#### **REVIEWS OF TOPICAL PROBLEMS**

### Structural models of water

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<u>Abstract.</u> Various conceptions on the structure of water are reviewed and different intermolecular interaction models underlying its description are discussed. To describe the structure of water, the method of integral equations for correlation functions borrowed from the theory of liquids is applied. Some numerical simulation results obtained with the Monte Carlo and molecular dynamics methods are also discussed in the context of water structural peculiarities.

### 1. Introduction

The understanding that liquids are far from being structureless substances came quite recently (i.e., in the 1930s) when it became clear that the continuous liquid-state model making no distinction between a gas and a liquid is inadequate for the description of many phenomena, including critical ones. X-ray diffraction studies of liquids, initiated at approximately the same time, revealed the presence in them of some order residing in the fact that the immediate vicinity of each molecule resembles the crystal-like packing, even if more loose and mobile than in crystals. Hence, the notion of short-range structural order in liquids. Such an interpretation holds equally well for gases (especially dense ones) that are also characterized by a certain short-range order. It should be recalled that crystals possess both short-range and long-range orders, meaning that crystallization is associated with the formation of long-range order. Moreover, amorphous states existing under the same thermodynamic condi-

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Received 22 June 2005 Uspekhi Fizicheskikh Nauk **176** (8) 833–845 (2006) Translated by Yu V Morozov; edited by A Radzig tions (density, temperature, etc.) as crystalline states exhibit only short-range order (as exemplified by an instantaneously frozen liquid) and are not crystals.

The structural approach to describing liquids provided a basis for the well-known dynamic (and at the same time structural) model of the liquid state developed by the eminent scientist Ya Frenkel for the analysis of kinetic properties of liquids and crystallization kinetics [1]. According to Frenkel, the motion of each molecule includes a vibrational constituent in a quasicrystal-like cell and translational jumps of this cell (a group of atoms in the immediate vicinity of the molecule) as a whole with the corresponding mean free path. In other words, the liquid is regarded as having properties of both crystals and gases. The composition of the properties depends on the thermodynamic state, i.e., temperature, pressure, and other macroparameters. Frenkel's theory appears to be the first consistent theory of liquids that still remains valid, as will be shown below in the discussion of later structural models of water. Indeed, it will be demonstrated that all the existing structural models, without a single exception, are to a certain extent compositional models, their composition elements being different types of elementary structures, or different types of the degrees of freedom inherent in various aggregate states, and so forth.

Fisher [2] and Eisenberg and Kauzmann [3] distinguish three types of structure in liquids, depending on their characteristic times:

(1) the instantaneous or I-structure of the close vicinity, essential for rapid processes with a characteristic time of  $\sim 10^{-15}$  s. Such a structure usually occurs in computer simulation experiments: for example, the time step in numerical integration of equations of motion in the molecular dynamics method is  $\Delta \tau \leq 10^{-15}$  s;

(2) the vibrationally averaged or V-structure with a characteristic time of  $\sim 10^{-12} - 10^{-13}$  s. It is the concept of V-structure that underlies the construction of various phenomenological models of the water structure, and

(3) the diffusion-averaged or D-structure described by molecular distribution functions that provide the main theoretical tool in the modern theory of liquids [4-6].

The conception of F-structure or inherent hidden structure, framed by Stillinger and Weber [7], appears especially useful and clear. The structure corresponds to the potential energy minimum for the nearest instantaneous I-structure.

The ideas of structural order in liquids are a component of the modern statistical theory of liquids based on the infinite system of linked integro-differential equations for the N-particle Bogoliubov-Born-Green-Kirkwood-Yvone (BBGKY) distribution functions [2]. These functions describe the probability of finding any group composed of N particles in one spatial configuration or another. It should be noted that such a definition of the structure also holds for gases and is consistent with the modern view of the crystal structure. Moreover, this definition is equally adequate for the description of metastable and even amorphous states [5]. In the latter case, however, the problem of applicability of the BBGKY system to the search for distribution functions remains to be clarified. The fundamental character of the description of a structure by a set of correlation functions is attributable to the fact that they serve to unambiguously express all thermodynamic and other macroparameters of a given system and thus establish the fundamental structureproperties relationship.

The system of BBGKY equations corresponds to the Gibbs distribution in the thermodynamic limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $\rho = N/V = \text{const.}$  However, the direct and rigorous application of the BBGKY equations is impossible because of the need for breaking off the infinite system of equations leading to a variety of sometimes unclear approximations. As shown in Refs [4, 6, 8], this system may be strictly transformed under conditions of pair additivity of interaction forces to a coupled, closed system of simply integral equations for one-and two-particle distribution functions: in the additive approximation, these functions alone are sufficient to define all macroparameters.

This system of two equations provides the principal tool for investigations into the structure and properties of liquids. It is worthwhile to emphasize that there is no need to solve the equations for the higher distribution functions in the additive approximation because they can be strictly expressed via the first two functions [6]. In the absence of an external field, the system of equations turns into the well-known Ornstein-Zernike (OZ) equation for the pair correlation function and the chemical potential definition [6]. However, certain problems of the theory and structure of liquids cannot be unambiguously resolved even in such a simple case. First and foremost, this concerns the problem of closure of the Ornstein-Zernike equation or the problem of deducing the form of bridge-functionals entering the equations [4-6]. Another important problem is related to the suitability of equations formally derived in the thermodynamic limit for the description of metastable and even amorphous states. This problem arises from the fact that no metastable states exist in the thermodynamic limit and the amorphous states are generally nonequilibrium ones even though their relaxation times may be regarded as infinite.

Water qualifies as a 'nontrivial' liquid in which intermolecular interactions cannot be described by spherically symmetric functions but depend on the mutual orientation between the molecules; this accounts for the complicated orientational dependence of the distribution functions. More problems emerge in the description of hydrogen bonds between water molecules. It is these bonds that are responsible for the unique tetrahedral short-range order which determines both the unusual properties of water distinguishing it from other liquids and the equally unconventional properties of numerous aqueous crystal structures.

