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Parameters of models and conditional sensitivity coefficients of radial distribution functions for water calculated by molecular dynamics data

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The influence of parameters of rigid models of the 12-6-1 type on the properties calculated in computer experiments, *viz.*, radial distribution functions and internal energy, was studied by the method of step-by-step transform of the water models supplemented by calculations of conditional sensitivity coefficients.

Key words: water, model potentials, molecular simulation, radial distribution functions, internal energy.

The intermolecular interaction potential plays the determining role in a theoretical study of properties of any system. A tendency to use as simple potential functions as possible always existed[1,2] and remarkably increased in recent years.[3—5] This is due to a necessity of performing arduous calculations over a variety of properties and intervals of thermodynamic state parameters (temperature (T) and pressure (P)). Water is the most typical example.[4—12]

More than 100 empirical potential functions have been proposed for water. Among them, the simplest and most efficient functions take into account only the Coulomb interaction of excess charges and the nonelectrostatic interaction between oxygen atoms,[2] most often using the Lennard-Jones (LJ) potential. When a new function is chosen, it is parametrized by a method of numerical experiment (Monte Carlo (MC) or molecular dynamics (MD)). This is a rather laborous and prolonged process and, as we have shown earlier,[13] it does not ensure a good final result. In our opinion, the use of the method of step-by-step transform of models (MSTM) and related determination of conditional sensitivity coefficients (CSC)[14] can substantially alleviate the problem and reject improper models prior to computer experiments. In addition, our calculations can estimate the influence of each parameter of the potential function on the shape of the potential hypersurface and properties calculated in computer experiments.

The true sensitivity coefficient $\alpha_i = \partial F/\partial\lambda_i$ is the partial derivative of the property F with respect to the parameter λ_i in the equation[15—17] determining the property F as a function of independent variables x_i

$$F = f(\lambda_1 x_1,...,\lambda_i x_i,...,\lambda_n x_n)\lambda_i.$$

In this situation, F is any property of water obtained by computer simulation, which is the function of the potential of pair interaction of particles $U(r,\lambda_1,...,\lambda_n)$ (r is the distance between the particles). The λ_i parameters are the force interaction constants, geometric characteristics of charges (when the latter are arranged not in the centers of atoms), and geometric parameters of molecules.

Such a calculation of the sensitivity coefficients is a very difficult procedure.[17] In addition, it produces only the characteristic of a model, which does not reveal the source of differences between different models. Meanwhile, the proposed method of step-by-step transform of models makes it possible to perform comparative analysis. In this work, the MSTM was applied to the study of rigid models of water with the three- and four-center arrangement of charges in the model molecule.

Calculation procedure

All known potentials of water can be classified by certain properties. Among empirical rigid models, we can distinguish several potentials for which the pair interaction function is written as the sum of the LJ potential and Coulomb components

$$U(r) = 4\varepsilon[(\sigma/r_{\mathrm{OO}})^{12} - (\sigma/r_{\mathrm{OO}})^6] + \sum_{i,j} q_i q_j / r_{ij}, \qquad (1)$$

where r_{OO} is the distance between the oxygen atoms belonging to two water molecules, and i and j are the centers of the localized positive and negative charges. This group of potentials includes the three-point[18] SPC,[19] SPC2,[20] TIPS,[21] and TIP3P [1] models and four-point[18] TIPS2,[22] TIP4P,[1] SRWK2,[23] WK,[24] and BF [25] models. These models are most widely used in practice and only they are considered below. For such potentials, the $U(r)$ function depends on six parameters: q_{H}, σ, ε, r_{OH}, r_{OM}, and $\angle$HOH, where q_{H} is the excess charge on the hydrogen atom, ε and σ are

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the constants of the LJ potential, r_{OH} is the O—H bond length in the water molecule, r_{OM} is the distance between the center of the oxygen atom and the excess negative charge displaced along the bisectrix of the HOH angle, and ∠HOH is the bond angle in the water molecule. In more complicated models, the number of parameters is much greater, and they can be different. For example, for the description of the nonelectrostatic interaction by the Buckingham potential,[26] the A, α, and B_6 parameters appear instead of σ and ε

