A simple method for evaluation of the self-consistency of the radial distribution functions and the orientation of water molecules in the first coordination sphere from the results of molecular dynamics calculations

V. E. Petrenko,[a]* *M. L. Dubova,*[a] *Yu. M. Kessler,*[a] *and M. Yu. Perova*[b]

[a]*Institute of Chemistry of Solutions, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 35 1869. E-mail: vep@ihnr.polytech.ivanovo.su
[b]*Ivanovo State University of Chemistry and Technology,*
7 prosp. F. Engel'sa, 153460 Ivanovo, Russian Federation.
Fax: +7 (093 2) 32 9502

A simple method for determination of the angular orientation of water molecules in the first coordination sphere from the radial distribution functions is proposed. A comparative analysis of the ability of the model potentials of pair interaction to take into account the effects of manybody interactions (MBI) was performed. The responses of the model pair potentials to the MBI effects in the first and second coordination spheres were found to be poorly correlated with each other. It was concluded that it is necessary to derive a new analytical type of potential functions of pair interaction.

Key words: intermolecular interactions, potential functions of pair interaction, radial distribution functions, computer simulation of liquids

In our studies on the properties of liquid water and aqueous solutions by computer simulation we placed special emphasis on two aspects of the problem.

1. The most widely used procedure for checking the adequacy of the empirical potential energy functions $U(r)$ of pair interaction between molecules in vacuum (r is the distance between the centers of oxygen atoms) using the results of computer simulation involves a comparison of the calculated radial distribution functions (RDF) of the oxygen and hydrogen atoms ($g_{OO}(r)$ and $g_{HH}(r)$, respectively) and the $g_{OH}(r)$ functions with the RDF obtained in X-ray, neutron, and electron diffraction studies of water.[1] These functions are also often used for the parametrization of the expressions for the function $U(r)$; however, the results obtained in different studies differ appreciably. The data[1] have long been considered as the most reliable. However, one can introduce several criteria for the self-consistency of data sets, which can be used equally for evaluation of the data on the RDF obtained either experimentally or in computer simulation.

The simplest parametric criterion has a clear physical meaning and can be expressed in the form

$$\delta_1 = r^{1m}{}_{OO} - r^{1m}{}_{OH} - r_{OH}.$$

Hereafter, $r^{km}{}_{ij}$ and $g^{km}{}_{ij}$ denote the coordinates of the kth maximum of the corresponding partial RDF, $k = 1$ or 2; i, j = O or H; and r_{OH} is the O—H bond length in the molecule of liquid water. According to this criterion, a data set is self-consistent if $\delta_1 \le 0$ and non-self-consistent if $\delta_1 > 0$. For a molecule of liquid water, the r_{OH} value must lie between 0.9572 Å (for an isolated molecule in vacuum) and 1.01 Å (for ice).[2] Neutron scattering studies showed[3] that r_{OH} = 0.966 Å, which differs from the value 0.98 Å recommended earlier.[1] Calculations of the δ_1 value using the experimental r_{OH} bond length (r_{OH} = 0.966 Å [3]) lead to δ_1 = 0.045,[1] −0.077,[4] 0.010,[5] −0.480[6]. Here, two sets of experimental data are non-self-consistent.

Generally, positive δ_1 values preclude a reliable determination of the mutual orientation of two neighboring molecules of liquid, while negative δ_1 values give no information on the accuracy of the coordinates of the RDF extrema found in the experiments. Analysis of the results of a recent neutron diffraction study[7] of water suggests that (a) the distance $r^{1m}{}_{OO}$ is shorter than that reported earlier,[1] and, therefore, the δ_1 value we calculated from the published data[1] is in fact smaller or even equals zero (unfortunately, only small-scale plots rather than tabulated data for the RDF have been reported[7]); (b) the error of determination of $g^{km}{}_{ij}$ is 14%; (c) $g^{1m}{}_{OO}$ equals ~2.3 instead of 3.09 (see Ref. 1); (d) positions of the maxima of the functions $g_{OH}(r)$ and $g_{HH}(r)$ are close to those reported earlier[1]; and (e) the estimates of the ratios of the maxima $g^{1m}{}_{OH}/g^{2m}{}_{OH} < 1$ and $g^{1m}{}_{HH}/g^{2m}{}_{HH} > 1$ are valid. Thus, the fulfilment of condition (e) and simultaneous observation of the second maximum of the function $g_{OO}(r)$ at ~4.5 Å should be considered as a necessary, but not sufficient condition when assessing the adequacy of the function $U(r)$.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1842—1846, November, 2000.

