

# Computer Simulation of the Structure of Water Clusters Containing Absorbed Ethane Molecules

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**Abstract**—The structure of water clusters that have absorbed ethane molecules is studied by the molecular dynamics method. Structural analysis is performed by the construction of Voronoi polyhedra for oxygen atoms and hybrid polyhedra whose centers coincide with the centers of oxygen atoms and the faces are formed according to the positions of hydrogen atoms. The  $(\text{H}_2\text{O})_{20}$  cluster can retain no more than four ethane molecules remaining at the same time stable. When a water cluster adds more than four ethane molecules, the volumes of Voronoi polyhedra acquire values close to the volume per molecule in the bulk liquid water. As the number of ethane molecules in a water cluster increases, the number of hydrogen atoms adjacent to oxygen, as well as the average number of units in cyclic formations composed of hydrogen atoms, also increases. In this case, the number of H–O–H angles formed by the nearest geometric neighbors close to  $89^\circ$  becomes dominant. The coefficient of nonsphericity reflecting the local arrangement of hydrogen atoms around the oxygen atoms decreases as the  $\text{C}_2\text{H}_6$  molecules are added to water cluster and approaches to the value of this coefficient for the rhombic dodecahedron in the case of adsorption of six ethane molecules.

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## INTRODUCTION

Water is a classical example of substance with a hydrogen bond. Hydrogen bonds are formed due to electrostatic and polarization interactions and perform one of the key biological functions. Bonds with the participation of hydrogen are also formed in other liquids, for example, in methanol. The presence of a bond network affects the structural characteristics of these liquids, in particular, radial distribution function that determines the range of spatial correlations. The mixing of two liquids with different types of H-bonds gives rise to the “competition” between such bonds.

Upon the hydration of hydrocarbon molecules, the hydrophobic effect is observed, which can be considered in the first approximation as the formation of the “shell” of free space in water around the hydrocarbon molecule. Regardless of the presence of the hydrophobic effect, clusters composed of water and hydrocarbon molecules can be formed in the gaseous phase. This is confirmed in experiments with expanding supersonic jet [1]. The possibility of the addition of  $\text{C}_6\text{H}_6$  molecule to the  $(\text{H}_2\text{O})_9$  cluster due to the formation of one hydrogen bond was revealed by the IR spectroscopy and the density functional theory [1]. In the process of cluster cooling, its H-bond with the  $\text{C}_6\text{H}_6$  molecule drifted from one water molecule to another. Because only one hydrogen bond is formed between the water cluster and the hydrocarbon molecule, whose range is limited by the region with a dimension of 0.35 nm, the shape of the hydrocarbon molecule is not the determining factor for its absorption by the cluster. Consequently, it can be

expected that water clusters can also capture molecules of nonaromatic hydrocarbons, including saturated compounds. Physicochemical properties of water clusters are mainly determined by their structure. The molecule of hydrocarbon added to the cluster violates the network of hydrogen bonds. Because of the small size of a cluster, local changes in the network of hydrogen bonds can be transformed into global changes with an increase in the number of absorbed molecules.

In the models of classical molecular dynamics (MD), Coulombic interaction between the molecules of water and hydrocarbons is set by the point charges distributed over the molecules. The contours of electron density in the models of extended systems can be revealed by the construction of Voronoi polyhedra (VP); moreover, two procedures for constructing VP can be used [2]. In the first case, the system of points that underlies the procedure of space discretization is formed by the centers of water molecule mass; in the second case, by the centers of all atoms, i.e., by oxygen and hydrogen. In both cases, similar contours of charge density were obtained. However, for the compensation of excess volume brought in by polyhedra constructed on the hydrogen centers, the VP faces were constructed for fictitious neighbors of hydrogen atoms shifted from the center to the distance of 60% of their true distance to the center.

For a system with a limited number of degrees of freedom, the VP can be constructed only for its interior part. However, even in this case, large changes in the VP shape should be expected if the number of points

determining the space discretization is small. The manifestation of “boundary” effects, i.e., effects related to a deficiency of points at the periphery, makes the VP substantially elongated and their volume greatly increases. One of the procedures for the construction of completed VP in such situation can be the use of fictitious point (the center of cluster mass) in the space discretization [3]. The VP for such fictitious point can usually be constructed even if the total number of points (molecules) is smaller than ten (however, it should necessarily be larger than four) [4].

