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Full Articles

Lattice model of a polar liquid

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The molecular model of a polar liquid based on the lattice gas theory was used to study the liquid—gas phase equilibrium. In this theory, the key unknown variables are the probabilities of various mutual pair positions of the molecules. The molecules are considered as non-polarizable point dipoles. The intermolecular interaction potential includes a dipole—dipole component depending on the molecular orientation and the Lennard-Jones contribution stabilizing the system with dipole interactions. The theory provides qualitative agreement with experimental data on the water—vapor equilibrium.

Key words: dipole liquids, atom—atom approximation, dipole—dipole potential, Lennard-Jones potential, pair distribution function, isotherms, phase separation curves.

Molecules in solution interact with one another and with the solvent. Most often, solvents are dipole media, and calculation of their properties remains a topical task. Apart from the continual model in which the solution is considered as an extended continuous medium, increasing attention has recently been attracted by methods based on discrete models of the solvent, which characterize in more detail the molecular properties of the reaction systems at the microscopic level and do not require the use of macroscopic characteristics like the dielectric constant.[1—3] Therefore, study of the solvent properties is associated with calculation of many-body interactions and taking account of the real solution structure.

A molecular statistic approach to systems with polyatomic molecules where intermolecular interactions depend on the mutual orientation of molecules was developed.[4,5] Within the bounds of the discrete lattice gas model (LGM), this approach is implemented by the notion of quasisorts of particles. These are identical molecules of the same substance oriented in space in different ways. This system can be treated as a mixture of several substances, interaction between the particles in which depends on the mutual orientation of molecules.

The purpose of this work is to construct a thermodynamically uniform lattice model of an aqueous system occurring in equilibrium with its vapor. The model of water formulated earlier[6—8] was based on the use of the tetrahedral diamond structure as the lattice, and mean-field approximation was used to calculate the intermolecular energy between the nearest neighbors.

In this study, the intermolecular interactions are taken into account as a combination of electrostatic di-

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pole—dipole (DD) and non-electrostatic Lennard-Jones (LJ) contributions. The effects of temperature and water density on the probability of different pair orientations of molecules were studied. The LGM equations were solved in the quasichemical approximation The algebraic equations describing the equilibrium distribution of molecules are based on the use of the cluster approach, which is suitable for the investigation of the equilibrium and dynamic characteristics of the multicomponent mixtures.[9]

In the modern statistical methods such as molecular dynamics and Monte Carlo and integral equation methods and lattice models, molecules are considered as the sets of interacting atoms, and the choice of the force field model is the key issue. The optimal parameters of this model are determined by fitting the theoretical and experimental data. The use of lattice models in which the solution can be obtained faster and simpler than in other methods is suitable for determining the effect of intermolecular interaction on the thermodynamic properties of the compound and comparing various techniques of detailed consideration of the structure of particles, some of the techniques using a molecule consisting of atoms as the particle, some other using a point dipole or polarizable dipole with van der Waals interaction.

Discrete model of a dipole liquid. At the molecular level, the LGM takes into account the proper volume of the molecules and the interaction between them. The space occupied by the system of particles is split into elementary cells with the volume $v_0 = \lambda^3$, where λ is the lattice constant corresponding to the size of a molecule, which rules out double occupation of a cell with different molecules. The molecules are located in the units, *i.e.*, centers of cells. The number of nearest neighbors will be designated by z.

Consider the lattice model for a mixture of polyatomic molecules that takes into account the pair interaction potential describing the orientational direction of bonds in more detail.[6] The statistical sum Q_{lat} of a system with N units is specified by the expression

$$Q_{\text{lat}} = \sum_{f=1}^{N}\sum_{i=1}^{\Phi}\exp[-\beta H(\{\gamma^i_f\})],$$

$$H(\{\gamma^i_f\}) = \sum_{h=1}^{N}\sum_{j=1}^{\Phi}\nu^j_h\gamma^j_h - 0.5\sum_{r=1}^{R}\sum_{h,g_r}^{N}\sum_{j,m}^{\Phi}\varepsilon^{jm}_{hg}(r)\gamma^j_h\gamma^m_{g_r},$$

$$\nu^j_h = -\frac{\ln(F^j_h)}{\beta},\ \beta = \frac{1}{k_{\text{B}}T}, \qquad (1)$$