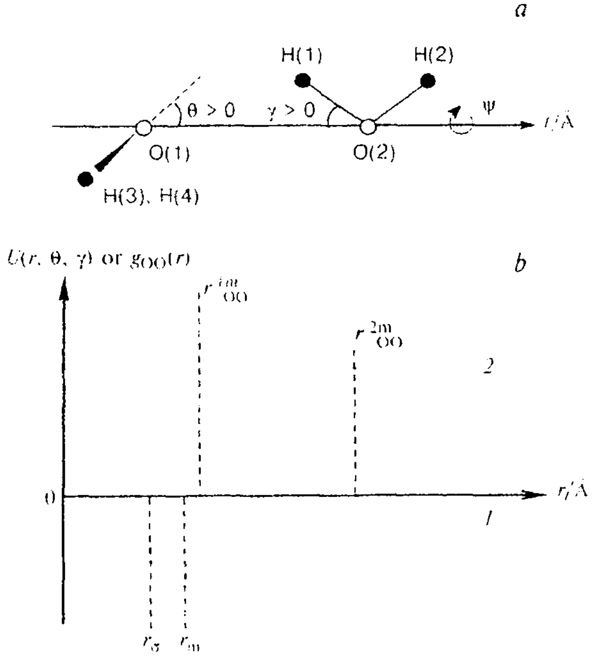

Fig. 1. Mutual orientation of the molecules in the *trans*-dimer of water (*a*); the potential function of pair interaction between water molecules in vacuum, $U(r, \theta, \gamma)$, for the *trans*-dimer of water (*1*) and the $g_{OO}(r)$ RDF for liquid water (*2*) (*b*).

The experimental data set reported in Ref. 4 does not meet these conditions completely; however, since in this case $\delta_1 < 0$, we used these data for determination of the mutual orientation of two molecules of liquid water. The notations of angles are given in Fig. 1, *a*. The plane of the first molecule is perpendicular to the drawing plane, which simultaneously is the symmetry plane of this molecule; the second molecule lies in the drawing plane. Using a graphical procedure described below, we found that $\theta = 61°$, $\gamma = -23.5°$, and α(H—O—H) = 110.5°. Taking into account the roughness of the graphical construction and the errors of experimental data,[4] our results are in fairly good agreement with the values $\theta = 78°$ [7] and α(H—O—H) = 102.6° [3] found from the neutron diffraction experiments. The use of non-self-consistent data[1,5] leads to the following values of the angles θ, γ, and α(H—O—H): 43°—62°, 8.6°, and 96.5° and 70.5°, 4.3°, and 96° for the data sets reported in the former and in the latter study, respectively.

2. It is known (see, *e.g.*, Refs. 8, 9) that the use of strongly different analytical functions $U(r)$ (including those obtained in the *ab initio* calculations) derived to be used in various models of the water molecule for the description of the properties of a fluid, which is often called computer water, leads to surprisingly qualitatively similar results. A formal explanation is almost trivial and lies in the fact that after a certain parametrization of the function $U(r)$ in order to reproduce particular physical properties of water the $U(r)$ functions obtained work fairly well in approximating an exact function, which is known to be done in a virtually uncountable number of ways. Physically, this can be rationalized[10,11] by taking into account the manybody interactions which change the orientation of a set of three arbitrarily chosen water molecules, due to the action of the pair potential $U(r)$, near $g^{2m}{}_{OO}$. Simultaneously, the absence of correlation between the $g^{1m}{}_{OO}$ and $g^{2m}{}_{OO}$ values has been shown.[11] In this work, we will consider how the orientation of the molecules in the first coordination sphere depends on the type of the function $U(r)$.