It is evident from the above that the description of water under ordinary and, as will be apparent from the following account, extraordinary conditions spans the entire range of problems awaiting theoretical solution. Many difficulties encountered in simple liquid models, such as hard sphere fluid or Lennard-Jones systems, described by the spherically symmetric interaction potentials have been overcome to a degree [2-6]. At the same time, the statistical theory of liquids proves insufficient for the description of water in many situations. For this reason, the analysis of water's structure and its relationship with the unusual properties of this liquid is often performed by means of numerical simulation using the molecular dynamics (MD) and Monte Carlo (MC) methods. In the meantime, new concrete phenomenological models of the structure of water continue to be developed and validated in an attempt to explain selected properties of the liquid.

The present review demonstrates and describes potential applications of the statistical theory of liquids based on the OZ equations. In addition, results of numerical experiments and phenomenological models are concerned with reference to the analysis and derivation of correlation functions.

### 2. Anomalous properties and the phase diagram of water

(1) It is common knowledge that maximum water density  $\rho$  under ambient pressure is attainable at a temperature of 4 °C and almost everyone guesses that the density of ice is less than that of the water on whose surface the ice floats. Heating usual ice to the melting point increases its density  $\rho$  by 8–9% [9]. This certainly contradicts the intuitive idea of the nature of solid state. New circumstances arise from the fact that cooling water below the melting point of ice, thus forcing the system into the metastable state up to the temperature  $T \sim 37-38$  °C, results in a decrease in metastable water density as well [9, 10].

(2) Many are aware that the isothermal compressibility of water exhibits anomalous behavior with respect to that of other liquids, dropping to a minimum at 46 °C. The compressibility of ordinary liquids always decreases with a fall in temperature, whereas the compressibility of water cooled down to below 46 °C increases and continues to grow in the metastable region.

(3) The behavior of aqueous solutions, for example, hydrocarbons, also looks surprising. Indeed, the dissolution of hydrocarbons has negative enthalpy. At the same time, the expected result should be positive because the interactions of hydrocarbons between themselves and with water are much weaker than between water molecules.

(4) The thermal expansion coefficient  $\alpha$  for ordinary liquids is always positive. The value of  $\alpha$  for water is significantly smaller than the expected one and decreases with decreasing temperature. The fall in  $\alpha$  is very rapid at temperatures below 4 °C, and at a sufficiently low temperature  $\alpha \leq 0$ .

It has recently been shown [11] that the unusual properties of water are especially well manifest after it is overcooled to below 0 °C. Indeed, a decrease in temperature causes such parameters as compressibility, heat capacity, and thermal expansion coefficient to tend extrapolatively to infinite values



**Figure 1.** T-P phase diagram of water: (a) C — critical point of a gas – liquid phase transition, and  $C^1$  — hypothetical critical point of a liquid – liquid phase transition in the metastable region. Line F — the line of a phase transition from the critical point  $C^1$ , dividing the low-density and the high-density phases. Line L and H denote the metastable limit of HDA and LDA phases. Line  $T_n$  is the hypothetical nucleation line (limit of the measurement feasibility). At P = 1 atm and  $T_n = -38$  °C,  $T_x$  is the line of crystallization from the amorphous state [10]; (b) instantaneous molecular-dynamic picture of coexisting LDL and HDL phases.

at the temperature  $T \approx -45$  °C. In fact, measurements are feasible only at temperatures as low as T = -38 °C. Hence the hypothesis of a second critical point in water at a negative temperature that implies the existence of a metastable region of phase transitions (in all probability, of the first order), in analogy with the gas-liquid phase transitions in the stable region of water existence with the parameters  $T_c = 647$  K,  $\rho_c = 0.328$  g cm<sup>-3</sup>, and  $P_c = 22$  MPa. Indeed, molecular dynamic experiments [12] have shown the possibility of a liquid-liquid phase transition between low-density metastable water (a low-density liquid, LDL) and high-density metastable water (a high-density liquid, HDL) with the critical parameters  $T_c = 220$  K,  $\rho_c = 1$  g cm<sup>-3</sup>, and  $P_c = 100$  MPa. A similar possibility was demonstrated by means of relevant thermodynamic approximations [13, 14].

One more unusual property is the existence of two forms of amorphous water (amorphous ice). Low-density amorphous ice (LDA) was described rather long ago [15]. Recent studies [16, 17] have revealed the existence of another form of amorphous ice, viz., high-density amorphous ice (HDA). A



Figure 2. The equation of water state V = V(P, T). Solid lines correspond to ice IV and ice XIV melting lines. Both liquid phases continuously pass into the corresponding amorphous phases.

partly real and partly hypothetical phase diagram of water is depicted in Fig. 1 [10]. Here, C is the real critical point of gas – liquid phase transition, and  $C^1$  is the hypothetical critical point of metastable liquid – metastable liquid phase transition. Figure 1 also shows a putative transition between two amorphous phases, which is reminiscent of the first-order phase transition LDA  $\rightleftharpoons$  HDA. It should be recalled that the existence of several amorphous phases is referred to in the literature as polyamorphism, in analogy with polymorphism, by which is meant the presence of a few crystal structures. By way of example, it is believed that water may exist in 30 crystalline forms, some of which are in all probability amorphous. Figure 2 presents a three-dimensional image of the equation of water state [9].

### 3. Phenomenological structural models of water

All anomalous properties of water can be accounted for by the peculiar structure of its molecule, and most importantly the electronic structure of the oxygen atom. Six electrons at the outer energy level behave as two unpaired electrons capable of making up a  $\sigma$ -bond with a hydrogen atom, and two unshared electron pairs give rise to two negatively charged centers. The sp<sup>3</sup>-hybridization of electron orbits is responsible for the tetrahedral character of saturated directed hydrogen bonds. It is the ability of water molecules to form no more than four tetrahedrally oriented hydrogen bonds that produces the unique intrinsic nature of the 'openwork', loosely packed structure of liquid water. Figure 3 depicts the linear configuration of two interacting water molecules in the gaseous phase. The equilibrium distance of an O-H hydrogen bond amounts to 1.78 Å, and its dissociation energy is about 5.5 kcal mol<sup>-1</sup>, i.e., over one order of magnitude smaller than the energy of covalent bonds and higher by the same amount than the dispersive interaction energy [18].

