New intermolecular interaction potential for simulation of water and aqueous solutions in a wide range of state parameters

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A new semiempirical method for derivation of additive effective potentials is proposed. Local features of the shape of the potential energy surface of water dimers are approximated by Gaussian functions. Optimum geometric parameters of nonlinear bifurcated and inverted dimers, obtained from quantum-chemical calculations are constants of the new BMW potential. Free parameters of the potential were chosen based on the results of Monte Carlo simulation of the structural and thermodynamic functions of water in a wide range of state parameters ($268\ \mathrm{K} \le T \le 673\ \mathrm{K}$, $0.1\ \mathrm{MPa} \le p \le 400\ \mathrm{MPa}$). Calculations revealed rather high concentrations of the bifurcated and inverted dimers in the systems of H-bonds of water models. Clustering of non-tetrahedral fragments of the network of H-bonds is responsible for a microheterogeneous structure of water on the microscopic level.

Key words: water, aqueous solutions, intermolecular interactions, hydrogen bond, potential, structure of liquids, computer simulation of liquids.

The role of water and aqueous solutions in many areas of human activity cannot be overestimated. These systems possess anomalous properties compared to other liquids. Despite intensive research, many structural properties of water are still to be determined. At present, the properties of liquids on the microscopic level are simulated using the molecular dynamics (MD) and Monte Carlo (MC) methods. The techniques allow the molecular coordinates and the intermolecular interaction energy for the compound under study to be calculated at prescribed values of state parameters.

To calculate the potential energy of molecular configurations (molecular ensembles comprising a large number of molecules), it is necessary to specify the intermolecular interaction potential[1—6] or use quantum chemistry methods. Using the density functional theory (DFT) approach, one can now determine[7] molecular configurations of water in relatively small unit cells (Carr—Parrinello Molecular Dynamics, or CPMD method).

The potential is responsible for all properties of the model of a substance. Energy calculations are carried out either with inclusion of non-additive polarizability effects in explicit form or using additive effective potentials. The potential can be derived[8] empirically, nonempirically, and semiempirically. In the first case, the form of the potential functions and the parameters of the potential are chosen depending on how the experimental properties of the substance under study are reproduced. The nonempirical approach involves fitting of parameters of the functions used to approximate the shape of the potential energy surface (PES) of a molecular cluster (most often, a dimer). The PES is calculated using quantum chemistry methods, which often requires considerable computational resources. Both procedures for derivation of the potential have significant drawbacks. The semiempirical approach combines the advantages of the empirical and nonempirical methods.

Nevertheless, all the methods mentioned above do not allow the potential to be derived unambiguously, because this problem belongs to the class of incorrect problems.[9] Indeed, all experimentally observed properties of a compound are determined by multidimensional integrals of some functions containing the potential. The form of the potential functions is unknown. The accuracy of approximation is determined in the integrated norm. In this case, the problem of deriving the potential has an infinite number of solutions. A consequence of incorrectness of the problem is that a variety of models with potentials with strongly different parameters quite correctly reproduce a broad range of experimental properties of a certain liquid. Indeed, hundreds of potentials for water have been

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 707—715, April, 2004.

proposed but the properties of water cannot be comprehensively described as yet. The goal of this work is to put forward a new method of deriving the potentials suitable for reproduction of experimental data.

Assessment of convergence of a computational procedure based on the integrated norm can introduce large errors when approximating the PES in local domains of the six-dimensional configuration space. What is more, the shape of the water dimer PES significantly changes in the presence of other molecules, which can lead to stabilization of certain configurations and to destabilization of other configurations of an isolated dimer. Local features of the shape of the dimer PES manifest themselves in different manner when reproducing various experimental properties of liquid. A characteristic feature of the PES of water dimer is a global minimum corresponding to the formation of a linear H-bond. Of course, such states of the dimer are characterized by a large statistical weight in the statistical ensemble and make the major contribution to the calculated characteristics of the liquid. However, additional local minima characterized by less pronounced effect on the macroscopic level can also be located on the PES. It is *a priori* unknown how particular features of the PES shape affect the structural properties of liquids.

In the recent decades, many phenomenological theories of the structure of water have been proposed.[10,11] Almost all of them put forward specific models for the mutual arrangement of and interaction between structural elements. Hot debates between supporters of continuum and multistructure theories do not die off. The results of computer simulation support the continuum models. In contrast to this, phenomenological theories based on the assumption of coexistence of several topologically different structures in liquids have not been confirmed as yet. Such topologically different structures can be distinguished among the configurations obtained in computer simulation but no unambiguous objective criteria for the determination of several characteristic structural elements are available so far.[12—14]

Multistructure theories are used[15] to explain the properties of the supercooled and crystalline states of water. Initially, the lower critical temperature corresponding to coexistence of two types of liquid water, namely, low-density amorphous (LDA) and high-density amorphous (HDA) water was hypothesized. Then, the existence of the LDA and HDA modifications of water was confirmed experimentally.[16] Depending on the preparation procedure, three amorphous states of water are formed at low temperatures and high pressures.[16,17] These are the LDA, HDA, and hyper-quenched glassy water (HGW). A new amorphous phase of water, namely, very high density amorphous (VHDA) water, was reported.[18] Heating of the HGW and LDA modifications of water to 148 K respectively results[16] in metastable viscous water-A and water-B differing in physicochemical properties. Thus, there is a wide variety of the crystalline, amorphous, and liquid modifications of water. Unfortunately, no potential suitable for reproduction of several experimentally observed phases of water by computational methods has been proposed to date.