$$U_{nel}(r) = A\exp(-\alpha r) - B_6/r^6.$$

The method of step-by-step transform of models involves transition from one model to another by a gradual change in the values of parameters of the model, and the value of only one parameter is varied at each stage. For each model appeared upon the transform, the $U(r)$ function (1) is minimized for the *trans*-dimer by r_{OO} and γ and θ angles (Fig. 1). As a result, the U_{min}, r_{min}, γ_{min}, and θ_{min} values are determined, as well as the r_σ value at which $U(r)$ crosses the abscissa and the asymmetry characteristic of $U(r)$ curve $2l_1/l$ for the equilibrium configuration.[14,18,27] These values for the SPC, SPC2, TIPS, TIP3P, TIP4P, SRWK2, BF, and WK models and for all considered by us 51 intermediate models are completely presented in Refs. 28 and 29. The radial distribution functions $g_{ij}(r)$ (RDF) and internal energy U_{int} were calculated for all models using the molecular dynamics method. Simulation was performed in the NVT ensemble at 300 K for the system containing 213 water molecules in a cubic cell with periodical boundary conditions using the SHAKE procedure.[30] The density corresponded to the experimental value for water equal to 0.997 g cm^{-3}. The Newton equations were integrated using the difference Verlet scheme. The temperature was maintained constant using an external thermostat. The time of each execution for the system to achieve equilibrium was 50 ps, and the equilibrium region in which the properties were calculated[28] was also 50 ps. Figure 2 illustrates the method of step-by-step transform: changes in the calculated values of the internal energy U_{int} and heights of the first peaks of the oxygen—oxygen RDF $g_{OO}{}^{1max}$ depending on two parameters of the model, *viz.*, the effective charge on the hydrogen atoms q_H and distance between the oxygen atom and displaced negative charge r_{OM}, while the other parameters of the model remained unchanged.

When studying a similar set of potentials, one can estimate the sensitivity of each characteristic of the $U(r)$ function or the Y property calculated with this function to a change in the parameter of the model λ through the finite differences $\Delta Y/\Delta\lambda$, *i.e.*, conditional sensitivity coefficients.[14,28,29]

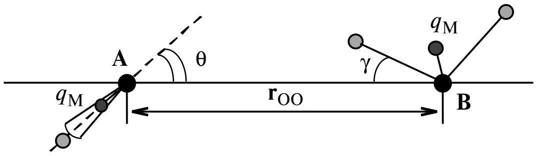

Fig. 1. Designations to minimization of $U(r)$. Molecule **A** (proton acceptor) is perpendicular and symmetrical to the figure plane, molecule **B** (proton donor) lies in the figure plane, and the θ angle is formed by the symmetry axis of molecule **A** and the $\mathbf{r}_{OO}$ vector. For the three-point models, q_M = 0, and for the four-point models, $q_M \neq 0$ and lies on the symmetry axis of the molecule with the displacement along this axis from the O atom toward the H atoms at the r_{OM} distance.