In the case of polyatomic molecules, the other way can be employed for the detailed analysis of the structure of a cluster. The local structure can be analyzed using convex polyhedra, for the construction of which the centers of all atoms are used. One kind of atom act as the centers of such polyhedra and the atoms of another kind act as their nearest neighbors, which set the positions of polyhedron faces. For example, in the case of water, it is convenient to use oxygen atoms as the centers and to choose hydrogen atoms as their nearest neighbors. Such hybrid polyhedra (HP) are easy to construct because the amount of hydrogen atoms is twice as large as that of oxygen atoms. However, the HP are not Voronoi polyhedra because, as a whole, they do not completely (without voids and overlaps) fill the space occupied by molecules. The VP faces present the cyclic formations composed of oxygen atoms, whereas the HP faces present the rings composed of hydrogen atoms.

The aim of this work is to study the absorption of ethane molecules by water clusters using the MD method and to determine the influence of these hydrocarbon molecules on the stability and structure of ultradispersed aqueous system.

## COMPUTER MODEL

Molecular dynamic simulation was performed on the basis of the DC model of water [5] obtained by the modification of a rigid four-center TIP4P model. The geometry of H<sub>2</sub>O molecule corresponds to the experimental parameters of water molecule in the gaseous phase:  $r_{OH} = 0.09572$  nm and the H–O–H angle is equal to 104.5° [6]. Electric charges ( $q_H = 0.519e$  and  $q_M = -1.038e$ ) are located in the centers of H atoms and in point  $M$  at the bisectrix of HOH angle at a distance of 0.0215 nm from the center of the oxygen atom. The values of charges and the position of point  $M$  are chosen so as to reproduce the experimental values of the dipole and quadrupole moments of water molecules [7, 8], as well as *ab initio* calculated energy of a dimer and the characteristic distance within it [9]. The stabilization of tetrahedral structure is determined mainly by the short-range Lennard-Jones (LJ) interaction through the oxy-

gen atoms. Polarizability  $\alpha_i$ , which is needed to calculate nonadditive energy of polarization interaction

$$U_{\text{pol}}(\mathbf{R}_{1\dots N}) = -1/2 \sum_i^N \mathbf{E}_i^0 \mathbf{d}_i^{\text{ind}}, \quad \mathbf{d}_i^{\text{ind}} = \alpha_i \mathbf{E}_i \quad (1)$$

and the induced force acting on a molecule  $k$  [10]

$$\mathbf{f}_k^{\text{ind}}(\mathbf{R}_{1\dots N}) = -\nabla_k U_{\text{pol}} = \sum_{i=1}^N \mathbf{d}_i (\nabla_k \mathbf{E}_i^0) + \sum_{i \neq k}^N \nabla_k (\mathbf{d}_i \mathbf{T}_{ik}),$$

is referred to point  $M$ . In these equations,  $R_i$  is the radius-vector of point  $M$  of  $i$ th molecule,  $\mathbf{E}_i^0$  is the strength of Coulombic field induced by fixed partial charges,  $\mathbf{E}_i$  is the strength of field induced in center  $i$  by both the charges and interaction between induced dipole moments and these charges, and  $\mathbf{d}_i^{\text{ind}}$  is the induced dipole moment of  $i$ th molecule; dipole tensor  $\mathbf{T}_{ij}$  is defined by the expression

$$\mathbf{T}_{ij} = \frac{1}{4\pi\epsilon_v} \frac{1}{r_{ij}^3} \left[ \frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - 1 \right],$$

where  $\epsilon_v$  is the electric constant.