Bernal and Fowler [19] appear to have been the first to notice the tetrahedral character of the coordination of molecules in liquid water. These authors may be regarded as pioneers of systematic studies on the structural properties of water, who proposed the first structural model of this liquid. Many new theories and models of water structure have been



**Figure 3.** Linear configuration of a water dimer. Five angles  $\theta_1$ ,  $\theta_2$ ,  $\chi_1$ ,  $\chi_2$ ,  $\varphi$  define the relative orientation between two molecules. This configuration corresponds to the global potential energy minimum for the TIP4P model. Here, r = 2.75 Å,  $\theta_1 = 57^\circ$ ,  $\theta_2 = 135^\circ$ ,  $\varphi = 180^\circ$ ,  $\chi_1 = 90^\circ$ , and  $\chi_2 = 0^\circ$ .

suggested since then but almost all of them in some way or other take into account the composite sense of Bernal and Fowler's ideas. Therefore, we shall describe the original model by these authors at somewhat greater length. According to Bernal and Fowler, three main forms of molecular arrangement are inherent in liquid water. The trydimite icelike structure (water 1) prevails at low temperatures, the quartz-like structure (water 2) predominates at moderate temperatures, and the densest one (water 3) acquires importance at high temperatures. In accordance with the Bernal and Fowler model, structural equilibrium occurs in water:

### Water 1 $\rightleftharpoons$ Water 2 $\rightleftharpoons$ Water 3,

which shifts from one side or the other with a change in temperature. This model provides a qualitative explanation for water's maximum density at  $4^{\circ}$ C.

All structural models of water can be conventionally divided into two classes: one constituted by discrete models, and the other by continuous ones. The former class includes, among others, the familiar cluster model by Némethy and Scheraga [20] that is actually a two-structure model of five states. This model is based on the assumption that water molecules either aggregate into compact structures (clusters) with 1-4 hydrogen bonds per molecule or exist as monomers with no hydrogen bonds linking them. These two structures are mixed up in equilibrium in accordance with the free energy minimum. The model is underlain by the assumption of the cooperative formation and breaking of hydrogen bonds, which implies that the creation of one such bond (by virtue of local energy fluctuations) decreases the potential barrier for the formation of the next one and eventually leads to the cascade generation of a cluster. The reverse cooperative process proceeds in a similar way: the breaking of a single hydrogen bond leads to the destruction of the entire cluster. Cluster formation and destruction are permanent processes. The density maximum is due to two factors. On the one hand, melting leaves intact a certain number of hydrogen bonds in water that gradually dissociate with a further rise in temperature; simultaneously, the coordination number, i.e., local density, increases. On the other hand, a temperature growth triggers the usual expansion mechanism inherent in all liquids. The former mechanism predominates up to 4 °C, and the latter at higher temperatures. Such an interpretation of the density maximum is in some way or other accepted in all current models of water structure.

Also worthy of note is a somewhat exotic clathrate model by Pauling [21], the basic element of which is a dodecahedron formed by hydrogen-bonded molecules and filled with free water. Individual dodecahedrons are in turn linked to one another into a sort of a spatial mesh. This model closely resembles the partial filling model proposed by Samoilov [22]. It is based on the idea that water molecules form a distorted, eroded structure of ice I, the cavities of which are partly filled with monomers; during molecular motion the lattice undergoes permanent rearrangement. The density maximum in water is attributed to the fact that a rise in temperature starting from 0°C leads, on the one hand, to stronger molecular vibrations about equilibrium positions in the structure and the corresponding growth of the effective molecular radius; on the other hand, the translational motion is also enhanced with increasing temperature and progressively more molecules enter the voids. The former process results in an increased volume, and the latter one in a higher density.

Very similar to this model is the so-called continuous model of bent bonds postulated by Pople [23], in which a hydrogen bond is described only by electrostatic interactions between protons of one molecule and the unshared electron pair of the other. The entire system is actually tied up by a flexible and extendable net of electrostatic interactions. Such net models are still successfully used in various physicochemical applications [23, 24] for the reason that many properties of liquids, such as diffusion, compressibility, etc. can be adequately, qualitatively interpreted as properties of the model net.

The modern theory of liquids is in principle capable of solving structural problems in the stable water region, i.e., at temperatures above 0°C. However, problems facing the theory in the region of metastable and especially amorphous states of water are still difficult to overcome. It is to such a case that the main instrument for the solution of structural and related problems in these states is computer simulation. And it is also for this reason that the structure of water continues to be described based on newly developed phenomenological structural models taking into consideration permanently emerging experimental data about the unusual novel properties of water. Surprisingly, the construction of these models remains compositional in character, as before, despite a variety of new structural elements proposed for them. By way of example, an original structural model in the form of a composition of low- and high-density amorphous ice has been developed based on the results of a thorough analysis of distribution functions found in scattering experiments in aqueous amorphous states [26]; this model takes into account that a structure in the amorphous state may be interpreted as the frozen structure of liquid water. This construction is supposed to uniformly describe the structure of water both in the stable region for  $T \ge 0$  °C and in the overcooled and amorphous states below 0°C. However, detailed calculations of correlation functions for amorphous ice by the Monte Carlo method [27-29] indicated that a simple composition of correlation functions of amorphous ice is too simple to be applied to the description of the properties of usual water.