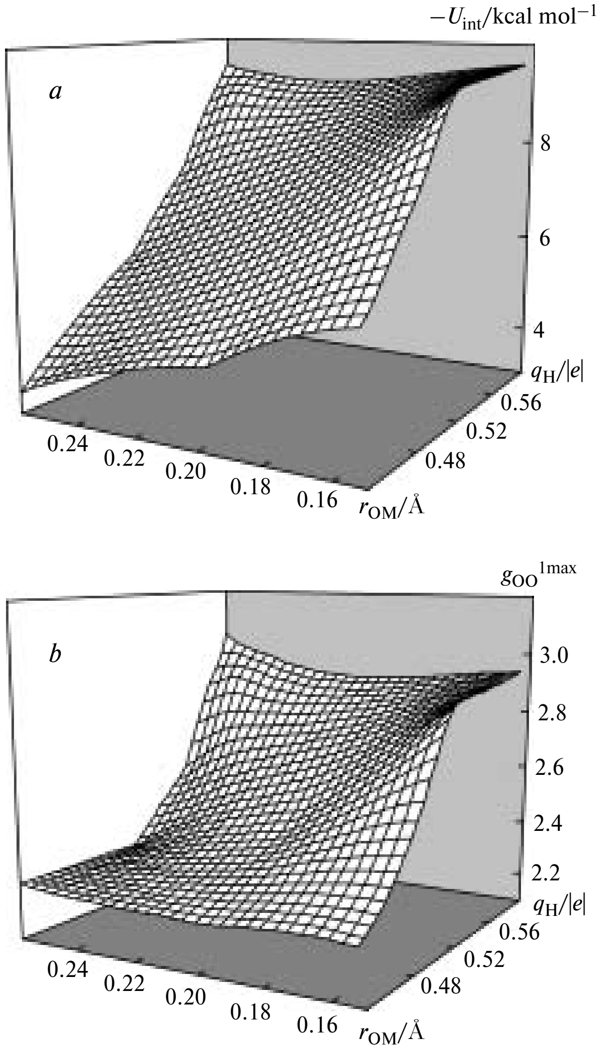

Fig. 2. Plots of U_{int} (*a*) and $g_{OO}{}^{1max}$ (*b*) *vs.* the q_H and r_{OM} parameters.

For parametrization of the empirical potentials, the LJ equation is often written in the form[1]

$$U_{LJ}(r) = A_{12}/r^{12} - A_6/r^6.$$

Therefore, we decided to consider the coefficients $A_{12} = 4\varepsilon\sigma^{12}$ and $A_6 = 4\varepsilon\sigma^6$ as λ in addition to ε and σ. Note that the signs at CSC do not coincide in the general case when calculated from A_{12} and A_6, on the one hand, and using ε and σ, on the other hand. For example, $\Delta U_{min}/\Delta\varepsilon$ and $\Delta U_{min}/\Delta\sigma$ have the same signs, while $\Delta U_{min}/\Delta A_6$ and $\Delta U_{min}/\Delta A_{12}$ have different signs, and the CSC $\Delta g_{OO}{}^{1max}/\Delta\varepsilon$, $\Delta g_{OO}{}^{1max}/\Delta\sigma$, and $\Delta g_{OO}{}^{1max}/\Delta A_6$, $\Delta g_{OO}{}^{1max}/\Delta A_{12}$ are characterized by the same relation of signs.

Results and Discussion

Analysis of the obtained CSC values[28,29] suggests the following.

The sign of $\Delta Y/\Delta\lambda$ for each transition depends on the λ parameter. This allows precision parametrization of the $U(r)$ function to be performed for obtaining the best coincidence in computer experiments between the calculated values and the physical experimental data. This "reliable" $U(r)$ function can be used to study properties, which are very difficult to measure or cannot be measured at all. In all cases, $\Delta Y/\Delta(\angle HOH)$ is much lower than the other $\Delta Y/\Delta\lambda$ (in this case, we do not mean $\lambda = A_{12}$ or $\lambda = A_6$ because A_{12} and A_6 are magnitudes of another order). This shows that the parametrization of any model related to a change in $\angle HOH$ cannot provide noticeable improvements and the choice of $\angle HOH = 109.47°$ (as in models of the SPC type, an angle in the regular tetrahedron) or $\angle HOH = 104.52°$ (as in models of the TIPS type, an angle between the O—H bonds in the water molecule in the gas phase) is not important from the viewpoint of final results.

In the series of transitions, all $\Delta Y/\Delta\lambda$ coefficients retain the sign and order of magnitude except for the $\Delta(2l_1/l)/\Delta\lambda$ coefficients, which are sign-variable and change in modulus up to three orders of magnitude, and the coefficients describing the influence of the λ parameters on the characteristics of the radical distribution functions $g_{ij}(r)$.[28,29] This confirms the role of asymmetry of the $U(r)$ function in the calculation of properties of the liquid phase and should be taken into account in comparison of the computer experimental results obtained using different potential functions.

The $\Delta Y/\Delta A_{12}$ values are very useful for the parametrization of models because the behavior of the repulsive potential branch (1) is determined, to a great extent, by a short-range repulsion, *i.e.*, its nonelectrostatic component. Hence, controlling the latter, one can gain the desired description of the left wall of the potential well. In this case, handling with the A_{12} parameter is simpler than the variation of the ε and σ values attaining the required combination.

Electrostatic attraction forces described in the considered models by the Coulomb potential $\Sigma q_i q_j/r_{ij}$ make the predominant contribution to long-range interactions. Based on the $\Delta Y/\Delta q_H$, $\Delta Y/\Delta r_{OH}$, and $\Delta Y/\Delta r_{OM}$ values, we can correct, in the first approximation, the behavior of the right branch of the potential curve. A finer parametrization should take into account the $\Delta Y/\Delta A_6$ values because the nonelectrostatic attraction makes a substantial, although not main, contribution to the long-range interaction forces. As for the transform of models to obtain a certain behavior of the potential curve in the region of a minimum, parametrization should be performed in the space of parameters. Special attention should be given to the $\Delta U_{min}/\Delta\lambda$ and $\Delta r_{min}/\Delta\lambda$ coefficients.