The additive component of ethane–water and ethane–ethane interactions was presented in the form of atom–atom functions set by the sum of repulsive, dispersive, and Coulombic contributions

$$\Phi(r_{ij}) = b_i b_j \exp[-(c_i + c_j)r_{ij}] - a_i a_j r_{ij}^{-6} + \frac{1}{4\pi\epsilon_v} \frac{q_i q_j}{r_{ij}},$$

where parameters  $a_i$ ,  $b_i$ , and  $c_i$  of the potential describing these interactions were taken from [11]. Electric charges  $q_C^{\text{ethane}} = -0.0939e$  and  $q_H^{\text{ethane}} = 0.0313e$  were assigned to C and H atoms in ethane molecule, respectively. The polarizability of C<sub>2</sub>H<sub>6</sub> molecule is referred to the center of its mass (point  $M$ ). The induced dipole moment of ethane molecule was determined using the second relation of Eq. (1) and its average value turned out to be close to the experimental value of 0.3 D [12].

The C<sub>2</sub>H<sub>6</sub> molecule has a stable conformation, in which free rotation around C–C bond is retarded; i.e., the molecule exists precisely in such conformation [13]. Distinct presentation of this conformation is given by the projection of C<sub>2</sub>H<sub>6</sub> molecule on the plane perpendicular to C–C bond (in the direction indicated by the arrow in Fig. 1). Three solid lines diverging at an angle of 120° from center  $C$  (the right-hand side of the figure) denote the links formed with carbon atom nearest to the observer; dotted lines denote the links with a remote C atom. The present model uses the following

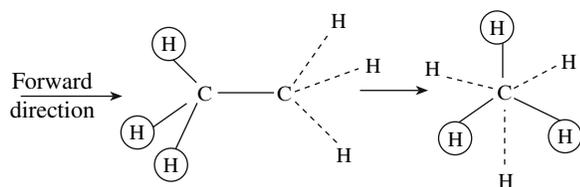


Fig. 1. Stable conformation of the ethane molecule.

characteristic distances between atoms in  $C_2H_6$  molecule:  $r_{CC} = 0.154$  nm and  $r_{CH} = 0.11$  nm [12]. In view of the symmetric distribution of electric charge in the  $C_2H_6$  molecule, its permanent dipole moment is equal to zero; however, an ethane molecule possesses a high polarizability ( $2.6 \text{ \AA}^3$ ) that is higher than that of water molecule ( $1.49 \text{ \AA}^3$ ) [12].

Equations of the motion of molecules were solved using the fourth-order Gear method [25]. Time step  $\Delta t$  of integration was  $10^{-17}$  s. The equilibrium state of  $(H_2O)_{20}$  water cluster that do not contain admixture molecules at  $T = 233$  K was originally established in the preliminary molecular dynamic calculation lasted for  $2 \times 10^6 \Delta t$ . Hereafter, the configuration of water cluster at time moment 20 ps was used as an initial configuration to simulate the  $(C_2H_6)_i(H_2O)_{20}$  system,  $1 \leq i \leq 6$ . No more than six ethane molecules were added to the water cluster by their original displacement to the regions admissible for interatomic interactions. Added  $C_2H_6$  molecules were originally arranged so that the least distance between atoms in ethane molecule and atoms of water molecules was no less than 0.6 nm. The  $C_2H_6$  molecule was placed so that its C–C axis would coincide with the ray connecting the center of the mass of  $(H_2O)_{20}$  cluster with the center of the mass of this molecule. Cut-off radius  $r_c$  of all interactions in the model amounted to 0.9 nm. In the case when more than one  $C_2H_6$  molecule was added to the water cluster, their C–C axes were located on the axes of rectangular coordinate system whose center coincided with the center of the mass of water cluster. The coordinate axes were filled successively with  $C_2H_6$  molecules; for example, in the presence of two ethane molecules, they were arranged on the same coordinate axis, though on different sides of the center of cluster mass. The newly formed system was put in equilibrium at  $0.6 \times 10^6 \Delta t$  time interval; then, the required physicochemical properties were calculated for the  $2.5 \times 10^6 \Delta t$  interval. We employed the scheme of the joint solution of equations describing the translational and rotational motions of molecules proposed by Sonnenschein [15]. This scheme was constructed on the use of Rodrigues–Hamilton parameters [16].