Some recent quantum-chemical studies[7,19] of water dimers revealed previously unknown local minima on the PES. It is of no importance whether they exist on the PES of an isolated dimer or are due to cooperative interactions in the molecular ensemble. We can assume that the states corresponding to such local minima serve as a basis for clearly distinguishable structures. This supports multistructure phenomenological theories of water and aqueous solutions.

Usually, the available potentials include contributions of the universal van der Waals and electrostatic components, the latter being calculated using the rough point charge approximation. As a result, the PES is described by a smooth function with a deep global minimum. It is not surprising that such potentials give a continuum picture of the structure of liquid water. But it is still hard to carry out a computer simulation using a multistructure model for water that is consistent with both the experimental data and the results of quantum-chemical calculations. Clearly, solving this problem requires a new type of potentials to be derived in order to describe a complex shape of the PES with several local minima that are comparable in depth with the global minimum.

If liquid water does contain a high concentration of associates with essentially nonlinear H-bonds, this can lead to significant changes in our view of the properties and structure of water on the microscopic level. The existence of non-tetrahedral fragments in the tetrahedral network of H-bonds is also of considerable importance from methodological standpoint. To which extent are our concepts of the structure of liquid water correct? Do the experimental data provide unambiguous information on the tetrahedral coordination of the water molecules or not?

In this work we report on a new method for derivation of semiempirical effective potentials. Taking a computer simulation of liquid water in a wide range of state parameters as an example, we demonstrate the applicability and advantages of the new class of potentials, analyze the experimental functions obtained by neutron diffraction, and give a structural interpretation of the results obtained.

Computer Simulation Procedure

Computer simulation of water was carried out by the Monte Carlo method using an original code and the standard Metropolis sampling algorithm in the NpT-ensemble[20] for a unit cell containing a total of 512 water molecules and a wide range of state parameters (268 K $\leq T \leq$ 673 K, 0.1 MPa $\leq p \leq$ 400 MPa). These states of water were chosen because they allow the results obtained to be compared with the data of neutron diffraction experiments.[21,22] Periodic boundary conditions and a spherical cut-off for the potential functions were applied. Water molecules were considered noninteracting if the distance between O atoms exceeded 10 Å. Markovian chains of length up to $500 \cdot 10^6$ configurations were generated. The portion of accepted configurations was about 0.5. Attempts to change the unit cell volume were undertaken after each 1024th successful atomic displacement and molecular rotation. The portion of accepted changes in the unit cell volume was 0.2 to 0.4. Calculations were carried out on a personal computer.

The total structure factors (F) for D_2O, H_2O, and equimolar mixture (HDO) were represented by weighted sums of the partial structure factors (S)[4]:

$$F_{D_2O}(q) = 0.092S_{OO}(q) + 0.422S_{OH}(q) + 0.486S_{HH}(q),$$

$$F_{H_2O}(q) = 11.92S_{OO}(q) - 30.74S_{OH}(q) + 19.82S_{HH}(q),$$

$$F_{HDO}(q) = 0.441S_{OO}(q) + 0.446S_{OH}(q) + 0.113S_{HH}(q). \quad (1)$$

The partial structure factors, $S_{ij}(q)$, were calculated using the Fourier transform of the atom—atom radial distribution functions (RDF) $g_{ij}(r)$:

$$S_{ij}(q) = \frac{12\pi d}{q}\int_0^{r_{\max}}[g_{ij}(r) - 1]\sin qr\,dr, \quad (2)$$

where d is the numerical density of atoms, r is the interatomic distance, and q is the wave vector.

The Potential

Quantum-chemical calculations[7,19] revealed at least two local minima corresponding to the bifurcated (or cyclic) and inverted water dimers (Fig. 1) in addition to the global energy minimum on the PES of water dimer. The bifurcated and inverted will be denoted BD and ID, respectively. The results of a CPMD study of water point to the existence of BD and ID in the system of H-bonds. Here, the intermolecular interaction energy was calculated using the density functional theory. A computer simulation of water with the cm4P-mTR model potential showed[23,24] that the BD and ID concentrations in the subcritical and supercritical regions of state parameters are rather high.

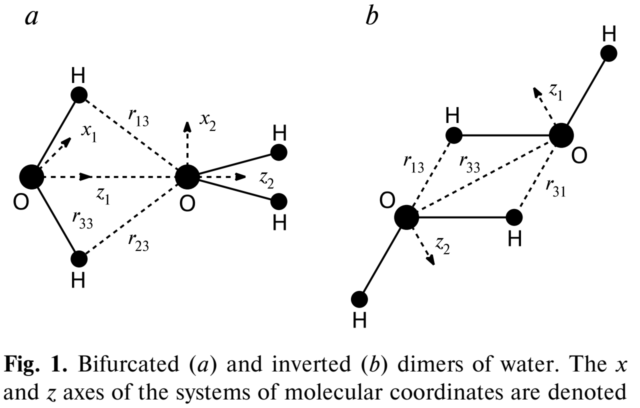

Fig. 1. Bifurcated (*a*) and inverted (*b*) dimers of water. The x and z axes of the systems of molecular coordinates are denoted by arrows. The intermolecular distances, r_{ij}, are denoted by dashed lines.