The configuration of a water dimer, $(H_2O)_2$, in vacuum is usually found from the results of minimization of the function $U(r)$ using the distance r_{OO} and the angles θ, γ, and ψ (see Fig. 1, *a*) as independent variables. By symmetry of the potential functions for any (rigid, flexible, polarizable, and flexible and polarizable) models of the water molecule and according to *ab initio* calculations, the global potential energy minimum corresponds to $\psi_m = 0$, while other parameters depend on the model used and vary between −10° and +10° for γ_m, 20° and 60° for θ_m, 2.7 and 2.9 Å for r_m, and −4.5 and −7.5 kcal mol^{-1} for U_m (see, *e.g.*, Refs. 4, 10; U_m and r_m are the coordinates of the minimum of the $U(r)$ function (Fig. 1, *b*)). Therefore, the *trans*-configuration of the water dimer (see Fig. 1, *a*) is the most energetically stable.

When using the function $U(r)$ in computer simulation of the properties of liquid water by the molecular dynamics, Monte Carlo, or integral equations methods, the manybody effects (environment) will change the mutual orientation of two neighboring water molecules, so that the θ and γ values will differ from θ_m and γ_m. For different functions $U(r)$, the differences $\theta - \theta_m$ and $\gamma - \gamma_m$ will also be different; hence they can serve as effective characteristics of specific behavior of these functions. Computer simulation allows determination of the angles θ and γ in a different manner; however, studies on this aspect are scarce. Since comparison of the properties of the functions $U(r)$ requires a large set of corresponding functions to be processed using the same computational procedure, it is appropriate to use the RDF reported in the vast majority of studies.

Calculation procedure

The calculation procedure proposed in this work is very simple and can as appropriately be used with the experimental RDF as with those obtained in computer simulation. However, in the former case the procedure always is more labor-consuming since it requires the determination of four parameters (the angles θ and γ, the bond length in the water molecule r_{OH}, and the bond angle H—O—H), whereas in the latter case the distance r_{OH} and the angle H—O—H for rigid models are parameters of the known potential function of pair interaction. The procedure involves determination of the coordinates of the points shared by two arcs (circumferences) by solving a corresponding system of equations. The order of operations is insignificant; however, different versions of the procedure take different times and give results of different accuracy.

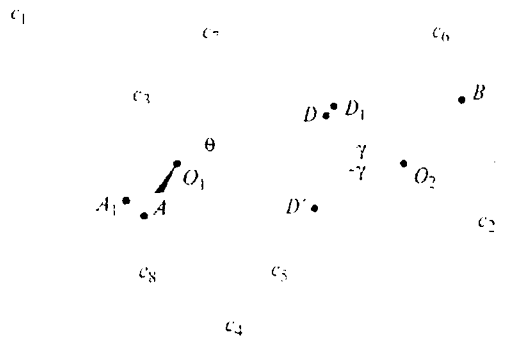

Fig. 2. Scheme of graphical construction used for determination of the angles of the mutual orientation of water molecules in the first coordination sphere and establishment of the sign of the angle γ.

Figure 2 illustrates one of the most convenient schemes for $\delta_1 < 0$. The absolute value of the angle γ is immediately calculated:

$$\cos\gamma = [(r_{OH})^2 + (r^{1m}{}_{OO})^2 - (r^{1m}{}_{OH})^2]/(2r_{OH}r^{1m}{}_{OO}),$$

but determination of its sign requires some additional operations. To make the calculations less labor-consuming, one should first obtain a graphical solution of the problem (see Fig. 2), which allows rejection of one intersection point for each pair of circumferences, except for the pair c_5—c_2.

Graphical construction and corresponding calculations are carried out as follows.