The dipole moment of the model molecule depends on its geometry, the position of the negative charge, and the value of the point charge q_H. The latter two parameters are determining. In effective pair potentials, the parameters are selected in such a way that the μ value would be close to the experimental dipole moment of the water molecule in the liquid phase (when the field imposed by surrounding molecules contributes to the dipole moment of the central molecule) $\mu_l \sim 2.6$ D [31] (WK model, *etc.*). Another variant is presented by the SRWK2 models, for which μ is closer to the experimental dipole moment of the water molecule in the gas phase ($\mu_g = 1.85$ D).[32] The third variant represents models of the TIPS type, for which μ is intermediate: ~2.2 D. In the step-by-step transform of models, the q_H and r_{OM} values were varied in such a way to obtain a set of potentials for which the dipole moment would range from 2.6 D for WK to 1.4 D. The calculation of $\Delta Y/\Delta r_{OM}$ was performed for pairs of models with the same q_H and different r_{OM}, and $\Delta Y/\Delta q_H$ were calculated for pairs with the same r_{OM} but different q_H. Analyzing the resulting CSC values, we revealed several regularities.

It is quite expected that the lower the q_H value, the lower $\Delta Y/\Delta r_{OM}$: a decrease in q_H decreases the contribution of electrostatic forces to the interaction of particles, and the relative position of charges in the molecule exerts a smaller effect on both the characteristics of potential curve and the calculated properties. It is of interest that $\Delta Y/\Delta A_{12}$ and $\Delta Y/\Delta A_6$ behave similarly when the charge decreases. This should be taken into account in the parametrization of the models. It is also noteworthy that the shorter the r_{OM} distance, the weaker the influence of the change in q_H on the potential well depth U_{min} and on the internal energy U_{int} calculated in computer experiment.

As for the properties of water obtained by calculation using the considered models,[28,29] the conclusion is evident: the lower the dipole moment (*i.e.*, the closer to $\mu_g = 1.85$ D), the lower the heights of the peaks $g_{ij}(r)$ and the higher the internal energy of the system (almost always $\Delta U_{int}/\Delta q_H < 0$, $\Delta U_{int}/\Delta r_{OM} > 0$, $\Delta g_{OO}{}^{1max}/\Delta q_H > 0$, $\Delta g_{OO}{}^{2max}/\Delta q_H > 0$, $\Delta g_{OO}{}^{1max}/\Delta r_{OM} < 0$, $\Delta g_{OO}{}^{2max}/\Delta r_{OM} < 0$, $\Delta(g_{OH}{}^{1max}/g_{OH}{}^{2max})/\Delta q_H > 0$, $\Delta(g_{OH}{}^{1max}/g_{OH}{}^{2max})/\Delta r_{OM} < 0$, $\Delta(g_{HH}{}^{1max}/g_{HH}{}^{2max})/\Delta q_H > 0$, and $\Delta(g_{HH}{}^{1max}/g_{HH}{}^{2max})/\Delta r_{OM} < 0$). This fact can be explained directly from the information specified in the values of parameters of the effective pair potential: if the parameters are selected in such a way that the dipole moment of the molecule would be close to μ_g, then the information is thus implied on the model that the interaction of particles in the system is weak. Correspondingly, *vice versa*: a high dipole moment of the model molecule implies that the particle interacts efficiently with the environment and the system should be characterized by high peaks of the radial distribution functions $g_{ij}(r)$ and a low internal energy.