We developed a novel intermolecular interaction potential for water. The geometric parameters of an isolated water molecule were taken from the widely used SPC/E potential. The molecule has three interaction centers. The O—H bond length is 1 Å and the H—O—H bond angle is 109.47°. Due to the lack of information on the PES shape in the vicinity of the energy minima and on the height of the potential barriers, the SPC/E potential was (to a first approximation) augmented with square well potentials suitable for rough description of the PES shape in the vicinity of local energy minima. A comparison of the results of calculations and experimental data showed that our procedure for derivation of the potential is correct. Then, the PES shape in the six-dimensional space was described using Gaussian functions with slightly corrected energy parameters of the starting potential SPC/E. The new potential was called the BMW potential.

The Gaussian functions have minima at the parameter values corresponding to the optimum geometric parameters of BD and ID obtained from quantum-chemical calculations.[16] A basic difference of the BMW potential from other potentials is that it directly includes the optimum geometric parameters of water dimers (they are considered constants). Augmentation of the potential with additional functions is due to the necessity of correcting the description of the PES shape in local spatial domains.

A conventional potential derivation scheme has fundamental drawbacks. It is a too complicated task to describe the PES shape at long distances from the molecule by choosing a particular variant of the intramolecular point charge distribution. Both an increase in the number of charged interaction centers and inclusion of atomic quadrupole moments lead to significant complication of the potential functions. Earlier,[25] it was shown taking the carbon tetrachloride molecule as an example that the point charge distribution is inappropriate for correct description of the PES shape. The procedure for deriving the potential proposed here allows this problem to be solved with ease.

The form of the potential functions and the numerical values of the free parameters of the BMW model were chosen based on the results of reproduction of the experimental properties of water. The van der Waals interactions were described using the (12-6) potential by Lennard-Jones with the parameters σ = 3.18 Å and ε = 0.6277 kJ mol^{-1}. The point electrostatic charges were placed on the atoms of a water molecule (0.405 e on each H atom and −0.81 e on the O atom). The major contribution to the energy of the interaction between the molecules m and n was calculated as follows

$$\begin{aligned} U_{mn}^{(1)} &= 4\varepsilon[(\sigma/r_{33})^{12} - (\sigma/r_{33})^6] + \\ &+ 1387.8\sum_{i,j=1}^{3} q_i q_j / r_{ij} - \\ &- 0.2092\exp[-(r_{33} - 4.4)^2/0.15], \end{aligned} \quad (3)$$

where r_{ij} is the distance between the atoms i and j (i = 1, 2 for H atoms; i = 3 for the O atom). The exponential term (Gaussian function) in expression (3) was introduced to correct the molecular energies in the vicinity of the second peak of the g_{OO} RDF at r = 4.4 Å. The scalar product of the dipole moment vectors of the molecules in the BD was considered positive (see Fig. 1, *a*). We calculated the following function s:

$$s = \exp[-(r_{33} - 2.97)^2 - (z_i z_j - 1)^4/0.1 - (x_i x_j)^8/0.003],$$

where z_i, z_j are the unit vectors directed along the molecular dipole moment vectors; x_i and x_j are the unit vectors perpendicular to the corresponding dipole moment vectors.

According to quantum-chemical calculations of the BD, the optimum intermolecular distance is $r_{33} = 2.97$ Å and the shortest distance between O and H atoms is $r_{13} = 2.47$ Å. We assumed that a BD exists if the magnitude of the product of the functions s and $s1$ exceeded 0.01, where

$$s1 = \exp[-(r_{13} - 2.47)^4/0.01 - (r_{23} - 2.47)^4/0.01].$$

The BD energy was calculated as follows

$$U_{mn} = U_{mn}^{(1)} - 7.1128 \cdot s1 \cdot s.$$

The potential energy of inverted dimers was calculated with the corresponding optimum geometric parameters ($r_{33} = 2.8$ Å, $r_{13} = r_{31} = 2.28$ Å). Then, the functions $s2$ and $s3$ were determined:

$$s2 = \exp[-(r_{33} - 2.8)^2 - (z_i z_j + 1)^4/0.1],$$

$$s3 = \exp[-(r_{13} - 2.28)^4/0.01 - (r_{31} - 2.28)^4/0.01].$$

The ID was considered existing when the magnitude of the product of these functions exceeded 0.01. The ID energy was calculated by the relationship

$$U_{mn} = U_{mn}^{(1)} - 8.368 \cdot s2 \cdot s3.$$

The BMW potential functions have a more complex form compared to many other additive potentials because the BMW model includes a large number of fitting parameters. However, it is much simpler than some published potentials.[26] One would expect a significant increase in the CPU time when calculating the intermolecular interaction energy. However, this is not the case. The reason is that the nonlinear dimers (BD and ID) exist in local domains of the six-dimensional configuration space. The energies of most molecular configurations are calculated conventionally and include only the $U^{(1)}$ contribution (see Eqn. (2)). The Gaussian functions rapidly tend to zero as their arguments deviate from the optimum values.