1. Circumscribe a circumference c_1 of radius $R_1 = r^{1m}{}_{OO}$ with its center at an arbitrary point O_1, which coincides with the center of the O atom of molecule 1.

2. Choose a point O_2 on the circumference c_1 which coincides with the center of the O atom of molecule 2, and circumscribe a circumference c_2 of radius $R_2 = r_{OH}$ with its center at point O_2.

3. Circumscribe a circumference c_3 of radius R_3 equal to the projection of r_{OH} on the drawing plane in which molecule 2 lies,

$$R_3 = r_{OH}\cos[\alpha(H-O-H)/2],$$

with its center at point O_1.

4. Circumscribe a circumference c_4 of radius R_4 equal to the projection of $r^{2m}{}_{OH}$ on the same plane,

$$R_4 = \{(r^{2m}{}_{OH})^2 - \{r_{OH}\sin[\alpha(H-O-H)/2]\}^2\}^{1/2},$$

with its center at point O_2.

The circumferences c_4 and c_3 intersect at a point A, which fixes the coordinates of the projections of the atoms H(3) and H(4) on the drawing plane.

5. Circumscribe a circumference c_5 of radius $R_5 = r^{1m}{}_{OH}$ with its center at point O_1. The circumferences c_5 and c_2 intersect at points D and D', one of which corresponds to the actual position of the H(1) atom (see Fig. 1, *a*).

6. Circumscribe a circumference c_6 of radius $R_6 = r^{2m}{}_{OH}$ with its center at point O_1, which intersects the circumference c_2 at point B. This allows determination of the sign of the angle γ using the H—O—H angle known from the model.

7. To check the self-consistency of the data obtained in computer simulation, let us circumscribe a circumference c_7 of radius R_7 equal to the projection of $r^{1m}{}_{HH}$ on the drawing plane,

$$R_7 = \{(r^{1m}{}_{HH})^2 - \{r_{OH}\sin[\alpha(H-O-H)/2]\}^2\}^{1/2},$$

with its center at point O_1.

Ideally, the circumferences c_2 and c_7 should intersect at point D. Actually, they intersect at point D_1, which allows introduction of the second self-consistency parameter, δ_2 (the angle $\alpha(D-O_2-D_1)$).

8. Circumscribe a circumference c_8 of radius R_8 equal to the projection of $r^{2m}{}_{HH}$ on the drawing plane,

$$R_8 = \{(r^{2m}{}_{HH})^2 - \{r_{OH}\sin[\alpha(H-O-H)/2]\}^2\}^{1/2},$$

with its center at point B. The circumference c_8 intersects the circumference c_3 at point A_1, which allows introduction of yet another self-consistency parameter, δ_3 (the angle $\alpha(A-O_1-A_1)$), since, ideally, points A and A_1 should coincide.

The parameters δ_2 and δ_3 are used in assessing the accuracy of determination of the angles γ and θ:

$$\gamma = [\beta_1(O_1-O_2-D) + \beta_2(O_1-O_2-D_1)]/2\pm\delta_2/2,$$

$$\theta = \pi - [\beta_3(O_2-O_1-A) + \beta_4(O_2-O_1-A_1)]/2\pm\delta_3/2.$$

If $\delta_1 = 0$, we immediately get $\gamma = 0$, while other operations remain the same as those described above. However, if $\delta_1 > 0$, we cannot determine the position of point D_1, since in this case the circumferences c_5 and c_2 share no points.