It is known that none of the models of water proposed in the literature can correctly reproduce the experimental radial distribution functions, even when the model is parametrized by them. The peculiarities of models parametrization by $g_{ij}(r)$ were considered[13,18]; hence, here we only remind that, according to the recent experimental data,[33] $r_{OO}{}^{1max}$ = 2.875 Å, $g_{OO}{}^{1max} \approx$ 2.3—2.5, $r_{OH}{}^{2max} \approx$ 4.5 Å, $g_{OO}{}^{2max} > 1$, $g_{OH}{}^{1max}/g_{OH}{}^{2max} < 1$, and $g_{HH}{}^{1max}/g_{HH}{}^{2max} > 1$. The experimental internal energy of water is –9.92 kcal mol^{-1}.[33] We have demonstrated[13] that the models cannot simultaneously be parametrized by $g_{ij}(r)$ and U_{int}. Here we present the results of studying in more detail the influence of a change in the parameters of the model on the properties of water obtained in computer experiments. Parametrization almost always requires to attain simultaneously a lower internal energy and lower RDF peaks or *vice versa*, *i.e.*, they should be changed in the same direction. However, in the majority of cases, the lower the internal energy, the higher the maxima in $g_{ij}(r)$, and their RDF have opposite signs with rare exception, which unfortunately is not regular. These results confirm the earlier conclusions.[13]

The following situation was considered when analyzing the influence of the parameters of models on the calculated radial distribution functions and internal energy. The basic was the SRWK2 model for which the dipole moment was μ = 1.878 D, r_{OM} = 0.26 Å, and $q_H = 0.6|e|$. The r_{OM} values were varied simultaneously with q_H in such a way that the dipole moment of the model molecule remained equal to 1.878 D. The models, whose r_{OM} were 0.15, 0.20 and 0.25 Å and q_H were 0.4482$|e|$, 0.5063$|e|$, and 0.5816$|e|$, respectively, were thus obtained. The results of calculations with these potentials were compared to each other. It turned out that the internal energy of the system increased with an increase in r_{OM} and, hence, q_H (see Fig. 2, *a*). The radial distribution functions for the models are presented in Fig. 3. The higher r_{OM} and q_H, the smaller the radii of the coordination spheres ($r_{ij}{}^{n\,max}$ decrease) and, simultaneously, the higher $g_{ij}{}^{n\,max}$ (see, *i.e.*, Fig. 2, *b*), and in the case of $g_{OO}(r)$ at high r_{OM}, the second maximum appears in a region of 4.5 Å.

This information can be very useful for the parametrization of the models. We clarified that the properties calculated in computer experiments are affected by the values and arrangement of the effective point charges in the model particles rather than the dipole moment.

Another regularity found by us is also valuable. We considered three groups of models, in each of which the $q_H{}^2/\varepsilon$ ratio remained unchanged and the q_H and ε values were varied obeying this criterion. The radial distribution functions and internal energy in the groups behave, in general, as expected: the higher q_H, the lower U_{int} and the higher $g_{ij}{}^{n\,max}$. Another fact is of interest: in each of the groups of models, the characteristic points of the potential curve $U(r)$ (r_{min}, r_σ, *etc.*) are arranged at the same distances. At the same time, as turned out, the position of the first maximum of the oxygen—oxygen radial distribution function ($r_{OO}{}^{1max}$) remains unchanged, but its height changes. This indicates an explicit relation between the behavior of the oxygen—oxygen radial distribution function in the region of the first maximum and the behavior of the repulsive branch of the potential curve. Thus, it becomes possible to modify the model during parametrization correcting the potential well depth and retaining its position and the r_σ value at variable $\partial U/\partial r|_{r=r\sigma}$ values and, thus, to correct the height of the first peaks of the oxygen—oxygen radial distribution function without changing its position.