The BMW potential thus derived is a semiempirical, additive effective potential. The free parameters of the BMW model are divided into two groups comprising constants chosen based on the results of quantum-chemical calculations of the dimer geometries and those obtained from comparing the experimental and calculated properties of water.

Results and Discussion

A single study is insufficient to calculate a large number of the properties of a liquid. Comprehensive treatment of a model for water can usually be carried out only by several independent research groups. First, we compared the calculated and experimental atom—atom RDF, structure factors, and thermodynamic functions. These are the most important characteristics, which provide valuable information on the properties of water on both microscopic and macroscopic levels.

The results of MC simulation of water show that optimum parameters of the potential can be determined with ease under external conditions similar to normal conditions. Earlier, the parameters of many widely used potentials were chosen using the NDIS-86 RDF set[27] determined under normal conditions. Since then, the experimental data were repeatedly refined and reviewed.[16,17] As a result, calculations using the potentials parametrized based on the earlier data give the RDF which are significantly different from the RDF included in the NDIS-97 and NDIS-2000 RDF sets. The BMW potential *a priori* includes an excess number of fitting parameters, which provides some flexibility ("degree of freedom"). According to calculations, considerable extension of the range of state parameters leads to much poorer reproduction of experimental data. The free parameters of the BMW potential were chosen in such a way that the differences between the calculated and experimental RDF be small in a wide range of the state parameters of water. We also implied rather high concentrations of BD and ID in the network of H-bonds.

The calculated water densities and the BD and ID concentrations in the network of H-bonds are listed in Table 1 (hereafter, commonly accepted notations[22] of the state parameters of water are used). For these points in the phase diagram of water, neutron diffraction studies have been carried out. The data are presented in the form of numerical density, which is independent of the isotope composition. The error in the density calculations is minimum at $T \geq 573$ K and does not exceed 4.2% throughout the entire range of state parameters.

In most cases the number of dimers that form nonlinear bonds is rather large and cannot be ignored in describing the topology of the network of H-bonds of water. Each molecule can be simultaneously involved in the formation of several H-bonds of any kind. Because of this, the number of molecules in the non-tetrahedral fragments can be much larger than the number of dimers. For instance, an isolated dimer comprises two molecules, while a BD—BD cluster comprises three water molecules that form two dimers. The number of the water states studied in this work is too small to plot a surface characterizing the dependence of the BD and ID concentrations on the pressure and temperature. However, we can say that the dimer concentrations increase with an increase in these parameters.

Table 2 lists the results of the MC simulation and MD calculations of thermodynamic properties of water performed using a number of models with polarizable potentials and several effective additive models. Direct inclusion of molecular polarizabilities causes no increase in the accuracy of reproduction of experimental data but re-

Table 1. Density of water and concentration of non-tetrahedral dimers calculated using the BMW model at different state parameters

State**	T/K	p /MPa	$d^* \cdot 10^2$/molecules Å^{-3}		Δd (%)	Number of dimers per 100 water molecules	
			Experiment	Model calculations		BD	ID
268a	268	27	3.38	3.47	2.6	4.26	5.74
268b	268	210	3.62	3.72	2.6	6.92	9.16
268c	268	400	3.81	3.91	2.6	9.33	12.71
298a	298	0.1	3.34	3.41	2.3	4.52	6.46
298b	298	210	3.57	3.69	3.4	8.04	11.78
423a	423	10	3.08	3.17	3.0	6.42	9.65
423b	423	190	3.34	3.42	2.5	7.68	12.12
573a	573	10	2.40	2.30	−4.2	1.08	1.43
573c	573	50	2.60	2.64	1.5	6.37	11.1
573d	573	110	2.78	2.76	−0.7	6.81	12.2
573e	573	197	2.96	2.96	0.0	7.61	13.4
573f	573	280	3.08	3.08	0.0	8.05	14.3
673a	673	50	1.94	1.93	−0.5	5.05	10.4
673b	673	80	2.21	2.19	−0.9	5.52	11.3
673c	673	130	2.45	2.44	−0.4	6.08	12.3
673d	673	340	2.92	2.91	−0.3	7.63	14.8

* Numerical density.

** See Ref. 22.

quires more computational resources. The BMW model is competitive with other models in reproducing the experimental values. To compare the properties of water calculated using the BMW model with the experimental data, we calculated the thermodynamic functions of water at $p = 0.1$ MPa in the whole temperature range of existence of the liquid phase (Fig. 2). With allowance for relatively small systematic error in the density and internal energy computations the calculated and experimental values are in excellent agreement. Any simulation procedure unavoidably introduces some errors. The BMW model correctly reproduces the temperature dependence of the thermodynamic properties of water and, hence, the thermal expansion coefficient and the specific heat capacity of water at constant pressure.