One of the advantages of the employed polarization potential of the interaction is the possibility of variations in the value of the dipole moment of every water molecule, irrespective of its surrounding charges. In order to compare our model with one of the most popular models

of unpolarized water molecules (SPC model), we calculated the excess (relative to the ideal gas) free energy  $\Delta G$  of an extended system ( $T = 273$  K) that is represented by 54 water molecules placed in the cubic cell [17]. Results of this calculation ( $\Delta G = -26.9$  kJ/mol) are in good agreement with the value of excess free energy for the SPC model ( $\Delta G = -25.1$  kJ/mol [18]). In our model, the  $\Delta G(t)$  function decreases more slowly at the initial part of calculation and increases more slowly at the final calculation stage.

A detailed analysis of the cluster structure was performed on the basis of the construction of Voronoi and hybrid polyhedra. The VP and HP were constructed around five oxygen atoms located closer to the center of cluster mass for every thousand time steps. Since the number of hydrogen atoms in a water cluster is twice as much as that of oxygen atoms, the probability of the construction of a completed polyhedron is higher in the case of VP. Moreover, this HP will have a larger number of faces and its volume will be more spherical than for VP. The construction of polyhedra was performed around the oxygen atoms of water molecules; however, the neighbors that set the position of faces can also be the centers of the mass of  $C_2H_6$  molecules or hydrogen atoms of ethane molecules in the cases of VP and HP, respectively.

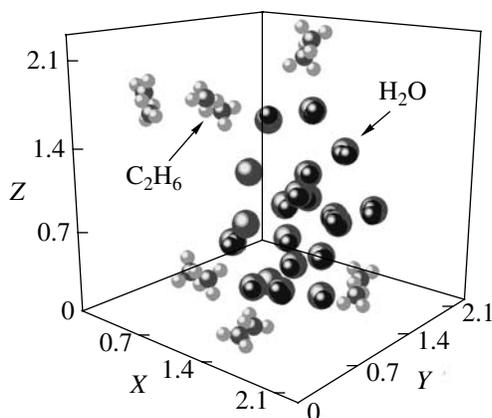
The degree of the uniformity of molecule distribution with respect to central molecule characterizes the nonsphericity of polyhedron determined by the expression [19]

$$\eta = \frac{S^3}{36V^2\pi},$$

where  $S$  is the surface area of polyhedron and  $V$  is its volume. By definition,  $\eta$  is equal to 1, 1.35, and 1.91 for the sphere, rhombic dodecahedron (VP with face-centered cubic lattice), and cube (VP with simple cubic lattice), respectively. For the VP of hexagonal ice, the nonsphericity is equal to 2.25 [20]; for the ideal tetrahedron, to 3.31.

When constructing HP, hydrogen atoms of the same  $H_2O$  molecule as the oxygen atom (the center of polyhedron) were excluded as neighbors. In order to exclude small-scale thermal fluctuations, i.e., in order to pass to the analysis of the averaged structure, sufficiently small faces were excluded in polyhedra. This was achieved by the removal of faces with lengths of  $l < 0.5\bar{l}$ , where  $\bar{l}$  is the mean length of the polyhedron face. The use of such a procedure in the construction of HP, in many cases, makes it possible to remove the double bonds of one molecule with the considered oxygen atom. Let us call polyhedra with excluded small faces simplified polyhedra.

The calculations were performed with a PENTIUM-IV computer operating at a processor clock frequency of 3.8 GHz. The calculation with time  $10^6 \Delta t$  for



**Fig. 2.** Configuration of  $(\text{C}_2\text{H}_6)_6(\text{H}_2\text{O})_{20}$  cluster corresponding to a time of 25 ps. Coordinates of molecules are presented in nm.

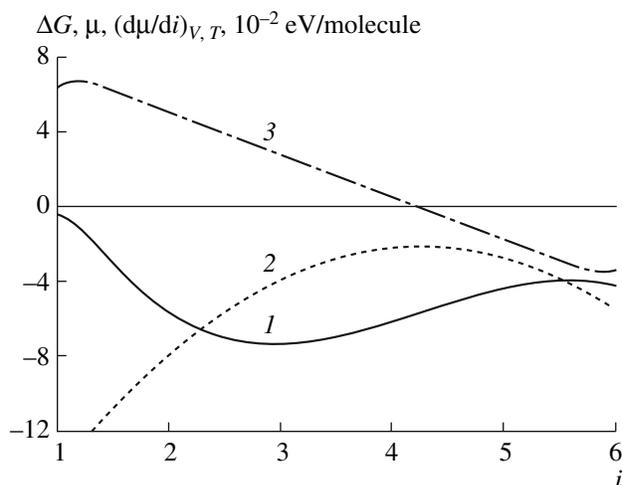
$(\text{C}_2\text{H}_6)_6(\text{H}_2\text{O})_n$  cluster took about 45 h of computer time.

