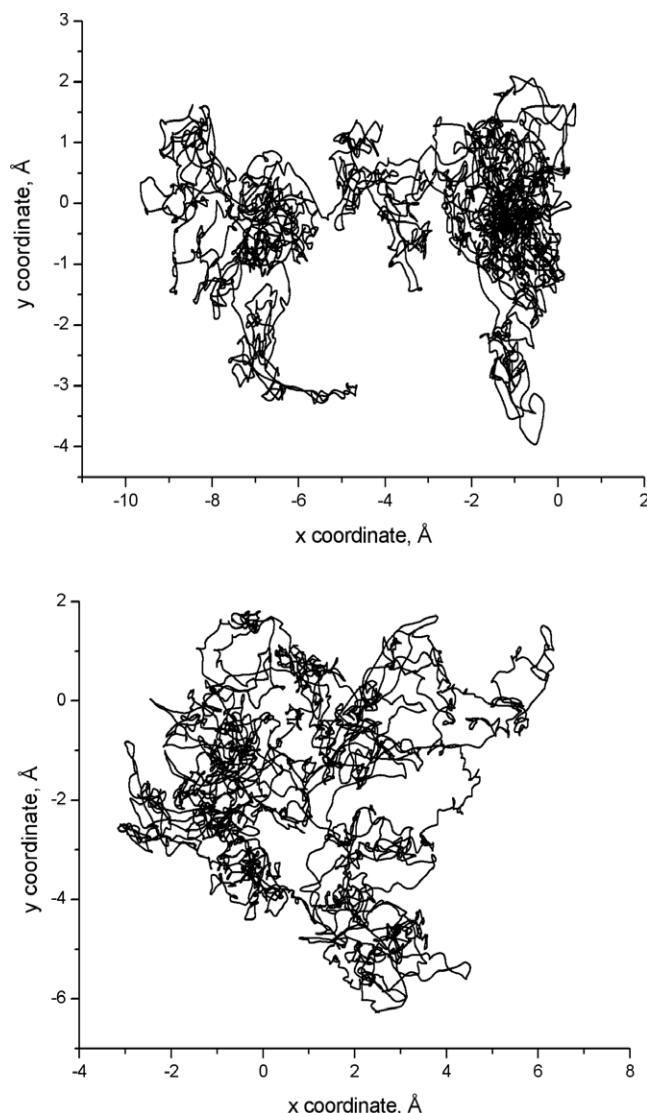


Figure 28. Wandering of water molecule oxygen atoms during 96 ps. Projections of the trajectories of water molecules on the x - y plane.

turns (up to 180°). Such turns occur rather rarely. Unlike slow jumps in diffusional motion, sharp changes of orientation occur very quickly (during 0.1–0.2 ps). All these changes of orientation occur against the background of fast oscillations. The period of these oscillations is about 50 fs. They are well known librational vibrations revealed by inelastic neutron scattering and by IR and Raman spectroscopy. Not all abrupt changes of water molecule orientations lead to the breaking of the hydrogen bond. Sometimes the proton participating in the hydrogen bond is changed but the bond between the molecules is preserved (see section 3.3.3.1b and [190]). Rotational motions of water molecules have been studied by many authors who performed computer simulation. I should like to attract the reader's attention to the paper [240], in which the dependence of the amplitudes of librations on the strength of hydrogen bonds (and hence on O–H stretching frequency) was demonstrated. In turn, long time reorientations responsible for the change of hydrogen bond partners do not depend on hydrogen bond strength.

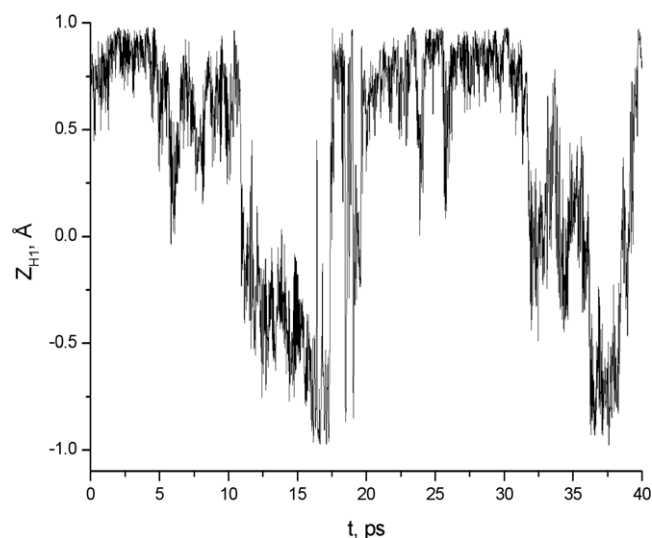


Figure 29. Dependence of the z coordinate of one of the hydrogen atoms of a water molecule on time. The origin of coordinates was shifted to the oxygen atom and moved together with it. The length of the O–H bond is about 1 Å, so if $z = \pm 1$ Å the O–H bond is directed along the z -axis. During the first 11 ps it was directed along the z -axis (upward), then it abruptly changed its direction and became perpendicular to the axis and started to change its direction slowly; at 16 ps the orientation became parallel to the z -axis (downward) but very soon the molecule turned back and OH bond again became oriented along the z -axis (upward). This orientation was maintained for ~ 15 ps, after which the O–H bond became oriented normally to the z -axis for ~ 7 ps. At the end of the 40 ps trajectory the OH bond was again directed along the z -axis upward. ($T = 297$ K, $d = 0.998$ g cm $^{-3}$.)