where $H(\{\gamma_f^i\})$ is the total energy of the system, F_h^j is the statistical sum of the internal states of the particle j located in unit h, $\varepsilon_{hg}{}^{jm}(r)$ is the interaction energy of particle j in unit h with particle m in unit g being at distance r from h, $1 \le r \le R$, R is the radius of the interaction potential, *i.e.*, the greatest distance at which the intermolecular interaction energy of a pair of particles still differs from zero, T is the absolute temperature, k_{B} is the Boltzmann constant. In the LGM, the γ_h^j values that are equal to 1 when particle j is located in unit h and otherwise are equal to 0 serve as the variables characterizing the state of the system. The indices i, j, and m characterizing the types of particles vary from 1 to Φ, where Φ is the total number of sorts of particles. The variables f, g, h correspond to the lattice units. The value f runs through all N units of the lattice and g runs through all $z_f(r)$ neighboring units in the r-th coordination sphere (CS) of the central unit f. The braces mean the set of states of all units $\{\gamma_f{}^j\} = \{\gamma_{f1}{}^{j1}, \gamma_{f2}{}^{j2}, ..., \gamma_{fN}{}^{jN}\}$. The particle i is a molecule of sort n existing in the orientation φ_n, which can be written as $i = \{n, \varphi_n\}$. The orientation of a molecule is defined by three spatial rotation angles, which are specified discretely. If the number of occurring orientations for a molecule of sort n is designated by Φ_n, then $\Phi = \Sigma^s{}_{n=1}\Phi_n$, where s is the number of sorts of molecules of a mixture together with free units (vacancies). The subscript s is used to designate vacancies ($\Phi_s = 1$, as the vacancies have no orientation).

The energy parameters $\varepsilon_{fg}{}^{jm}(r)$ depend on the sorts of particles i and m and on the mutual positions of units f and g at distance r, because the change of positions of polyatomic molecules described by subscript g with the values i, m, and r remaining the same leads to changes of most closely located atoms of these molecules.

The introduction of coordination numbers is related to the traditional view of the short-range order in the arrangement of molecules in the liquid phase. This leads to the conclusion that the diamond structure with the coordination number $z = 4$ was chosen as the spatial structure of water (Fig. 1, *a*). At high pressure, other types of lattice are possible for water and for other dipole liquids, for example, simple cubic lattice (Fig. 1, *b*).

Lattice model of water. Specific properties of water are caused by the presence of directed hydrogen bonds between the molecules.[10,11] A water molecule has four tetrahedrally directed polarities, two positive and two negative ones. The polarities are oriented in four directions from the center to the vertices of the tetrahedron of the sp^3-hybridized oxygen. A pair of hydrogen-bonded molecules (Fig. 2, *a*) is oriented in such a way that opposing polarities have opposite signs and has a lower energy than a nonbonded pair of molecules (Fig. 2, *b*). Figure 3 schematically illustrates the interaction of two molecules in our model. Water molecules are considered as point dipoles whose orientations are selected discretely (the dipoles in Fig. 3 point either to the neighboring water molecules that are not shown or to the opposite direction). In addition to the DD potential between the oxygen atoms of water molecules, there is the LJ force that can be assumed to be centered at the point of the dipole.

Equations of the model. The ensemble-average values of one or the product of several γ_f^i values are called corre-