Results and Discussion

The calculated values of the non-self-consistency parameters of RDF, the angles γ_m and θ_m, as well as their differences $\gamma - \gamma_m$ and $\theta - \theta_m$ for several model pair potentials are listed in Table 1 (for the standard notations of the potential functions and their parameters, see Refs. 8—11). It is now required to ascertain whether the values found in this work correlate with other parameters obtained in computer simulation. First of all, let us elucidate the effect of changes in the mutual orientation of the nearest molecules, which are due to the transfer of two water molecules from the gas to condensed phase and responsible for the nonzero differences $\gamma - \gamma_m$ and $\theta - \theta_m$, on the distance (r_{13}) between the first and the third molecule, the latter being in the second coordination sphere of the former.[10,11] In computer simulation, r_{13} becomes $r^{2m}{}_{OO}$ and θ_m becomes θ. As can be seen in Fig. 3, there is no correlation between the differences $r^{2m}{}_{OO} - r_{13}$ and $\theta - \theta_m$. This confirms the conclusion drawn earlier[10,11] that the compositions of the first and second coordination spheres can be to some extent different from each other. That is why the values $g^{1m}{}_{OO}$ and $g^{2m}{}_{OO}$ for different models of water (a total of 31 models were considered) do not correlate,[11] which seems to be quite surprising at first glance.

Even a very simple analysis of the values of the angles θ and γ leads to intriguing conclusions. First of all, noteworthy is that these values do not correlate (the plot is not shown). On the other hand, an increase in θ leads to an increase in the Coulomb repulsion between the

Table 1. Parameters δ_1—δ_3 of the non-self-consistency of RDF, the equilibrium values of the angles γ_m and θ_m (see Fig. 1, *a*), and their changes $\gamma - \gamma_m$ and $\theta - \theta_m$ due to manybody effects

Model	Reference	δ_1/Å	δ_2	δ_3	γ_m	$\gamma - \gamma_m$	θ_m	$\theta - \theta_m$
			deg					
SRWK2	10	−0.0042	2.5	−10.1	8.0	3.1	91.0	−21.9
TIP3P	10	−0.1320	14.7	−5.1	−4.0	11.7	21.0	44.3
SPC2	10	−0.0330	8.4	−3.9	−2.0	14.2	23.0	36.6
Watts	4	−0.0400	15.5	−11.7	−3.2	−16.6	19.7	47.1
RWK1	4	−0.0272	1.0	4.2	4.0	11.1	67.4	2.7
RWK2	4	−0.0072	10.3	−15.5	2.4	3.4	52.6	9.8
BNS	4	−0.0600	7.9	−12.3	0.0	16.0	55.0	−2.5
RWL	4	−0.0300	10.0	−16.6	2.5	9.0	25.8	35.6
ST2	4	−0.0400	4.3	−1.4	−1.0	14.1	52.0	12.2
HF	4	−0.0470	7.6	−12.8	5.5	20.3	49.4	15.5
MCY	4	−0.0572	4.1	−25.4	4.0	12.3	37.1	20.5
TIP4P	12	−0.2170	8.9	−21.1	1.0	34.0	48.0	5.3
TIPS2	12	−0.1049	2.2	−10.9	1.0	21.1	47.0	9.8
BF	12	−0.1247	6.4	−20.0	2.0	21.9	52.0	12.3
TIP3P	12	−0.1132	4.6	−3.5	−4.0	27.0	21.0	45.1
SPC	12	−0.0060	4.8	−3.6	−3.0	8.1	21.0	38.6
ST2	12	−0.0295	5.1	−4.4	−1.0	12.3	52.0	12.3
ST2	13	−0.0600	4.2	−1.4	−1.0	11.2	52.0	14.2
DM	13	0.0700	—	19.4	0.0	22.8	55.0	20.3
MP	13	−0.0600	1.3	−5.4	−2.0	13.5	24.0	34.1
MCY	13	−0.0272	7.4	−14.0	4.0	7.1	37.1	20.5
ST4	14	−0.005	9.0	−5.9	0.0	15.6	66.0	6.9
Wall	15	−0.1270	8.0	−8.3	−4.0	26.6	22.0	37.8

H atoms owing to shortening of the corresponding interatomic distance. This can be compensated by an increase in the angle γ to the point where a decrease in the O(1)...H(1) Coulomb attraction can be compensated by an increase in the H(3)...O(2) and H(4)...O(2) Coulomb attraction (see Fig. 1, *a*). Additionally, in computer simulation for the models considered the maximum probability of finding the nearest neighbor corresponds to a distance r^{1m}_{OO} such that $r^{1m}_{OO} > r_m$ (see Fig. 1, *b*). Hence, in the condensed phase the global potential energy minimum is shifted along the r axis with respect to the corresponding minimum in the gas phase (r_m). Probably, the value r_σ corresponding to $U(r) = 0$ is also shifted toward longer distances. This seems to be the reason why $g_{OO}(r) \equiv 0$ already at $r > r_\sigma$ (see Fig. 1, *b*). All these changes are due to manybody interactions in the liquid phase; it seems that we are the first who succeeded in revealing their role at a microscopic level using the angles θ and γ.