At present, the NDIS-97 and NDIS-2000 sets of the atom—atom RDF are thought to be the most reliable. Recently, calculations of the RDF using experimental data are carried out by the reverse Monte Carlo (RMC) method,[28,29] which permits generation of molecular con-

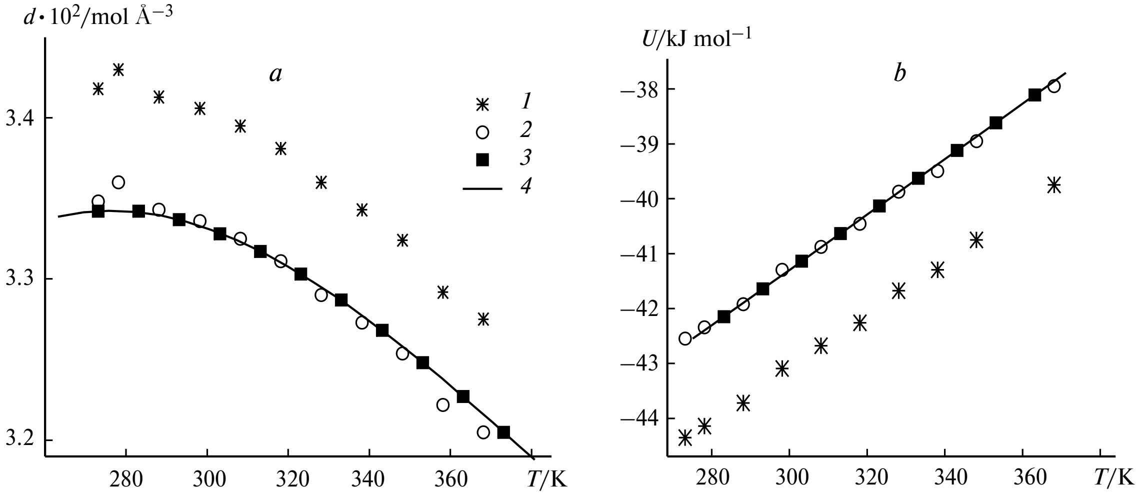

Fig. 2. Numerical density (*a*) and internal energy (*b*) plotted *vs*. temperature at $p = 0.1$ MPa. The dependences calculated using the BMW model (*1*), curve *1* shifted by arbitrary constant (*2*), experimental data (*3*), and polynomial approximation of the experimental data (*4*).

Table 2. Thermodynamic characteristics of several models for water[6] including the BMW model

State	Method	$-U$ /kJ mol^{-1}	$d \cdot 10^2$ /Å^{-3}
298a	BSV	42.72	3.622
	CC	39.38	2.956
	DC	41.27	3.542
	TIP4P	42.52	3.644
	SPC/E	47.48	3.52
	BMW	44.07	3.41
	Experiment	41.53	3.34
573e	BSV	26.57	2.776
	CC	22.54	2.304
	DC	24.97	2.608
	TIP4P	29.96	2.887
	SPC/E	33.98	2.96
	BMW	30.90	2.96
	Experiment	30.05	2.96
573a	BSV	2.96	0.152
	CC	2.23	0.140
	DC	2.76	0.164
	TIP4P	8.21	0.242
	SPC/E	29.82	2.22
	BMW	27.36	2.30
	Experiment	26.72	2.40
673b	BSV	16.22	1.647
	CC	12.17	1.207
	DC	15.07	1.539
	TIP4P	20.55	1.857
	SPC/E	26.53	2.138
	BMW	23.94	2.19
	Experiment	23.09	2.21

Note. The models for water with polarizable potentials are as follows: Brodholt-Sampoli-Vallauri (BSV), Chialvo-Cummings (CC), and Dang-Chang (DC) models; the models for water with additive potentials are the SPC/E, TIP4P, and BMW models.

figurations in such a way that the RDF or the structure factors of the model be close to the experimental values. This method does not require the intermolecular interaction potential to be specified. The computational procedure, which is based on minimization of the difference and at the same time does not involve determination of the energy characteristics of molecular configurations, has many drawbacks. In this case, it is highly probable to generate such configurations that are rare to occur or impossible in real liquid. The empirical potential structure refinement (EPSR) version of the RMC method provides a way for the system under study to be located in the more probable regions of the configuration space. Here, the configuration sampling procedure is performed using an effective potential augmented with an empirical potential to minimize the difference between the calculated and experimental functions. This approach was employed to derive the NDIS-2000 set of RDF. The main potential (SPC/E)[22] was augmented with an empirical correction in such a way that the experimental structure factors be best reproduced. However, this also allowed only one out of manifold of possible solutions to the incorrect problem to be obtained; therefore, one can expect publication of new RDF sets calculated using experimental data in the nearest future.

A major drawback of the EPSR procedure is that each point in the phase diagram of a substance requires a particular empirical potential. To perform any calculations, a large experimental data set is necessary. The data obtained in neutron diffraction experiments include errors that can hardly be allowed for. When determining the partial structure factors and the RDF from experimental data, the properties of water are assumed to be independent of the isotope composition. This is a rough approximation. At small q values, the errors in determination of the differential cross sections dramatically increase. Incorrect inclusion of correction for inelastic neutron scattering in the NDIS-93 set led