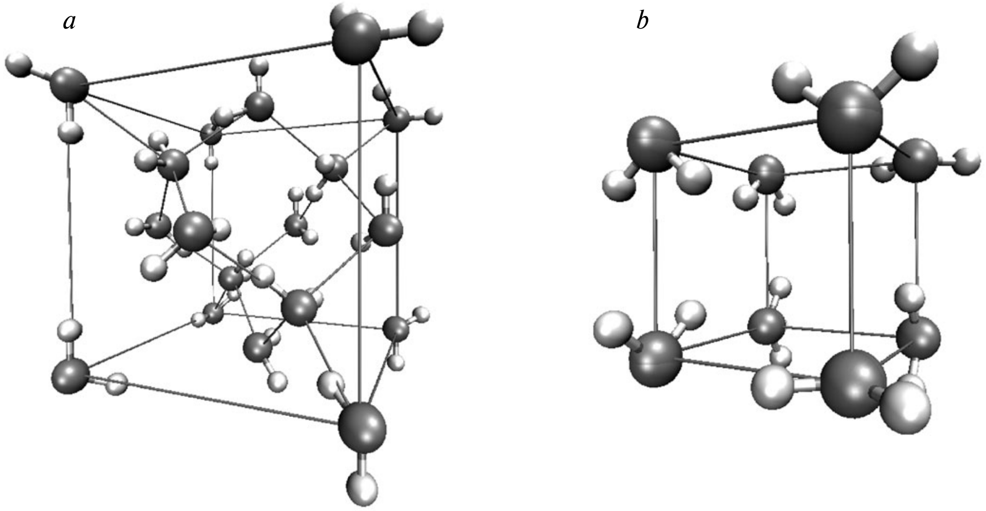

Fig. 1. Lattice structures of water with the numbers of nearest neighbors $z = 4$ (*a*) and 6 (*b*).

lators and mean the probability of detection of a sort i particle in unit f, and sort j particle in unit g, an so on:

$$\theta_f^{\,i} = \langle\gamma_f^{\,i}\rangle,\ \theta_{fg}^{\,ij} = \langle\gamma_{fg}^{\,ij}\rangle.$$

In terms of the quasichemical approximation, for pair correlators $\theta_{fg}^{\,ij}$, one can obtain the relations[9]

$$\theta_{fg}^{\,ij}\theta_{fg}^{\,lk} = \theta_{fg}^{\,ik}\theta_{fg}^{\,lj}\exp[-\beta(\varepsilon_{fg}^{\,ij} + \varepsilon_{fg}^{\,lk} - \varepsilon_{fg}^{\,ik} - \varepsilon_{fg}^{\,lj})], \qquad (2a)$$

which form a closed system together with the normalization conditions

$$\sum_{i=1}^{\Phi}\theta_{fg}^{ij} = \theta_g^i,\ \sum_{j=1}^{\Phi}\theta_{fg}^{ij} = \theta_g^i,\ \sum_{i=1}^{\Phi}\theta_f^i = 1 \qquad (2b)$$

The pressure P in the system can be written as follows:

$$a_f^i P_i = \frac{\theta_f^i\Lambda_f^i}{\theta_f^s},\ \Lambda_f^i = \prod_{r=1}^{R}\prod_{g=1}^{z(r)}\sum_{j=1}^{\Phi}\frac{\theta_{fg}^{ij}(r)}{\theta_f^i}\exp[\beta\varepsilon_{fg}^{ij}(r)]. \qquad (3)$$

The $\Lambda_f^{\,i}$ values called non-ideality functions take into account direct correlations between the interacting particles in the quasichemical approximation, $a_f^{\,i} = \beta F_f^{\,i}\exp(\beta\varepsilon_f^{\,i})/F_i^0$ is the local Henry coefficient, all partial pressures $\{P_i\}$ $(1 \le i \le s - 1)$ are identical, $\{P_i\} = P_{H_2O}$, as in a rarefied vapor in the absence of a real external field, all orientations of molecules i are equally probable. For the same reason, within the framework of this model variant, one can consider $a_f^{\,i} = a = 1$. Since the system is isotropic in the absence of an external field, all $\theta_f^{\,i}$ values are equally probable.

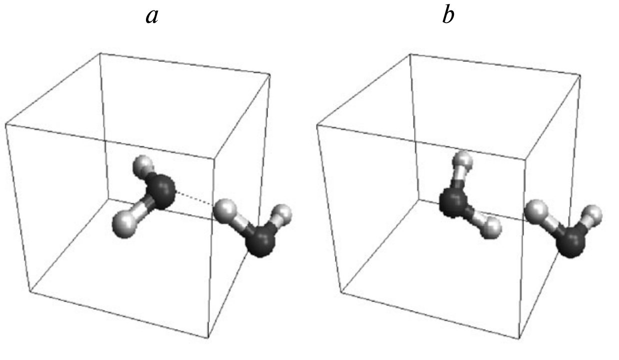

Fig. 2. Bonded (*a*) and non-bonded (*b*) configurations of a water molecule in the lattice; the dashed line denotes hydrogen bond.