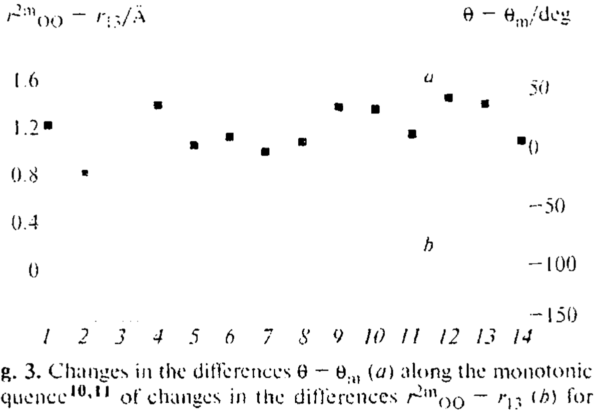

Fig. 3. Changes in the differences $\theta - \theta_m$ (*a*) along the monotonic sequence[10,11] of changes in the differences $r^{2m}_{OO} - r_{13}$ (*b*) for different model potentials: DM (*1*), SRWK2 (*2*), Ev (*3*), Wall (*4*), RWK1 (*5*), TIPS2 (*6*), BNS (*7*), TIP4P (*8*), SPC2 (*9*), MP (*10*), ST2 (*11*), TIP3P (*12*), SPC (*13*), and ST4 (*14*).

Despite the fact that there is no correlation between g^{1m}_{OO} and g^{2m}_{OO},[11] one can assume that the structure and dynamics of the molecules in the first and second coordination spheres are related, though in a complex manner. On the one hand, the values g^{1m}_{OO} do not correlate with the angles θ referring to the first coordination sphere; on the other hand, there is a correlation between the θ and g^{2m}_{OO} values, which characterize the second coordination sphere (Fig. 4, the correlation coefficient is 0.62). From physical considerations it is clear that the probabilities of finding neighbors O(1)...O(2) and O(1)...H(1), O(1)...H(2), O(2)...H(3), and O(2)...H(4) (see Fig. 1, *a*) are closely related with one another. It is convenient to use the ratio of the first and second peak heights for the RDF $g_{OH}(r)$, $g_{12} \equiv g^{1m}_{OH}/g^{2m}_{OH}$, as a generalized characteristic of these probabilities. We found that similarly to g^{1m}_{OO} the parameter g_{12} correlates neither with θ nor with γ, which indicates its "insensitivity" to the mutual orientation of the molecules in the first coordination sphere. At the same time, a correlation between g^{1m}_{OO} and g_{12} does exist (Fig. 5, the correlation coefficient is 0.93).

The calculated values of the angles θ and γ are the most probable time-average (or, by ergodicity of the system, ensemble-average) values. For a given pair of

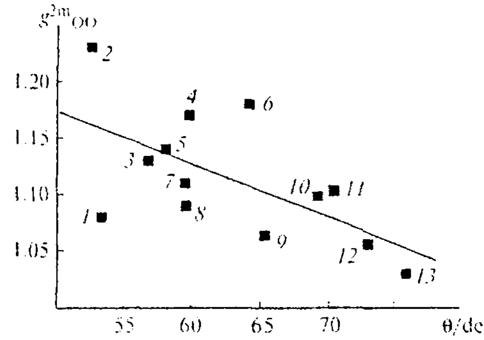

Fig. 4. Correlation between g^{2m}_{OO} and θ (the correlation coefficient is 0.62) for different model potentials: TIP4P (*1*),[12] BNS (*2*),[4] TIPS2 (*3*),[12] Wall (*4*),[15] MP (*5*),[13] ST2 (*6*),[4] SPC2 (*7*),[10] SPC (*8*),[12] TIP3P (*9*),[10] SRWK2 (*10*),[10] RWK1 (*11*),[4] ST4 (*12*),[14] and DM (*13*).[13]