## 4. Model description of intermolecular interactions in water

The degree of adequacy inherent in the description of intermolecular interaction forces in water determines the adequacy of all structural and physical corollaries of theoretical and computer applications. The discrepancies arising from their comparison with the results obtained in real experiments and the interpretations thereof may reflect the approximate character of both the model description of interactions and theoretical and computer approaches to their investigation, emphasizing the paramount importance of reliable simulation of intermolecular interactions. The general procedure in such cases consists in approximating the results of quantum-mechanical computations of potential energy surfaces by a set of functions compatible with the apparatus of the analytical method being used, e.g., with the relevant equations for correlation functions. For example, the three-point Matsuoka - Clementi - Yoshimine (MCY) model [30] is based on the *ab initio* calculations of a water dimer and represented in the form of an additional scheme of pair interactions:

$$U_{\alpha\beta}(r) = \frac{A_{\alpha\beta}}{r^{12}} + \frac{C_{\alpha\beta}}{r^6} + \frac{Z_{\alpha}Z_{\beta}e^2}{r} , \qquad (1)$$

where coefficients A and C describe the attraction and repulsion in dispersion forces, while  $Z_{\alpha}$  and  $Z_{\beta}$  are the charges on the interacting centers.

The disregard of many-particle interactions in such calculations leads to equilibrium distances r(OO) = 2.98 Å, whereas in the real condensed phase the equilibrium distance r(OO) = 2.76 Å. Other known models having the form of Eqn (1) are the simple point charge model (three-point SPC model) [31] and its SPC/E modification [32] taking into consideration the polarizability of water molecules. One more three-point model is referred to as the transferable intermolecular potential with three points (TIP3P) [33]. The four-center TIP4P model [34] has been derived from TIP3P by introducing a new virtual center on the bisectrix of the HOH angle in the direction of the hydrogen atoms with the displacement of the oxygen negative charge toward this center. This model is reported to fairly well reproduce many experimental characteristics of stable water. Another model is the five-point ST2 model [35] with tetrahedrally arranged charges and the neutral center of the tetrahedron involved in van der Waals intermolecular interactions. Finally, the central force (CF) model [36] is distinguished from all the rest in that it makes no distinction between the descriptions of intra- and intermolecular interactions. Both oxygen and hydrogen atoms are considered here to be independent material points interacting with one another in the same way as with atoms of other surrounding molecules. As a matter of fact, water is regarded as a simple mixture of oxygen and hydrogen atoms with such interaction potentials that ensure the formation of stable water molecules with adequate structure and properties.

The above-listed variety of model interaction potentials for water covers almost the entire spectrum of characteristic features inherent in many other phenomenological models. The cited literature sources report specific details and parameters of point models describing intermolecular interactions in water; therefore, they are not discussed here. Nor do we consider here polarization models constructed so as to correctly reproduce not only dipole moments but also higherorder moments. This purpose is actually achieved by either redefining and specifying parameter values in the aforementioned point models or introducing new virtual interaction centers. However, these models are very difficult to apply in the method of integral equations of the theory of liquids, discussed in the next section.

# 5. Method of integral equations for correlation functions, as applied to water

The OZ equation for the pair correlation functions h(r) in a spatially homogeneous system in which intermolecular interactions are described by spherically symmetric interaction potentials has the form [4-6]

$$\gamma(r_{12}) = h(r_{12}) - C(r_{12}) = \rho \int C(r_{13}) h(r_{23}) \,\mathrm{d}r_3 \,. \tag{2}$$

This seemingly simple integral equation, on the one hand, conceals a few problems that are very difficult to resolve. On the other hand, it provides a basis for many methodical approaches employed in the theory of both simple and complex liquids. In equation (2), the notation is employed:

$$h(r) = g(r) - 1 = \exp\left[-\frac{\Phi(r)}{kT} + \omega(r)\right] - 1.$$
 (3)

Here, g(r) is the usual radial correlation function defined in the following way:

$$g_2(r_1, r_2) = V^2 \iint \frac{1}{Q_N} \exp\left[-\frac{U_N(r_1, r_2, \dots, r_N)}{kT}\right] dr_3 \dots dr_N,$$
(4)

where  $Q_N$  is the configuration integral, and  $U_N$  is the potential energy of the system. In a simple case,  $g_2(r_1, r_2) =$  $g(|r_2 - r_1|) = g(r), \ \omega(r) = \omega(r; T, \rho)$  is the thermal potential depending on the thermodynamic state of the system, and  $\rho = N/V$  is the density. Moreover,  $\omega(r) = \gamma(r) + B(r)$ . The problem reduces to determining the relationship C = C(h(r))in Eqn (2) or (which is virtually the same) to calculating the bridge-functional B(r) that is known to consist of an infinite series of irreducible diagrams [37]. This problem has not been completely solved to date even though good approximations to B(r) (or closures of the OZ equation) have been suggested. The radial correlation function g(r) serves to express all macroscopic parameters in the additive representation of the total potential energy of the system [4-6, 37]. Moreover, Eqn (2) is exact by itself and absolutely corresponds to the virial expansions of the function h(r). All these data are well known and presented here for the purpose of further applications.

### 5.1 Structure and properties of water in the central force model

Certain drawbacks of the central force model [36, 38] proposed by Lemberg and Stellinger are compensated for by its obvious advantages lying in the realization of equations. To begin with, water is treated as being a simple mixture of hydrogen and oxygen atoms in a ratio of 2:1, with no need to specially distinguish the orientational dependence of correlation functions and hydrogen bonds. Figure 4 shows CF potentials of water (dashed lines) and their small CF1 modification (solid lines) [39]. An insignificant difference between the potentials, almost unapparent at first sight, leads to a much greater difference in the resulting pressure; it exposes the strong parameter dependence of the properties of the model. Charges on hydrogen atoms are equal for either model,  $q_{\rm H} = 0.3283e$ , where *e* is the proton charge. The charge on the oxygen atoms is  $q_{\rm O} = -2q_{\rm H}$ . The noninteger values of the charges are not artifacts but reflect screening associated with polarization effects produced by the con-



**Figure 4.** Potential energy  $U_{\alpha\beta}(r)$  in kT units at T = 25 °C for the CF (dashed lines) and CF1 (solid lines) models of water.

tributions of triple and higher-order interactions to the effective pair potential [39]. The OZ equation in the Fourier variables assumes the algebraic form

$$\tilde{\gamma}(k) = \frac{\rho \tilde{C}^2(k)}{1 - \rho \tilde{C}(k)} \tag{5}$$

with the closure  $C(r) = F(\gamma(r))$ .