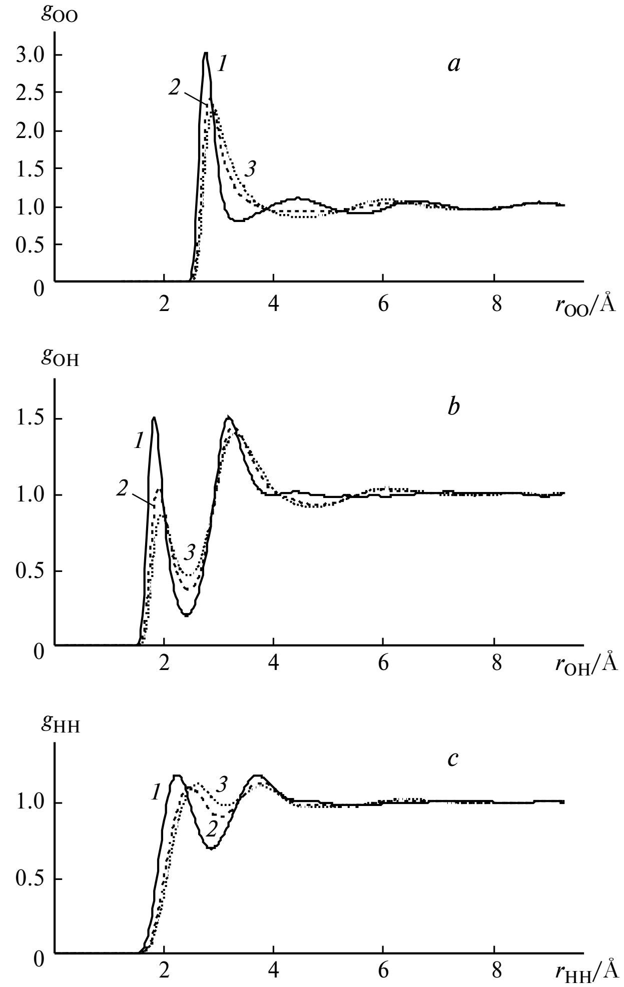

Fig. 3. Radial distribution functions $g_{OO}(r)$ (*a*), $g_{OH}(r)$ (*b*), and $g_{HH}(r)$ (*c*): *1*, SRWK2 model; *2*, model of the SRWK2 type with r_{OM} = 0.2 Å at μ = 1.878 D; and *3*, model of the SRWK2 type with r_{OM} = 0.15 Å at μ = 1.878 D.

Let us consider the use of the obtained results for the development of a new rigid three- or four-point model. The main idea is to reject variants of the models providing unsatisfactory RDF and U_{int} values without MD experiment. For this purpose, one can use the CSC and the correlations found by us,[28] which obey the equation[34,35]

$$y = ax + b. \quad (2)$$

Table 1. Parameters of Eq. (2) for calculations using the correlation equations (energy in kcal mol^{-1}, distances in Å)

Position	Parameter							Refs.
	y	x	a	b	S^a	R^b	N^c	
1	U_{int}	U_{min}	1.686	1.165	0.91	0.91	69	29
2	$-U_{\mathrm{int}}$	$\partial U(r)/\partial r\|_{r=r\sigma}$	0.188	−0.617	0.63	0.96	53	34
3	U_{int}	W^d	$0.942 \cdot 10^{-2}$	−6.947	1.43	0.82	58	29
4	$g_{\mathrm{OO}}{}^{\mathrm{1max}}$	U_{int}	−3.385	$-3.277 \cdot 10^{-2}$	0.74	0.87	30	14
5	P_1	$g_{\mathrm{OO}}{}^{\mathrm{1max}}$	1.910	1.201	0.17	0.93	28	14
6	g_{OO} (r = 4.5 Å)	$\partial U(r)/\partial r\|_{r=r\mathrm{infl}}{}^e$	0.138	0.403	0.06	0.92	53	34

[a] Root-mean-square deviation.

[b] Correlation coefficient, Eq. (2).

[c] Number of models.

[d] $W = U_{\mathrm{min}} g_{\mathrm{OO}}{}^{\mathrm{1max}} l_1/(r_{\mathrm{OO}}{}^{\mathrm{1max}} - r_{\mathrm{min}})$.

[e] r_{infl} is the abscissa of the inflection point in the $U(r)$ curve at $r > r_{\mathrm{min}}$.[34]

The $U(r)$ function for the chosen model is minimized and its characteristic parameters[27] including the derivatives are determined (Table 1). Then U_{int} is calculated by position 1 and, for checking, the same value is calculated by positions 2 and 3. Then $g_{\mathrm{OO}}{}^{\mathrm{1max}}$ is determined by position 4, the ratio