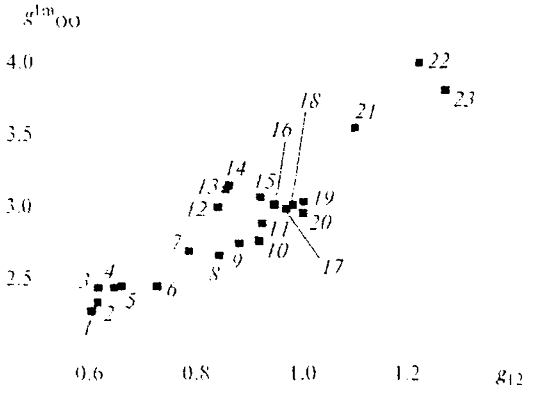

Fig. 5. Correlation between g^{1m}_{OO} and g_{12} (the correlation coefficient is 0.93) for different model potentials: DM (*1*),[13] RWL (*2*),[4] HF (*3*),[4] MCY (*4*),[13] MCY (*5*),[4] RWK2 (*6*),[4] BF (*7*),[12] BNS (*8*),[4] TIP3P (*9*),[12] SPC (*10*),[12] TIP4P (*11*),[12] ST4 (*12*),[14] ST2 (*13*),[4] ST2 (*14*),[13] ST2 (*15*),[4] TIPS2 (*16*),[12] Wall (*17*),[15] SRWK2 (*18*),[10] SPC2 (*19*),[10] TIP3P (*20*),[10] Watts (*21*),[4] RWK1 (*22*),[4] and MP (*23*).[13]

molecules they are retained over the course of the mean lifetime of the hydrogen bond (~10 ps). Deviations from these values are due to simultaneous changes in the three angles θ, γ, and ψ (see Fig. 1, *a*) and the distance O(1)...O(2) (translational vibration ν_2). For a water dimer in the gas phase, the frequencies of these vibrations can be assessed reliably.[10] We calculated all four frequencies (ν_2, ν_θ, ν_γ, and ν_ψ) and ascertained that there is no correlation between any of them and monotonic sequences of (i) the differences $\theta - \theta_m$ and $\gamma - \gamma_m$ and (ii) the values g^{1m}_{OO} and g^{2m}_{OO}. On the other hand, the assumption that the dynamic behavior of molecules in a local volume under consideration has no effect on the state of molecules in the nearest local volume casts some doubt. We believe that the search for vibrational modes corresponding to large-amplitude motions instead of the calculated ν_i modes, which correspond to small-amplitude motions, provides some way out. Such "large-amplitude" modes can be associated with the preparation of molecule 2 for escape from the nearest environment of molecule 1.

This work is the last in a series of studies[9–11] devoted to derivation of a new parametrization of the potential functions of pair interaction. Summing up, two major conclusions can be drawn, which are significant for the next step of investigations.

It is impossible to judge the efficiency of the functions $U(r)$ from the absolute values of the differences $\theta - \theta_m$ and $r^{2m}_{OO} - r_{13}$. It is of much greater importance to modify the analytical form of the function $U(r)$ in order to get a correct response to the manybody effects rather than to "guess" it in order to obtain zero differences. It is this approach that can provide agreement between the results of computer simulation and those obtained in physical experiments.

Weak correlation between the events in the first and second coordination spheres also requires modification of the analytical form of the function $U(r)$ in order to correct its behavior at distances $r > r_m$ as compared to that of the functions shown in Fig. 1, *b*.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32064).

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Received February 16, 2000;
in revised form May 30, 2000