The structure of an aqueous system at low pressures is largely determined by the ability of water molecules to form tetrahedrally directed hydrogen bonds; this gives rise to a regular open structure with the coordination number $z = 4$ (ice Ic). Although at high pressures (~2000 MPa), this ordered state becomes less stable than ice VII; however, at pressures of up to 100 MPa, this structure is regarded as the major one in this work.

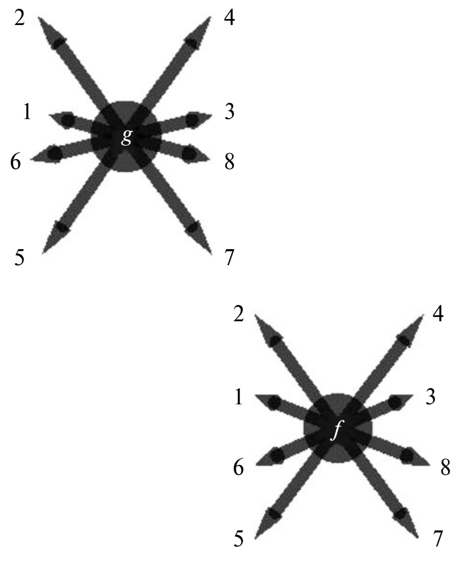

Fig. 3. Schematic view of the considered orientations of two neighboring water molecules. The numbers of arrows reflect the spatial orientations of molecules.

System energetics. Consider how two point dipoles with the moments μ, the LJ radius σ, and LJ energy ε interact at distance r. We assume that r acquires a number of discrete values $r_0 = 1.12\sigma$, r_1, r_2, r_3, ..., which correspond to the distance from lattice coordination spheres to the center. If orientation (i) of the first dipole located in unit f, the orientation (j) of the second dipole located in unit g, and the direction from the first to second dipole are specified by unit vectors n_1, n_2, n_{12}, then the interaction of the dipoles is described by the following equation:

$$\begin{aligned}
\beta\varepsilon_{fg}^{ij}(r) &= \\
&= \beta\left\{\frac{(d_1,d_2)-3(d_1,n_{12})(d_2,n_{12})}{r^3}+4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]\right\} = \\
&= \frac{\mu^2}{kTr_0^3}\,\frac{(n_1,n_2)-3(n_1,n_{12})(n_2,n_{12})}{\left(\dfrac{r}{r_0}\right)^3} + \\
&\qquad + \frac{1}{kT}4\varepsilon\left[\left(\frac{\sigma/r_0}{r/r_0}\right)^{12}-\left(\frac{\sigma/r_0}{r/r_0}\right)^{6}\right] = \\
&= \frac{p}{T}F(n_1,n_2,n_{12},r/r_0)-\frac{q}{T}i_n, \qquad (4)
\end{aligned}$$

where p and q are positive and are given by $p = \mu^2/(kr_0^3)$, $q = \varepsilon/k$, i_n = 1.000, 0.103, 0.040, 0.013, ... (for the diamond lattice). The F(...) value in the first summand for $r = r_0$ varies from –2 to 2.

The possible orientations of the dipole moment of a water molecule in the lattice units were chosen to point to the four nearest neighboring units of the first coordination sphere (or to the opposite direction). Then the set n_1 comprises eight unit vectors: $\varphi_1 = (-1, -1, -1)/\sqrt{3}$, $\varphi_2 = (-1, -1, 1)/\sqrt{3}$, $\varphi_3 = (-1, 1, -1)/\sqrt{3}$, $\varphi_4 = (-1, 1, 1)/\sqrt{3}$, $\varphi_5 = (1, -1, -1)/\sqrt{3}$, $\varphi_6 = (1, -1, 1)/\sqrt{3}$, $\varphi_7 = (1, 1, -1)/\sqrt{3}$, $\varphi_8 = (1, 1, 1)/\sqrt{3}$. These vectors for a pair of neighboring units are shown in Fig. 3. In view of the possibility of occupation of this unit by a vacancy, this set is supplemented by zero vector $\varphi_9 = (0, 0, 0)$. The positions $\vec{r}(g)$ of the nearest neighbors in the diamond lattice, *i.e.*, the coordinates of units g with the central unit f located at the center of coordinates where the shortest distance between the units r_0, are as follows: $\vec{r}(1) = r_0(-1, -1, 1)\sqrt{3}$, $\vec{r}(2) = r_0(-1, 1, -1)\sqrt{3}$, $\vec{r}(3) = r_0(1, -1, -1)\sqrt{3}$, $\vec{r}(4) = r_0(1, 1, 1)\sqrt{3}$. Table 1 illustrates the dependence of the energy $\varepsilon_{f1}{}^{ij}(1)$ (dimensionless) of the electrostatic interaction of the dipoles (*i.e.*, the function F(...) in Eq. (4)) located in the units (central f and neighboring g = 1) on the orientation of dipoles φ_i, φ_j. It can be seen from this Table that only two different interactions, except for sign, are possible in the first coordination sphere. One of these is a stronger interaction (repulsion or attraction depending on the sign) of the orientations i = 2, 7 and j = 2, 7 (see Fig. 3) where the direction between the units coincides with the dipole orientations. The other type of interaction is encountered 16 times more frequently but it is 3 times weaker and is implemented at the expense of other orientations. The same dependence $\varepsilon_{f1}{}^{ij}(r)$ for the CS with r = 1, 2, 3, 4 as a function of orientations i,j is shown in Fig. 4.