For an *n*-component system, one has

$$h_{\alpha\beta}(r_{12}) = C_{\alpha\beta}(r_{12}) + \sum_{s=1}^{n} \rho_s \int_V C_{\alpha s}(r_{13}) h(r_{23}) \,\mathrm{d}\mathbf{r}_3 \tag{6}$$

or, in the Fourier variables, it comes out as

$$\hat{h} = \hat{C} + \hat{C}\hat{\rho}\hat{h}, \qquad (7)$$

where  $\hat{h}$  and  $\hat{C}$  are the matrices of the corresponding functions, and  $\hat{\rho}$  is the diagonal concentration matrix. By analogy with (5), one finds

$$\hat{\gamma} = \hat{C}(I - \hat{\rho}\hat{C})^{-1} - \hat{C}.$$
 (8)

Here, *I* is the unit matrix, and  $\hat{\gamma} = \hat{h} - \hat{C}$ . Equation (8) is an exact solution to the OZ equation (1). A few changes and assumptions are in order for the further discussion. Because the potential functions presented in Fig. 4 contain the divergent Coulomb terms, Eqn (8) needs to be renormalized accordingly. One way to its renormalization leading to the Debye-Hückel screening consists in the separation of the interaction potential into the short-range part (s) and the long-range component (l):

$$U_{\alpha\beta} = U^{\rm s}_{\alpha\beta} + U^{\rm l}_{\alpha\beta} \,. \tag{9}$$

Then, we obtain

$$C = C^{\rm s} - \beta U^{\rm l}_{\alpha\beta} \,, \tag{10}$$

where  $\beta = 1/kT$  (do not confuse this with the subscript!), and

$$h = h^{s} + q \,. \tag{11}$$

Here, matrix q is the renormalized Coulomb potential

$$q_{\alpha\beta}(r) = -\frac{\beta q_{\alpha} q_{\beta}}{4\pi r} \exp\left(-\chi r\right), \qquad (12)$$

where  $\chi$  is the inverse Debye length [39].

The main idea behind another approach to the renormalization of Eqn (8) [40] is to assess the asymptotics of functions C and h bearing in mind charge screening and the choice of the corresponding convergent functions. By introducing the matrix

$$\hat{V} = I + \hat{\rho}\hat{q} \,, \tag{13}$$

equation (8) may be rewritten in a truncated form as

$$\rho\gamma^{s} = V\rho C^{s} (I - V\rho C^{s}) V - \rho C^{s}, \qquad (14)$$

$$\gamma^{\rm s} = h^{\rm s} - C^{\rm s} \tag{15}$$

with the reduced renormalized closure

$$C_{\alpha\beta}^{\rm s} = \exp\left(-\beta U_{\alpha\beta}^{\rm s} + \gamma_{\alpha\beta} + q_{\alpha\beta} + B_{\alpha\beta}\right) - 1 - \gamma_{\alpha\beta} - q_{\alpha\beta} \,. \tag{16}$$

As mentioned above, the central and still incompletely resolved problem in the theory of correlation functions for liquids consists in the search for the bridge-functional  $B = B(\gamma(r))$  [4-6, 37, 41]. It is supposed that the most adequate approximation for a system with interactions including the long-range Coulomb components is the hypernetted chain (HNC) approximation B = 0. The actual applicability of one closure or another is determined by the so-called thermodynamic consistency criterion or the comparison with the results of numerical simulation [42]; this markedly restricts the possibilities of the theory. Effective approximate closures are known for simple systems with spherically symmetric interaction potentials, such as Percus-Yevick, Verlet, and Martynov-Sarkisov closures [43-45], whereas no theoretically substantiated closures exist in the case of complex systems with Coulomb components of the interaction potential. In the above-cited approach [39], the modified bridge-functional B was employed, which has been found in numerical experiments for a system of hard spheres based upon a consideration of the universality and permissible transmissibility of these functions. The correlation functions of the model in question and those obtained in experiment [46] are presented in Fig. 5. It should be recalled that Katzoff [47] was the first to construct correlation functions for water based on the results of X-ray scattering experiments in which the principal finding was the first maximum at  $r \approx 2.9$  Å, and the second one at  $r \approx 4.5$  Å. Figure 6 compares experimental [48] and theoretical

$$S_{\rm T}(k) = D_{\rm OO}(k) S_{\rm OO}(k) + D_{\rm OH}(k) S_{\rm OH}(k) + D_{\rm HH}(k) S_{\rm HH}(k)$$
(17)

structural functions, where  $D_{\alpha\beta}(k)$  are the weight factors, and  $S_{\alpha\beta}(k)$  are the particle structural functions:

$$S_{\alpha\beta}(k) = 4\pi\rho \int_0^V dr \, r^2 h(r) \, \frac{\sin kr}{kr} \,.$$
(18)

## 5.2 Atom – atom (center – center) approach to the description of water structure

The description of complex molecules with the help of the atom-atom representation has much in common with the



**Figure 5.** Radial correlation functions for the CF1 model (solid lines) at temperature T = 25 °C and density  $\rho = 1.0$  g cm<sup>-3</sup> and experimental correlation functions (dashed lines) [46]. Dotted lines show correlation functions for the SPC/E model. The last two functions are given at density  $\rho = 0.997$  g cm<sup>-3</sup>.