3.3.4. Second critical point and separation of liquid water into two phases. The most non-trivial idea about water, that had a great impact on water science, stimulated innumerable publications and caused ardent discussions, was undoubtedly the second critical point conjecture [241]. Discovery of the phase transition between two forms of amorphous ice (title of the paper [242] is ‘An apparently first-order transition between two amorphous phases of ice induced by pressure’) inevitably led to the conclusion that such a transition could also occur at higher temperature, when solid amorphous ices are softened and become liquid. It was natural to suppose that the difference between these two phases becomes less and less pronounced when temperature increases and disappears at some critical temperature, because no phase transitions occur above the ice melting temperature. The idea was taken up by many researchers. Preliminary results of this activity were summed up in the well known paper by Mishima and Stanley [243]. According to the estimation of Ponyatovskii *et al*, the critical temperature T_{cr} is 230 K and the critical pressure P_{cr} is 17.4 MPa [244]. Many other estimations of these parameters based on either extrapolation of experimental data or on the results of computer simulation were proposed. They are reviewed in [124] (pp 1699–1707). According to all these evaluations, T_{cr} is close to T_H . Suggested estimates of P_{cr} vary in a wide range of up to 300 MPa. The latest estimation and discussion of the modern state of the art of the problem can be found in [245]. The authors made special

experiments in order to refine the pressure dependence of T_H (shown schematically in figure 23) and analysed all available experimental and computational data. They came to the conclusion that $145\text{ K} < T_{cr} < 175\text{ K}$ and $P_{cr} \approx 200\text{ MPa}$. Their conclusion is in a sense paradoxical: ‘Although the existence of a second critical point has become more realistic, the location seems to be less favourable to the water model of the second-critical-point interpretation’. It is very important that they connect the second critical point with the position of the minimum of the $T_H(p)$ curve.

The second critical point conjecture is not the unique interpretation of the properties of water at very low temperatures. In 1972 Anisimov *et al* [246] demonstrated that the temperature dependence (for supercooled water) of many dynamic properties of water (viscosity, dielectric and magnetic relaxation times, inverse self-diffusion coefficient) can be described in terms of a simple formula similar to the relation describing the behaviour of properties near the critical point:

$$y = y_0[(T - T_s)/T_s]^{-\gamma}.$$

According to Angell [247], who used more recent and exact experimental data, $T_s = 228\text{ K}$ and γ is close to 1.6. The authors of [246] and Angell insisted that T_s is not a critical point in the sense that water is segregated into two phases below this temperature, although their T_s is close to some estimations of T_{cr} suggested later. In fact, at ambient pressure T_s is close to T_H and is some kind of lowest limit of stability for liquid water. The concept of the stability limit was developed by Speedy [247]. It is discussed in detail in [124] and more briefly in [10]. It seems that the authors of [245] try to reconcile conceptions of the second critical point and of the stability limit. Anyhow, if they are right and T_{cr} is much lower than has been thought before, there is little hope that separation of water into two phases with different densities will be observed in the experiment. Crystalline ices are stable in this ‘no man’s land’, as Mishima and Stanley called the region of the phase diagram between T_H and the glass transition temperature [243]. Meanwhile transitions between different liquid phases have been observed many times in computer experiments [241, 249–254].

4. Conclusion

The list of publications on water is inexhaustible. No one knows them all. It was a difficult problem for me to choose from those I am acquainted with the 254 publications I cite in this paper. Of course the choice of the problems which I intended to discuss here is very personal. As a crystallographer by education and by way of thinking I preferred to discuss structural aspects and properties related to the structure. This is why I did not touch on many interesting and important questions.

One of the brightest peculiarities of water is its wide structural diversity. Three new crystalline ice modifications has been discovered during the last decade. The diversity of amorphous ices has been the subject of intensive studies and discussions during the last quarter of a century. As to liquid

water, the possibility of coexistence of two phases differing in density is not proven yet. Structural diversity in the case of liquid water can be manifested in its structural heterogeneity; therefore, considerable attention has been given to this question in the paper.

The general picture of the structure of liquid water which was formed at the end of the 1960s has withstood the test of time. As before, water is thought to be a continuous three-dimensional approximately tetrahedral hydrogen-bonded network. Attempts to revive mixture models stimulated by discovery of water polyamorphism cannot shake this paradigm: both components are hydrogen-bonded networks. The difference between uniform and mixture models lies in the structural heterogeneity. Achievements of x-ray spectroscopy are not a serious menace to the traditional model either: the lowest estimations of the number of hydrogen bonds per molecule far exceed the percolation threshold for three-dimensional networks. So these estimations do not contradict the conception of the infinite network. The last publications on XAS spectroscopy of water instil hope that the average number of hydrogen bonds in which molecules participate is slightly below four. It is not yet possible to present an intelligible picture of water molecule motion in the liquid. Development of the methods of ultrafast spectroscopy supported by computer simulations and theoretical studies will undoubtedly provide us with such a picture. An enormous number of publications is devoted to supercooled water. The key to understanding many of the properties of this remarkable substance lies in water at temperatures below the melting point.

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