Table 1. Energies $\varepsilon_{f1}{}^{ij}(r)$ of the dipole—dipole interaction of the neighboring water molecules for eight considered orientations φ_1—φ_8 in the first coordination sphere

φ	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
φ_1	0.67	–0.67	0.67	–0.67	0.67	–0.67	0.67	–0.67
φ_2	–0.67	–2.00	0.67	–0.67	0.67	–0.67	2.00	0.67
φ_3	0.67	0.67	0.67	0.67	–0.67	–0.67	–0.67	–0.67
φ_4	–0.67	–0.67	0.67	0.67	–0.67	–0.67	0.67	0.67
φ_5	0.67	0.67	–0.67	–0.67	0.67	0.67	–0.67	–0.67
φ_6	–0.67	–0.67	–0.67	–0.67	0.67	0.67	0.67	0.67
φ_7	0.67	2.00	–0.67	0.67	–0.67	0.67	–2.00	–0.67
φ_8	–0.67	0.67	–0.67	0.67	–0.67	0.67	–0.67	0.67

Solution of the system of equations for pair functions. Consider the liquid water—vapor equilibrium where a unit may be occupied by a water molecule dipole oriented in a definite way or by vacancy. The system of equations (2) for this case was solved in the following way. Among the possible pair correlators $\theta_{fg}{}^{ij}$, the correlators containing vacancies $\theta_{fg}{}^{is}(r)$ и $\theta_{fg}{}^{sj}(r)$ can be chosen as the independent ones. Then using Eq. (2a), it is possible to express particle—particle type correlators through independent values

$$\begin{aligned}
\theta_{fg}^{ij}(r) &= \frac{\theta_{fg}^{is}(r)\theta_{fg}^{sj}(r)}{\theta_{fg}^{ss}(r)}\,\bullet \\
&\bullet \exp\left\{-\beta\left[\varepsilon_{fg}^{ij}(r)+\varepsilon_{fg}^{ss}(r)-\varepsilon_{fg}^{is}(r)-\varepsilon_{fg}^{sj}(r)\right]\right\}. \qquad (5)
\end{aligned}$$

By substituting expression (5) to the normalization equations (2b) and assuming that the interaction energy with the vacancy is zero, we finally obtain the non-linear set of equations

$$\theta_{fg}^{is}(r)+\frac{\theta_{fg}^{is}(r)}{\theta_{fg}^{ss}(r)}\sum_{j=1}^{s-1}\theta_{fg}^{sj}(r)\exp[-\beta\varepsilon_{fg}^{ij}(r)] = \theta_f^i \qquad (6a)$$

$$(1 \le i \le s-1),$$

$$\theta_{fg}^{si}(r)+\frac{\theta_{fg}^{si}(r)}{\theta_{fg}^{ss}(r)}\sum_{j=1}^{s-1}\theta_{fg}^{js}(r)\exp[-\beta\varepsilon_{fg}^{ji}(r)] = \theta_f^i \qquad (6b)$$

$$(1 \le i \le s-1).$$

The correlator between the vacancies $\theta_{fg}{}^{ss}(r)$ can also be excluded using Eq. (2b) as

$$\theta_{fg}^{ss}(r)+\sum_{j=1}^{s-1}\theta_{fg}^{sj}(r) = \theta_f^s = 1-\sum_{j=1}^{s-1}\theta_f^j. \qquad (6c)$$