## RESULTS OF CALCULATIONS

The configuration of the  $(\text{C}_2\text{H}_6)_6(\text{H}_2\text{O})_{20}$  cluster at a time of 25 ps is shown in Fig. 2. As is seen, the  $\text{C}_2\text{H}_6$  molecules were not mixed with  $\text{H}_2\text{O}$  molecules. Five out of six  $\text{C}_2\text{H}_6$  molecules are in close contact with water molecules of  $(\text{H}_2\text{O})_{20}$  cluster. The sixth  $\text{C}_2\text{H}_6$  molecule (at the top left) is connected with a cluster via the other ethane molecule. The orientation of C–C axis is not matched to the direction set originally and is not directed tangentially to the aggregate surface, as is observed for linear acetylene molecules. The same water molecule can form hydrogen bonds with two different  $\text{C}_2\text{H}_6$  molecules, as well as one ethane molecule can interact with two water molecules via the H bond.

The behavior of excess free energy  $\Delta G$ , chemical potential  $\mu$ , and the derivative  $(\partial\mu/\partial i)_{V,T}$  for the  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters with the variations in number  $i$  of ethane molecules in a cluster is presented in Fig. 3. The  $\Delta G(i)$  dependence has the minimum in the vicinity of  $i = 3$ ; the  $\mu(i)$  function, the maximum near the  $i = 4$ . At  $i > 4$ , derivative  $(\partial\mu/\partial i)_{V,T}$  becomes negative, which testifies to the thermodynamic instability of water clusters that have absorbed more than four ethane molecules.

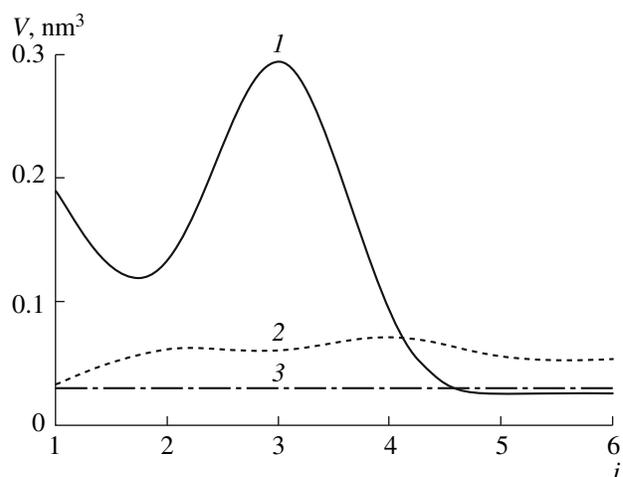
Because of the deficiency of the nearest neighbors, Voronoi polyhedra for small clusters (even when they are constructed for the centers of molecules near the centers of cluster mass) appeared to be elongated, i.e., they have substantial volume. As the cluster grows due to the addition of  $\text{C}_2\text{H}_6$  molecules, large fluctuations of average volume  $\bar{V}$  of VP are observed (Fig. 4). However, when more than four ethane molecules are added to the water cluster, the average volume  $\bar{V}$  of VP sig-