**Figure 6.** Structural function  $S_{\rm T}^{\rm x}(k)$  for the CF1 model (solid line) at  $T = 25 \,^{\circ}{\rm C}$  and density  $\rho = 1.0 \,{\rm g \ cm^{-3}}$ . Experimental structural function (dashed line) [48] was obtained at  $\rho = 0.997 \,{\rm g \ cm^{-3}}$ .

method of central forces in terms of form but is totally different from it in essence. With this approach, the system of interest is no longer regarded as a two-component mixture of spherically symmetric oxygen and hydrogen atoms; rather, it is treated as a one-component system in which intermolecular interaction is the sum of interactions between individual atoms. In this method, unlike the central force approach, the geometry of water molecules is given from the very beginning, while atom-atom interactions and correlation functions have only the intermolecular sense. The site-site Ornstein-Zernike (SSOZ) equations and the reference interaction site model (RISM) were first considered by Chandler and Andersen [49]. In this description, the geometry of water molecules is introduced by the matrix of intramolecular correlation functions [50]

$$\omega_{\alpha\beta}(r) = \frac{\delta(r - l_{\alpha\beta})}{4\pi l_{\alpha\beta}^2} \tag{19}$$

or, in the form of the Fourier variables, as

$$\omega_{\alpha\beta}(k) = \frac{\sin k l_{\alpha\beta}}{k l_{\alpha\beta}} , \qquad (20)$$

where  $l_{\alpha\beta}$  is the distance between atoms  $\alpha$  and  $\beta$  inside the molecule. Thus, the method distinguishes between intra- and intermolecular correlations that are combined in the central force model.

Now, the SSOZ-equations in the Fourier variables look like [40, 49-51]

$$h(k) = \omega(k) C(k) \omega(k) + \omega(k) C(k) \rho h(k).$$
(21)

For convenience, we have omitted hats over the matrices. It is important to emphasize that Eqn (21), unlike Eqn (7), is not strict on its own accord, being at variance with exact virial expansions. It can be rewritten in a form analogous to formula (14):

$$\rho\gamma = \omega\rho C (I - \omega\rho C)^{-1} \omega - \rho C. \qquad (22)$$

When the interaction potential contains Coulomb components, the renormalized equation takes the form of formula (14) with the sole difference that now

$$V = \omega + \rho q \,. \tag{23}$$

Evidently, for structureless particles, one has  $\omega \rightarrow 1$ .

The exact form of the atom-atom approach is the Chandler-Silbey-Ladanyi (CSL) equations [52] in which the pair (total) correlation function h(r) is represented as the sum of four terms:

$$h_{\alpha\beta}(k) = h^{\rm o}_{\alpha\beta}(k) + h^{\rm l}_{\alpha\beta}(k) + h^{\rm r}_{\alpha\beta}(k) + h^{\rm b}_{\alpha\beta}(k) , \qquad (24)$$

where each term corresponds to different subclasses of diagrams in the expansion of function h(r). The matrix of the direct atom – atom correlation functions  $C^i$  (i = 0, 1, r, b) is represented in a similar way.

The CSL equations may be written down in the matrix form [53] resembling SSOZ equations:

$$\hat{H}(k) = \hat{C}(k) + \left[\hat{C}(k) + \hat{S}(k)\right]\hat{\rho}\left[\hat{H}(k) + \hat{S}(k)\right].$$
(25)

Here, the following notation was used:

$$\hat{\rho} = \begin{pmatrix} \rho & \rho \\ \rho & 0 \end{pmatrix},\tag{26}$$

$$\hat{H}(k) = \begin{pmatrix} \hat{h}^{\circ}(k) & \hat{h}^{\mathrm{r}}(k) \\ \hat{h}^{1}(k) & \hat{h}^{\mathrm{b}}(k) \end{pmatrix}, \qquad (27)$$

$$\hat{C}(k) = \begin{pmatrix} \hat{C}^{\mathrm{o}}(k) & \hat{C}^{\mathrm{r}}(k) \\ \hat{C}^{\mathrm{l}}(k) & \hat{C}^{\mathrm{b}}(k) \end{pmatrix},$$
(28)

$$\hat{S}(k) = \begin{pmatrix} 0 & 0\\ 0 & \rho^{-1}\omega(k) \end{pmatrix},$$
(29)



**Figure 7.** OO radial correlation function  $g_{OO}(r)$  for the SPC model of water at  $T = 25 \,^{\circ}$ C and  $\rho = 0.997 \,\text{g cm}^{-3}$ : I - CSL-HNC (hypernetted chain approximation, B = 0) (solid line);  $2 - \text{CSL-HNC}+B^0$  approximation (dashed line),  $B^0$  - bridge-functional found by computation of the first irreducible diagram in the expansion of B; 3 - SSOZ-HNC approximation (dotted line), and 4 - numerical experiment (Monte Carlo method) (full circles) [33].



Figure 8. OH radial correlation function  $g_{OH}(r)$  for the SPC model of water at T = 25 °C and  $\rho = 0.997 \text{ g cm}^{-3}$ . Notations are the same as in Fig. 7.

where the structural matrix  $\omega$  is determined by formula (19), as before. The closures of the CSL equations are defined in analogy with formula (16):

$$h^{i}_{\alpha\beta} = h^{i}_{\alpha\beta}(U_{\alpha\beta}, B^{i}_{\alpha\beta}), \qquad (30)$$

$$C^{i}_{\alpha\beta} = C^{i}_{\alpha\beta}(U_{\alpha\beta}, B^{i}_{\alpha\beta}), \qquad (31)$$

which have exact diagrammatic expansions but are not presented here. It should be noted that the approximate choice of the bridge-functionals actually reduces to naught the advantages of the exact system of CSL equations, making them approximate, too. Figures 7–9 present the OO, OH, and HH atom–atom correlation functions in the approximations considered above and obtained in numerical experiments. A significant scatter in the data is well apparent along with their marked deviation from the results of numerical experiments. Here, the correlation CSLfunctions do not seem to be more exact than in the SSOZ approximation.



**Figure 9.** HH radial correlation function  $g_{\rm HH}(r)$  for the SPC model of water at  $T = 25 \,^{\circ}\text{C}$  and  $\rho = 0.997 \text{ g cm}^{-3}$ . Notations are the same as in Fig. 7.