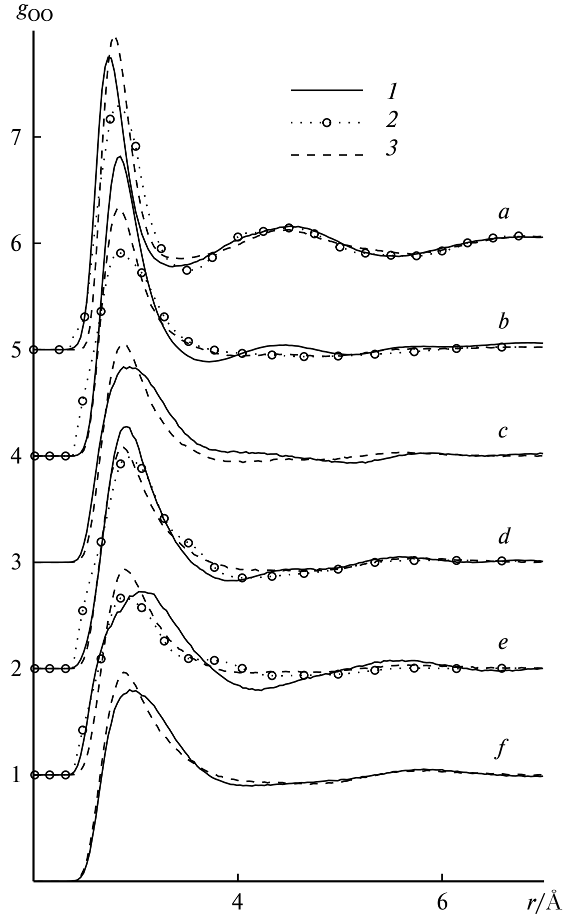

Fig. 3. The g_{OO} RDF of the states 298a (*a*), 423b (*b*), 573a (*c*), 573f (*d*), 673a (*e*), and 673d (*f*) calculated using the NDIS-2000 set (*1*), NDIS-97 set (*2*), and BMW models (*3*). For clarity, the plots are shifted along the *y* axis.

to a crisis[3,4,21] in the studies on structural properties of water.

When calculating the structure factors based on the results of computer simulation, we also assumed that the properties of water are independent of isotope composition. The limitation imposed on the upper limit of integration in Eq. (2) due to the small size of the unit cell can lead to the appearance of additional extrema in the $S(q)$ and $F(q)$ curves and introduce errors in the determination of these functions at small q values. Since the BMW model treats the water molecule as a rigid species, we took the intramolecular components of the g_{HH} and g_{OH} RDF from the corresponding functions of the NDIS-2000 set.

The NDIS-97 and NDIS-2000 experimental data sets contain a large number of functions. Therefore, we will illustrate the consistency between the calculated and experimental data taking a small number of curves as examples. The RDF determined using molecular configurations obtained from MC simulation of the model of water with the BMW potential and the RDF from the NDIS-97 and NDIS-2000 function sets are shown in Figs. 3 and 4. The RDF are "the most distant" objects from the experimental data. The shape of these curves is most sensitive to the influence of admissions and errors in calculations, which are unavoidable while processing experimental data. The partial structure factors characterizing correlations in the arrangement of H atoms in the wave vector space are shown in Fig. 5. The experimental structure factors are obtained from the total structure factors by solving the system of equations (1). Of course, the error in determination of the partial structure factors considerably increases. In some portions of the curves, systematic shifts along the abscissa axis can appear. In Fig. 6 we present the calculated and experimental total structure factors $F(q)$ for H_2O, D_2O, and their equimolar mixture. Note that the experimental structure factors include a difficult-to-allow-for contribution of inelastic neutron scattering.[21] At $q < 1.1$ Å^{-1}, the accuracy of determination of the $F(q)$ values is very low.

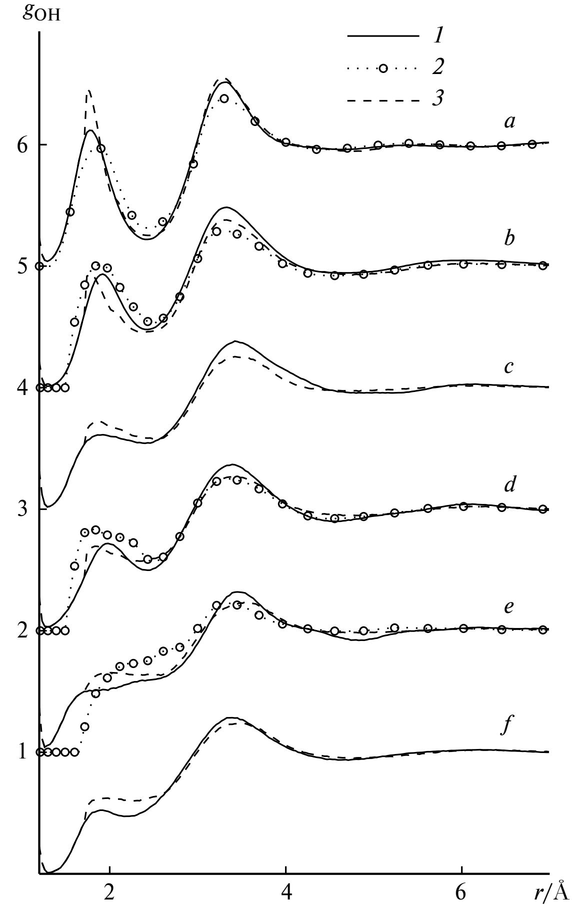

Fig. 4. The g_{OH} RDF. For notations, see Fig. 3.