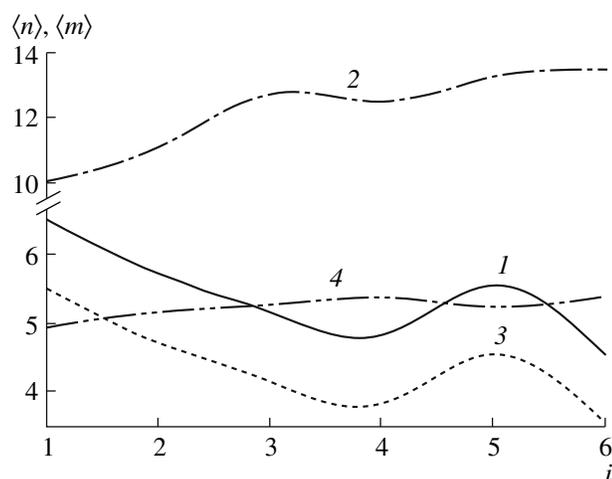
**Fig. 3.** Dependences of (1) excess free energy  $\Delta G$ , (2) chemical potential  $\mu$ , and (3) coefficient of stability  $(\partial\mu/\partial i)_{V,T}$  on the number of  $i$   $\text{C}_2\text{H}_6$  molecules in  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters.

nificantly decreases, reaching a value that corresponds to the volume per molecule of liquid water [12]. The  $\bar{V}$  value of hybrid polyhedra is not subjected to any large fluctuations due to the addition of ethane molecules to a cluster. At  $i > 4$ , the  $\bar{V}$  values of HP become larger than corresponding volumes for common VP constructed for the centers of oxygen atoms.

The dependences of the average number  $\bar{n}$  of faces in simplified polyhedra for  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters and the average number  $\bar{m}$  of sides of faces on the number  $i$  of captured  $\text{C}_2\text{H}_6$  molecules are shown in Fig. 5. Generally, in the case of simplified VP, the  $\bar{n}(i)$  and  $\bar{m}(i)$



**Fig. 4.** Average volumes of (1) Voronoi and (2) hybrid polyhedra as a function of  $i$  and (3) the volume per molecule of liquid water at 298 K [12].

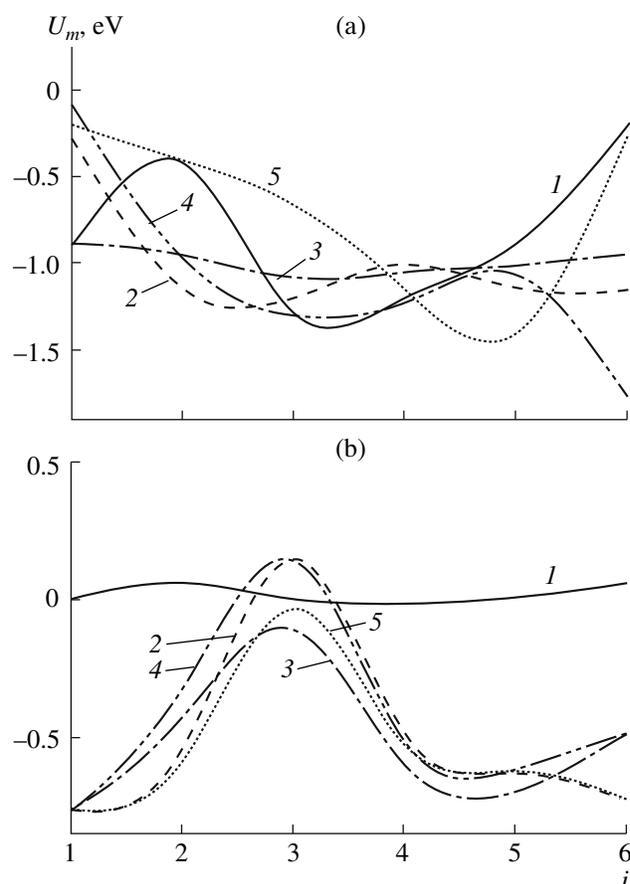


**Fig. 5.** Average number of faces  $\bar{n}$  in (1) simplified Voronoi polyhedra (SVP) and (2) simplified hybrid polyhedra (SHP) and the average number of sides  $\bar{m}$  in (3) SVP and (4) SHP faces as functions of  $i$  for  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters.

dependences decrease with an increase in  $i$  (curves 1 and 3); however, at  $i = 5$ , they are characterized by the maximum. On the contrary, for simplified HP, the  $\bar{n}(i)$  and  $\bar{m}(i)$  functions tend to increase. For all of considered  $i$  values, the  $\bar{n}$  and  $\bar{m}$  values are smaller for simplified VPs than for analogous HP.