#### 5.3 Orientational structure in water

The total two-particle correlation function (TCF) for complex molecules depends on radial r and angular  $\Omega$  variables:

$$g_{ij} = g(r_{ij}, \Omega_{ij}). \tag{32}$$

For water,  $\Omega_{ij}$  is a set of the five angles defined in Fig. 3. Although the OZ equation can be applied directly to any complex molecular system but in reality such a procedure is very difficult, if not impossible, to perform, either for water or for other liquids. The difficulties stem first and foremost from the dimensions of the integrals being calculated and the necessity of their repeated numerical integration in iterational procedures. More important, however, is that the real analysis of a many-dimensional surface represented by a huge amount of numerical data all the same requires the use of its projections, the atom – atom approximation being one of the variants of this approach. In fact, the atom – atom correlation functions in this approximation are certain integrals of the total correlation function; this accounts for the partial loss of information (namely, a part of the orientational structure).

A possible solution consists in using the expansions of the binary correlation function in terms of the spherical harmonics and deriving the equations for coefficients of these expansions [54, 55]. The description of the orientational structure is feasible bearing in mind that TCF is exactly defined [56] in the low-density limit, i.e., for two isolated interacting molecules. It is also possible to consider the approximation consisting in the factorization of orientational distribution functions, and thereby in diminishing the dimension, with the choice of factorization methods based on the behavior in the low-density limit. It is supposed that TCF may be represented as the product

$$g(r, \Omega(1, 2)) = g(r) g\left(\frac{\Omega(1, 2)}{r}\right).$$
(33)

Here, the first multiplier is the radial correlation function for the two distinguished centers on water molecules (in the given case, oxygen atoms):

$$g(r) = \frac{1}{\bar{\Omega}^2} \int g(r, \Omega(1, 2)) \, \mathrm{d}\Omega(1, 2) \,. \tag{34}$$



**Figure 10.** Orientationally averaged interaction energy of water molecules: I — gaseous phase (solid line), liquid phase (dashed line),  $T = 25 \,^{\circ}$ C, P = 1 atm; 2 — orientationally averaged interaction (solid line) smoothed over the gaseous phase (initial approximation) as compared with the exact form (dashed line) obtained in a numerical experiment. Curves 2 are shifted by 2 kcal mol<sup>-1</sup> upward.

For nonlinear molecules, one has  $\overline{\Omega} = 8\pi^2$ . The second multiplier  $g(\Omega(1,2)/r)$  presents the orientational correlation function (OCF) and is the conventional probability that two water molecules reside in a certain angular configuration at a given distance between the centers. The normalization condition reduces to

$$\frac{1}{\bar{\Omega}^2} \int g\left(\frac{\Omega(1,2)}{r}\right) \mathrm{d}\Omega(1,2) = 1.$$
(35)

At low densities, the TCFs (similar to all other distribution functions) largely depend on the interaction potential [6, 57]:

$$g(r,\Omega(1,2)) = \exp\left[-\beta U(r,\Omega(1,2))\right],$$
(36)

where U is the intermolecular interaction energy. Then, for the radial correlation function (RCF), one obtains

$$g(r) = \frac{1}{\bar{\Omega}^2} \int \exp\left[-\beta U(r, \Omega(1, 2))\right] d\Omega(1, 2).$$
(37)

For the OCF, we have

$$g\left(\frac{\Omega(1,2)}{r}\right) = \bar{\Omega}^2 \frac{\exp\left[-\beta U\left(r,\Omega(1,2)\right)\right]}{\int \exp\left[-\beta U\left(r,\Omega(1,2)\right)\right] d\Omega(1,2)}, \quad (38)$$

where

$$\int d\Omega(1,2) = 2\pi \int \sin \theta_1 \, d\theta_1 \sin \theta_2 \, d\theta_2 \, d\varphi \, d\chi_1 \, d\chi_2 \,.$$
 (39)

The meaning of all these formulas is as follows. It is assumed, apart from the factorization hypothesis, that the qualitative behavior of the OCF in the liquid is the same as in the gaseous phase. In other words, it is largely determined by the interaction potential, which makes it possible to take into account the indirect part of the mean-force potential in the OCF by means of relevant corrections. Figure 10 shows orientationally averaged intermolecular potentials in the gaseous phase and in a liquid, calculated with the use of the



Figure 11. OO radial correlation function at T = 25 °C, P = 1 atm (solid line), and P = 10,000 atm (dashed line).

4-center TIP4P potential [34] having the form reminiscent of formula (1):

$$U = 4\varepsilon \left[ \left( \frac{\sigma}{r_{\rm OO}} \right)^{12} - \left( \frac{\sigma}{r_{\rm OO}} \right)^6 \right] + \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{r_{\alpha\beta}} , \qquad (40)$$

with parameters  $\sigma = 3.1536$  Å and the depth of the OO well equal to  $\varepsilon = 0.155$  kcal mol<sup>-1</sup>. The OO radial correlation function for this potential is depicted in Fig. 11. The marginal distribution functions determining the probability of the values of individual angles and a pair of angles are written down in the following way:

$$g\left(\frac{\Omega_i}{r}\right) = \frac{\int g\left(\Omega(1,2)/r\right) d\Omega(1,2)_{j'i}}{\int d\Omega_{j'i}},$$
(41)

$$g\left(\Omega_{i},\frac{\Omega_{j}}{r}\right) = \frac{\int g\left(\Omega(1,2)/r\right) d\Omega(1,2)_{k'i,j}}{\int d\Omega_{k'i,j}},\qquad(42)$$

where i, j = 1-5. Figures 12–14 present certain marginal correlation functions illustrating the orientational structure of water.



**Figure 12.** Distribution function  $g(\theta)$  in a gas (solid lines) and a liquid (dashed lines): I - r = 2.8 Å in gas,  $r \le 2.8$  Å in liquid; 2 - r = 3.2 Å in gas,  $2.8 \le r \le 3.4$  Å in liquid, and 3 - r = 4.5 Å in gas,  $3.4 \le r \le 5.6$  Å in liquid. Curves I and 2 are shifted by 2 and 1 units upward, respectively.