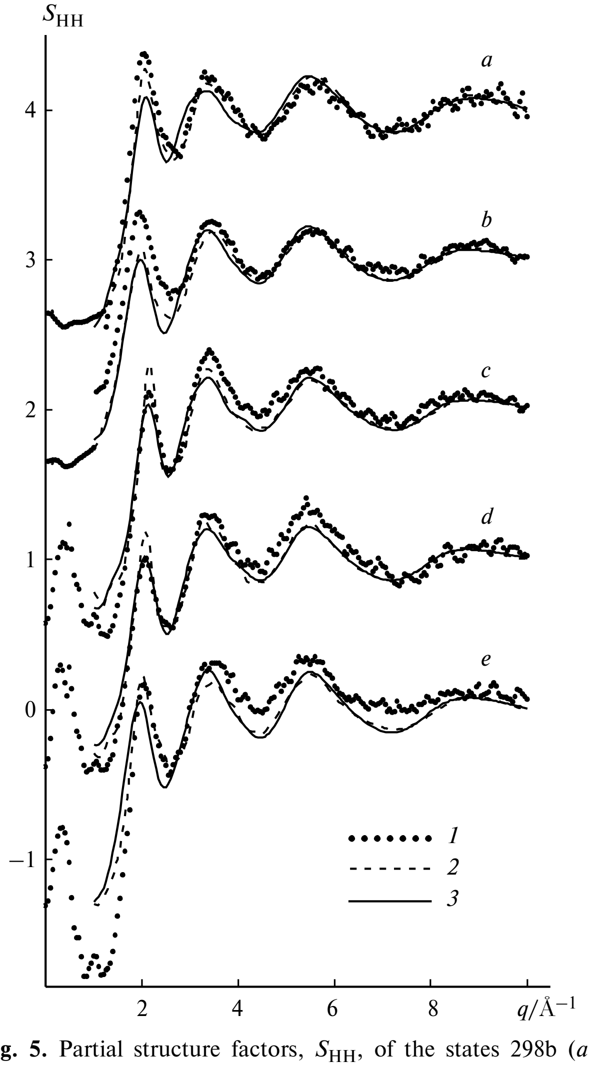

Fig. 5. Partial structure factors, S_{HH}, of the states 298b (*a*), 298a (*b*), 268c (*c*), 268b (*d*), and 268a (*e*). Experimental data (*1*) and the results of calculations using the NDIS-2000 RDF set (*2*) and the BMW model (*3*). For clarity, the plots are shifted along the *y* axis.