Energies  $U_m$  for five  $m$ -membered rings formed by oxygen atoms in  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters are shown in Fig. 6a as functions of  $i$ . Five-membered rings are the most stable with respect to the addition of  $\text{C}_2\text{H}_6$  molecules; the largest scatter in the values of energy was obtained for six-membered rings. At  $i = 6$ , these rings demonstrated the lowest (among other  $m$ -membered rings) values of energy. At  $i = 1$ , they have one of the largest values of energy. Three- and seven-membered rings in water clusters that absorbed six ethane molecules are also characterized by the largest values of energy.

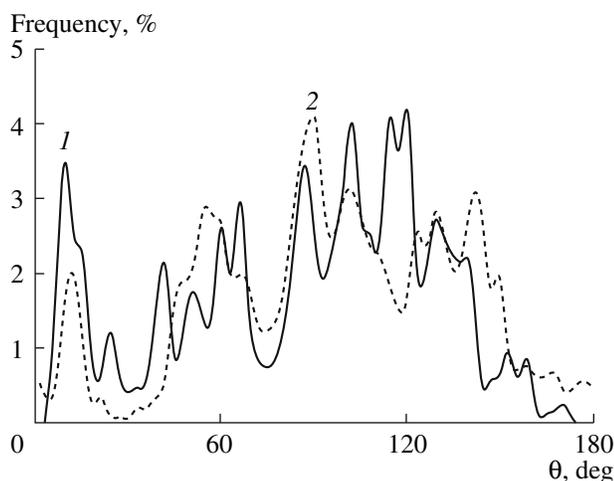
The rings formed by hydrogen atoms give one-type  $U_m(i)$  dependences (Fig. 6b). Typical pattern of  $U_m(i)$  function does not extend to the rings formed by three hydrogen atoms. In this case, the  $U_m(i)$  function has steadily large values. Note the presence of a maximum in the  $U_m(i)$  dependence at  $i = 3$  for the rings of other types. Moreover, the  $U_m(i)$  values at the point of the maximum are positive for four- and six-membered rings. The presence of this maximum indicates that the addition of a third ethane molecule to a cluster tends to produce an energy-stressed state in a cluster. This state is determined by the distribution of hydrogen atoms, i.e., by the energy-unfavorable orientation of molecules. However, after one more  $\text{C}_2\text{H}_6$  molecule is added to the cluster, the energy-stressed state caused by the approach of hydrogen atoms vanishes.



**Fig. 6.** Energies of  $m$ -membered rings formed by (a) oxygen and (b) hydrogen atoms in  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters as functions of  $i$  at various  $m$ : (1) 3, (2) 4, (3) 5, (4) 6, and (5) 7.

The notion of the mutual arrangement of neighboring atoms (molecule) results in the angular distribution of the nearest geometric neighbors. The  $\theta$  angles considered here are formed, in one case, by the paired set of oxygen atoms and the center of the studied atom (oxygen), while in the other case, they are formed by the paired set of hydrogen atoms located in the vicinity of the same center. Figure 7 demonstrates the angular distributions ( $\theta$  distributions) of nearest geometric neighbors determined when constructing VP and HP for the  $(\text{C}_2\text{H}_6)_6(\text{H}_2\text{O})_{20}$  cluster. These spectra are characterized by a large number of peaks. Maximum values of  $\theta$  distributions are matched to angles  $119^\circ$  (VP) and  $89^\circ$  (HP). Note that the first peak at  $11^\circ$  in the  $\theta$  distribution for HP becomes noticeably weaker and the peak at  $119^\circ$  vanishes completely, giving way to the minimum. At the same time, when passing to HP, peaks at  $89^\circ$  and  $142^\circ$  become higher and a new peak emerges at  $55^\circ$ .