**Figure 14.** Distribution function  $g(\varphi)$  in a gas (solid lines) and a liquid (dashed lines). Notations are the same as in Fig. 12.

### 5.4 Structure of low- and high-density water

Reports on the possibility of using SSOZ and CSL integral equations for the investigation into the structure and properties of metastable water in the negative temperature region are still lacking in the literature. Apart from the problems related to the description of intermolecular interactions in water, the approximate character of equations themselves, and the search for their closures, there is an additional unresolved fundamental problem concerning the possibility of application of the equations in the atom - atom approximation to the description of water properties in the metastable region under the conditions of stable crystalline state. In the case of simple systems, the OZ equation is suitable for the description of both the metastable gas-liquid transition region [5, 58] and the metastable states in the crystal parameter region [5]. Such a possibility was demonstrated in numerous applications of the OZ equation to simple systems. A limited substantiation of the applicability of the OZ equation to describing metastable states was given in the review [5].

The real possibility of studying the structure and properties of metastable and especially amorphous states in water, aqueous, and other systems composed of complex molecules is provided by computer or real experiments and their combination. For example, it is possible to experimentally measure by the neutron diffraction method [59] the particle atom-atom structural factors (18) at a certain temperature



**Figure 15.** Atom – atom radial correlation functions of low-density (solid lines) and high-density (dots) water, obtained in computer experiments taking into consideration structural factors measured in metastable states.

(T = 268 K in the cited work) within a pressure range corresponding to the interval from low-density (LDL) to high-density (HDL) water. However, the particle (atom – atom) structural factors alone are insufficient to unambiguously define the atom – atom correlation functions (in ordinary situations, the retrieval of correlation functions from scattering data is unambiguous). Therefore, the atom – atom correlation functions are determined in computer simulation experiments from the experiments' ability to reproduce real particle structural factors. The SPC/E model of interactions is used initially. An additional condition is the aforementioned assumption about the structure of water as a linear combination of the constituent structures of low- and high-density water [26, 60, 61]:

$$\rho(T, P) = \alpha(T, P) \rho_{\rm H}(T) + \left[1 - \alpha(T, P)\right] \rho_{\rm L}(T), \qquad (43)$$

$$\rho g_{ij}(r) = \alpha(T, P) \rho_{\rm H}(T) g_{ij}^{\rm H}(r) + \left[1 - \alpha(T, P)\right] \rho_{\rm L}(T) g_{ij}^{\rm L}(r),$$

$$S_{ij}(k) = \alpha(T, P) S_{ij}^{\rm H}(k) + [1 - \alpha(T, P)] S_{ij}^{\rm L}(k), \qquad (45)$$

where  $\alpha(T, P)$  is the mole fraction of the high-density structure.

The self-consistency of experimental data, the results of numerical experiments, and conditions (43) – (45) allowed the atom – atom correlation functions in the metastable region to be reconstructed. They are shown in Fig. 15. Analysis of these functions and selected structural features in self-consistent calculations leads to the conclusion that the form of low-density water ( $\rho_L \approx 0.0295$  molecules Å<sup>-3</sup>) is that of an open hydrogen-bonded tetrahedral structure. Conversely, the

OOO angle in high-density water ( $\rho_{\rm H} \approx 0.0402$  molecules Å<sup>-3</sup>) is no longer tetrahedral and hydrogen bonds between the molecules localized in the first and second coordination spheres are broken. This important structural finding needs to be specially emphasized.

All structural changes result from a rise in pressure and largely occur between the first and the second coordination layers. The results of molecular-dynamic calculations near the water melting point were also considered in the framework of a two-structure model but in a somewhat different interpretation [62]. Water is a mixture of molecules that may exist in two states. Time variations in the local correlation functions constructed in the vicinity of the molecules under study were observed in the course of dynamic calculations [63] (the TIP4P model was additionally used for this purpose). It was revealed that each molecule alternately exists in two different states (periods): the structured one (when the local hydrogenbonded structure is well apparent), and the destructured one (in which the same structure is poorly manifested). These findings in a way bring us back to Frenkel's ideas of the character and mechanism of molecular diffusion in liquids at the structural level, with due regard for the modern concept of liquid structure. The degree of structuring is characterized by the local structure index (LSI) [63] that is the second moment of the radial correlation function. The LSI criterion plays the role of an order parameter and describes the degree of local structural fluctuations. The comparison with the experimental (neutron-weighted) correlation function [12] gives reason to assert that 'structured' molecules belong to the LDA type structure, whereas 'destructured' ones are HDA type molecules. Thus, water contains two types of clusters that permanently transform into each other and back. In other words, this concept of the structure of water does not



**Figure 16.** Radial correlation functions in a structured cluster (a) and the descructured region (b). Results were obtained from molecular-dynamic computations.



**Figure 17.** Instantaneous molecular-dynamic picture of the distribution of 'structured' (open circles) and 'destructured' (full circles) molecules: (a) T = -10 °C; (b) T = 72 °C at usual pressures; (c) T = -21 °C, and (d) T = 72 °C at high pressures.

practically differ from other composite models with the sole exception that its structural elements are now elements of amorphous structures. Figure 16 presents two types of local correlation functions, and Fig. 17 depicts the instantaneous dynamic distribution of structured and destructured molecules under various thermodynamic conditions.

### 6. Conclusion

This review considered concepts of the structure of water and its description with the use of correlation functions. These concepts have fundamental theoretical substantiation. Surprisingly, discussions of what is the liquid structure (in our case, water) are still underway, motivated by the desire to explain many physico-chemical phenomena in plainly obvious crystallographic terms. Such a crystallographic approach is doubtlessly justified in concrete applications.

A large volume of data on water properties and many related problems have remained beyond the scope of this paper. But even such specialized discussion of selected structural issues as this highlights the difficulties facing the theory of liquids and its limited potential for solving the said problems.

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