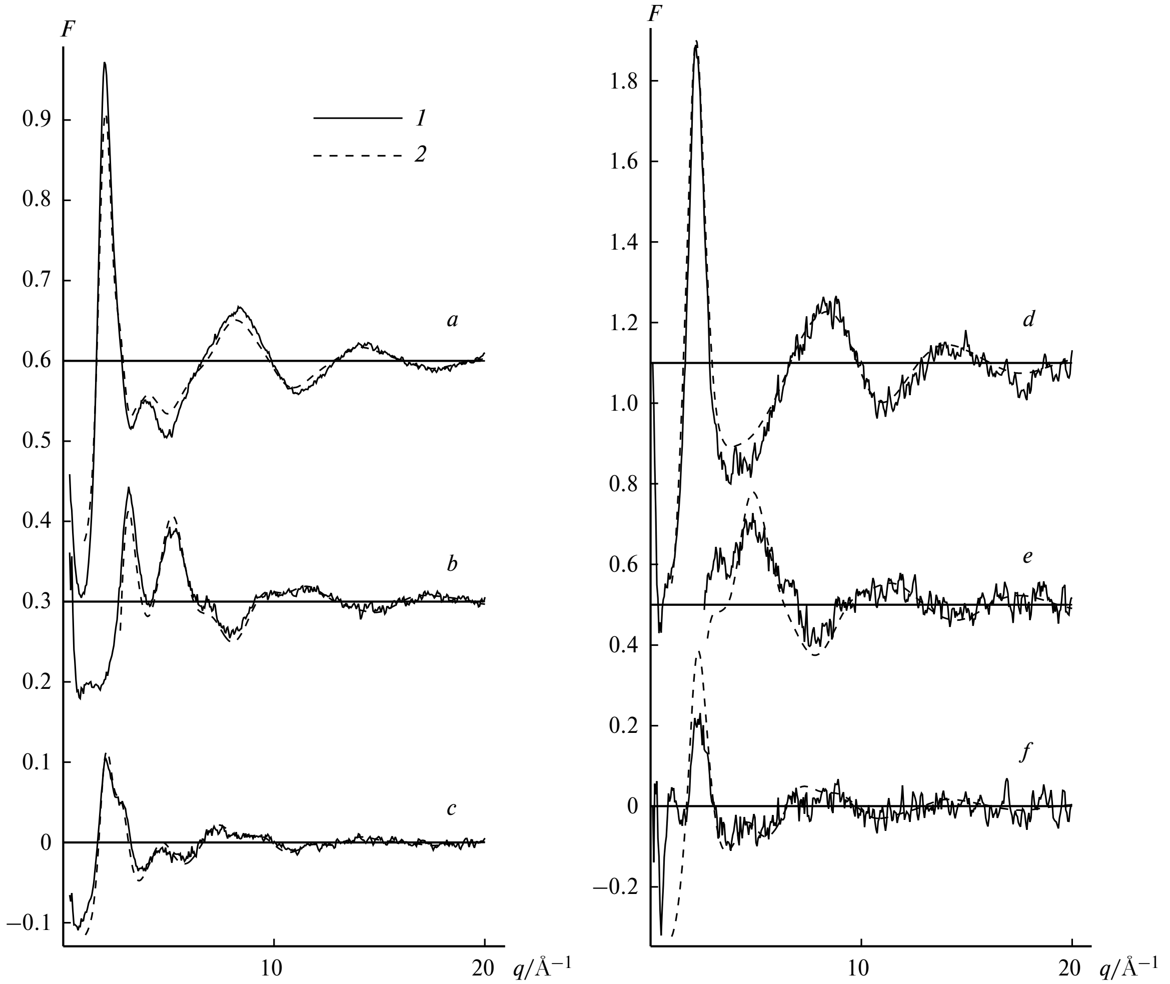

Fig. 6. Total structure factors F_{D_2O} (*a*, *d*), F_{H_2O} (*b*, *e*), and F_{HOD} (*c*, *f*) of the states 298a (*a*—*c*) and 673d (*d*—*f*): experimental data (*1*) and the curves calculated using the BMW model (*2*).

The results obtained in our study suggest that in a wide range of state parameters the properties of water calculated using the BMW model are quite consistent with the most reliable data of neutron diffraction experiments. In many cases the calculated RDF pass between the corresponding curves from the NDIS-97 and NDIS-2000 function sets.

Analysis of molecular configurations suggests that the system of H-bonds of water in the BMW model is inhomogeneous. Non-tetrahedral fragments are defects of the tetrahedral network of H-bonds and are therefore displaced by this network. Dimers (both BD and ID) form clusters, one of which is shown in Fig. 7. A group of molecules 1—6 should be pointed out, which form a chain BD—ID—ID—BD—ID. The H atoms denoted as "A" and "B" belong to the molecules that form two-fold bonds.

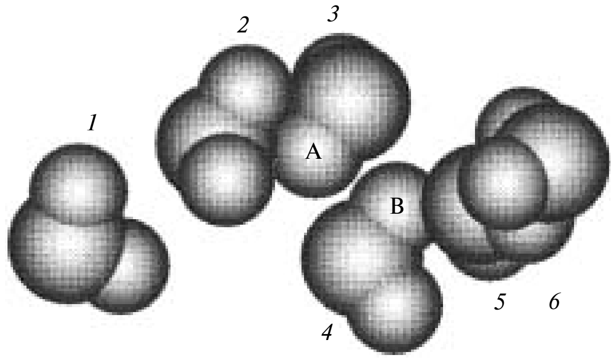

Fig. 7. Cluster comprised of six molecules (*1*—*6*) that form nonlinear H-bonds. The cluster was found in a molecular configuration (other molecules in the unit cell are not shown); the capital lettes "A" and "B" denote the molecules that form two-fold H-bonds.

Thus, the structural and thermodynamic functions of water calculated using the BMW model are consistent with experimental data on the properties of water in a wide range of state parameters. Therefore, there are grounds to suggest that the system of H-bonds of water can contain not only tetrahedrally coordinated molecules but also a large number of non-tetrahedral bonds. In the

BMW model, water is characterized by heterogeneous network of H-bonds on the microscopic level, which is consistent with numerous phenomenological theories based on the assumption of coexistence of several structures. Local extrema on the PES strongly affect the structural properties of water. The proposition that the results of computer simulation provide an unconditional support of continuum models should be revised.

It is believed that the structure of a liquid can be completely described using the RDF set only. Long-term experimental investigations allowed the RDF of water to be determined for a broad range of state parameters. However, the RDF can be interpreted in a different way. Even in the hypothetical case (knowledge of exact RDF sets) it is impossible to establish the laws of mutual arrangement of the molecules and the topological properties of the system of H-bonds of water. The RDF are integrated characteristics. Determination of the RDF by either experimental or computational methods always involves averaging over statistical ensemble. The inverse problem, *i.e.*, reconstruction of molecular configurations, belongs to the class of incorrect problems and has multiple solutions.

The linear, bifurcated, and inverted dimers have different total dipole moments. In both aqueous electrolyte solutions and aqueous solutions of polar and nonpolar substances the dynamic equilibria between various molecular states in the system of H-bonds of water can be shifted. Based on the assumption of rather high concentration of non-tetrahedral fragments in the system of H-bonds, current views of the structure of water and aqueous solutions may be significantly changed.

The authors express their gratitude to Dr. F. Muguet (Ecole Nationale Supérieure de Techniques Avanceés, ENSTA, Paris, France) for fruitful discussions and to Dr. A. Soper (Rutherford Appleton Laboratory, United Kingdom) for his interest in this work and providing tabulated experimental data.

This work was carried out with the financial support from the Russian Foundation for Basic Research (Project No. 04-03-32363-a).

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Received March 1, 2003