The coefficient of nonsphericity  $\eta$  reflecting the uniform arrangement of hydrogen atoms adjacent to oxygen atoms in the  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters decreases from 3.77 at  $i = 1$  to 1.49 at  $i = 6$  (Fig. 8). Among the ideal crystal packings and distributions of H atoms over



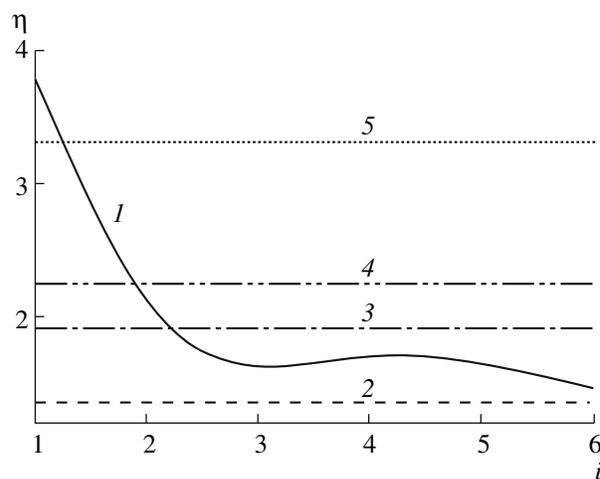
**Fig. 7.** Angular distributions of neighboring atoms of (1) oxygen and (2) hydrogen around the centers (oxygen atoms) in the  $(\text{C}_2\text{H}_6)_6(\text{H}_2\text{O})_{20}$  cluster.

the vertexes of geometric figures, the best correspondence with respect to  $\eta$  at  $i = 1$  is observed for the packing of ideal tetrahedrons ( $\eta = 3.31$ ); at  $i = 6$ , for face-centered cubic lattice ( $\eta = 1.35$ ). When the water cluster absorbs two ethane molecules, the value of the coefficient of nonsphericity is close to the value  $\eta = 2.25$  for the VP of hexagonal ice. At other  $i$  values, parameter  $\eta$ , which determines the arrangement of hydrogen atoms with respect to oxygen in  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters, is in between the values of coefficient  $\eta$  for the cube ( $\eta = 1.91$ ) and that for the rhombic dodecahedron ( $\eta = 1.35$ ).

## CONCLUSIONS

The dependence of the chemical potential of  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters on the number  $i$  of absorbed ethane molecules passes through the maximum at  $i = 4$ . The thermodynamic stability of  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters decreases with the addition of ethane molecules. When more than four  $\text{C}_2\text{H}_6$  molecules are added to the  $(\text{H}_2\text{O})_{20}$  cluster, the cluster becomes unstable (derivative  $(\partial\mu/\partial i)_{V,T} < 0$ ).

The analysis of the structure of  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters was performed on the basis on the construction of Voronoi and hybrid polyheda. Large fluctuations of the average VP volume and fairly steady values of the average HP volume are observed. Except for the case of  $i = 1$ , the values of the average HP volume is approximately twofold larger than the volume per molecule in the liquid water. The exclusion of small faces of polyheda permits us to pass to the analysis of their averaged structure. On average, every oxygen atom in these clusters is in the nearest neighborhood with 5–6 hydrogen atoms and 10–14 more remote oxygen atoms. Oxygen atoms in clusters form rings composed more often of 5–6 atoms. Four to five atoms are found with a high prob-



**Fig. 8.** Dependences of (1) the coefficient of nonsphericity for hybrid polyheda in  $(\text{C}_2\text{H}_6)_i(\text{H}_2\text{O})_{20}$  clusters and coefficient  $\eta$  for (2) rhombic dodecahedron, (3) cube, (4) the VP cell for hexagonal ice, and (5) ideal tetrahedron on number  $i$ .

ability in analogous rings of hydrogen atoms. In general, rings composed of 6 oxygen atoms and 5 hydrogen atoms are the most energy-favorable. For the nearest geometric neighbors, angles  $\angle\text{OOO} = 119^\circ$  and  $\angle\text{HOH} = 89^\circ$  are encountered most often. Unlike Voronoi polyheda, the coefficient of nonsphericity for hybrid polyheda has much lower values that are comparable to analogous characteristics for the VP of crystal lattices and regular tetrahedron. Moreover, coefficient  $\eta$  for the HP rapidly decreases when passing from the water cluster with one ethane molecule to the water aggregate containing two  $\text{C}_2\text{H}_6$  molecules. The  $\eta$  value changes insignificantly with further addition of ethane molecules to the cluster and is in between the  $\eta$  values for the rhombic dodecahedron and the cube.

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