For an isotropic system, the probabilities $\theta_f{}^i$ of unit occupation by dipole molecules oriented in different ways

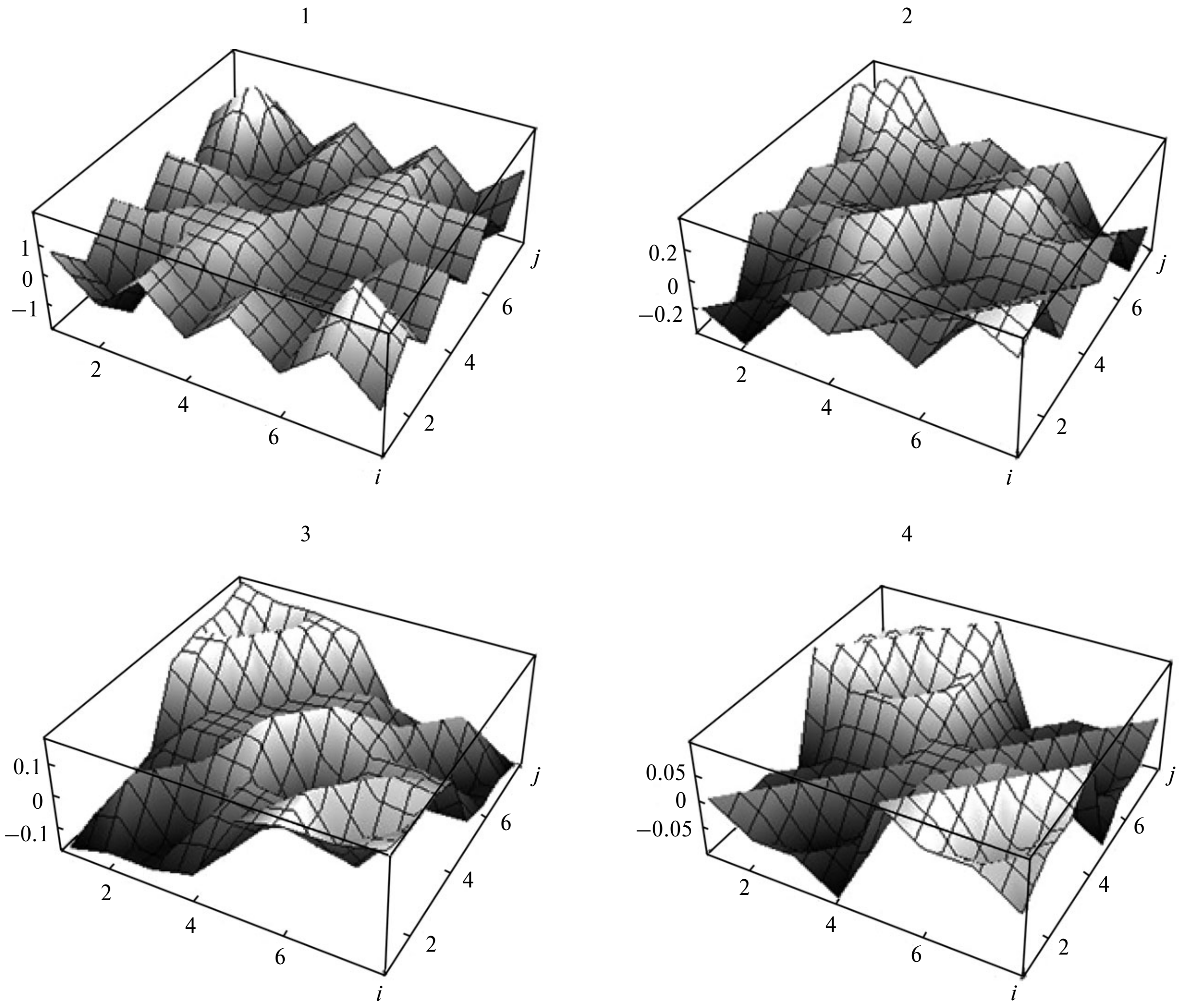

Fig. 4. Potential reliefs for the contribution to the dipole—dipole interaction to the energy $\varepsilon_{f1}{}^{ij}$ for the first four CS. The numbers of spheres r = 1, 2, 3 and 4 are indicated above. The values along x and y axes are i and j.