$$P_1 = g_{\mathrm{OH}}{}^{\mathrm{1max}}/g_{\mathrm{OH}}{}^{\mathrm{2max}}$$

is found by position 5, and finally, g_{OO} (r = 4.5 Å) is determined by position 6. The potential is considered appropriate when the calculated values are close to the experimental data obtained in diffraction experiments (see summary tables in Refs. 13 and 34). In this case, the MD experiment can be carried out, and the result can be verified by position 4 in Table 1. If the coincidence is absent, one should correct the parameters of the $U(r)$ function using the CSC as reference.[29] It should be immediately noted that for the three-point models, for which the potential curve is written as Eq. (1), no substantial success can be achieved.[13] This is also seen distinctly from the CSC values[29]: as mentioned above, an increase (algebraic) in U_{int} simultaneously decreases all three key values of other magnitudes, namely, $g_{\mathrm{OO}}{}^{\mathrm{1max}}$, P_1, and $g_{\mathrm{OO}}{}^{\mathrm{2max}}$, and *vice versa*. Therefore, variation of the parameters of the potential can only somewhat improve, in the best case, the coincidence of the MD or MC calculated values with the data of physical experiments but does not allow them to coincide completely. This conclusion is also confirmed by the results in the work,[36] whose authors concluded that three-point models of the SPC and TIP3P types cannot be parametrized by the properties of ice Ih even when the polarizability is taken into account. However, this parametrization is possible for four-point models of the TIP4P type. This conclusion has completely been confirmed later[37] by a more detailed study of the possibility of parametrization of the same models by the properties of liquid water at 298 K. Indeed, we found that the coincidence of the signs of the CSC [29] $\Delta U_{\mathrm{int}}/\Delta\lambda$ and some other $\Delta Y/\Delta\lambda$ (this is a necessary condition for successful parametrization) is observed only for some four-point models and is never observed for three-point mod-

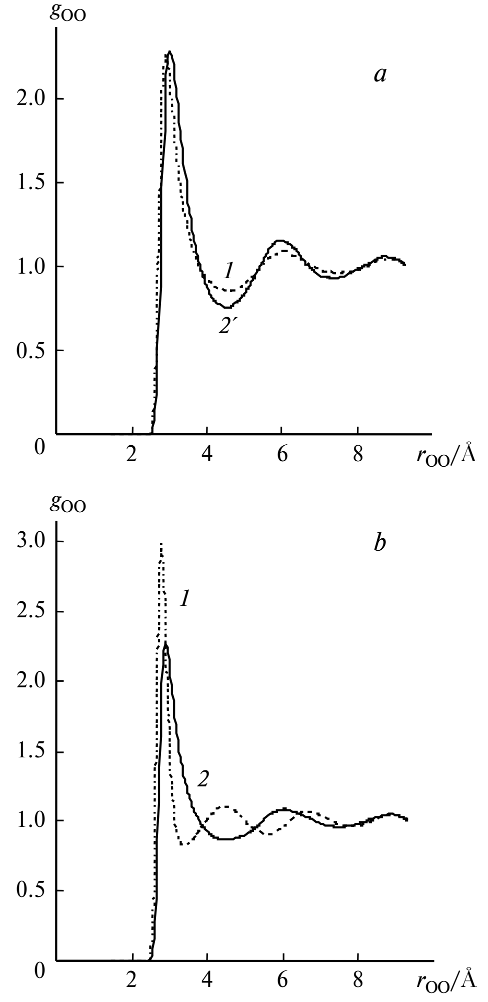

Fig. 4. Oxygen—oxygen radial distribution functions for models of the TIP4P type with q_{H} = 0.4428|e| (*a*) and 0.52|e| (*b*) and r_{OM} = 0.15 (*1*) and 0.26 Å (*2*).

els. For example, in the case of transition for models of the BF type, this is true for $\Delta P_1/\Delta(\angle \mathrm{HOH})$, $\Delta g_{\mathrm{OO}}{}^{2\max}/\Delta A_6$, and $\Delta(g_{\mathrm{HH}}{}^{1\max}/g_{\mathrm{HH}}{}^{2\max})/\Delta r_{\mathrm{OH}}$, while for the TIP4P models, it holds true for $\Delta g_{\mathrm{OO}}{}^{1\max}/\Delta r_{\mathrm{OM}}$. The radial distribution functions of the latter pair of models are compared to another pair of transition models for TIP4P in Fig. 4. This figure clearly indicates the direction of necessary changes in the oxygen—oxygen RDF to coincide with the results of physical experiments ($U_{\mathrm{int}} = -10$ kcal mol^{-1}, $g_{\mathrm{OO}}{}^{1\max} = 2.4$, $P_1 = 0.65$, $g_{\mathrm{OO}}{}^{2\max} = 1.1$). The question how the three-point models can be improved by the introduction of the non-Coulomb interaction of other pairs of atoms except O...O, for example, H...H or O...H, remains yet unclear and is being studied by us presently.

The revealed regularities should undoubtedly find practical use for parametrization of models. The results of this work are only a part of the continued study, whose final purpose is to obtain the model potential for water without disadvantages of the models known presently.

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