are equal: $\theta_f{}^i = \theta/s$, where θ is the total water concentration. System (6) contains unit number g; however, there is no need to solve it for all of the possible g but it is sufficient to solve it for any single value, for example, $g = 1$. The solutions for other g can be derived based on the fact that the correlators $\theta_{fg}{}^{is}$, $\theta_{fg}{}^{si}$ in the fixed coordination sphere (r = const) depend actually only on the angle between the direction to the vacancy $\vec{r}(g)$ and the dipole orientation $\vec{\varphi}_i$:

$$\theta_{fg}{}^{is}(r) = \vartheta(|\vec{r}_g \cdot \vec{\varphi}_i|),\ \theta_{fg}{}^{si}(r) = \vartheta(|\vec{r}_g \cdot \vec{\varphi}_i|).$$

System (6) should be solved separately for different coordination spheres. For example, for the first CS of the diamond lattice, system (6) has the form

$$\left(1 - \frac{3\theta}{4}\right)\vartheta(1) + \left(e^{\frac{-2p+q}{T}} + e^{\frac{2p+q}{T}} - 2\right)\vartheta(1)^2 + \frac{3}{4}\theta\vartheta(2) +$$

$$+ 3\left(e^{\frac{-2p+3q}{3T}} + e^{\frac{2p+3q}{3T}} - 2\right)\vartheta(1)\vartheta(2) = \frac{1}{8}(1-\theta)\theta,$$

$$\left(1 - \frac{\theta}{4}\right)\vartheta(2) + 3\left(e^{\frac{-2p+3q}{3T}} + e^{\frac{2p+3q}{3T}} - 2\right)\vartheta(2)^2 + \frac{1}{4}\theta\vartheta(1) +$$

$$+ \left(e^{\frac{-2p+3q}{3T}} + e^{\frac{2p+3q}{3T}} - 2\right)\vartheta(1)\vartheta(2) = \frac{1}{8}(1-\theta)\theta,$$

where $\vartheta(1)$ is the correlator of the dipole directed toward the vacancy and $\vartheta(2)$ is the correlator for other orientations of the particle with the vacancy (see Fig. 3).

As the principal set of interaction parameters in relation (4), we choose p = 1000 K and q = 500 K for which the optimal interaction energy of a pair of neighboring molecules located in a diamond lattice with the density of 1 kg L^{-1} (the shortest distance between the molecules is 2.69 Å) is 5 kcal mol^{-1}, which is close to the experimental binding energy of two water molecules. When a simple cubic lattice is used, the distance between the molecules increases to 3.1 Å at the same density.

The pair functions of the first coordination sphere $\theta_{fg}^{ij}(1)$ corresponding to $g = 1$ depending on the change of the numbers of orientations *i* and *j* are shown in Fig. 5 for three concentrations of water molecules $\theta = 0.10$, 0.25, and 0.85 at $T = 700$ and 500 K. One can see that as the system density increases, the absolute values of the functions θ_{fg}^{ij} increase by an order of magnitude, which is reflected in the value of the function along the *y*-axis. The proper appearance of the surface is retained, and all figures clearly indicate that as the density and the temperature change, the above-noted correlators $i = 2, 7$ and $j = 2, 7$ (see Fig. 3 and Table 1) corresponding to the maximum absolute magnitude of DD interaction predominate as regards the magnitude among all the correlators $\theta_{fg}^{ij}(1)$.

This behavior of the pair functions $\theta_{fg}^{ij}(1)$ is related to the use of the quasichemical approximation in which direct correlations distinguish separate pairs of molecules irrespective of the state of other molecules. If one takes into account multiparticle interactions, for example, the electron polarization of molecules, the values of the pair correlator functions will depend on the density of the local environment.

The concentration behavior of the pair functions of the fist ($\theta_{fg}^{ij}(1)$) and second ($\theta_{fg}^{ij}(2)$) CS are shown in Fig. 6 for the maximum and minimum interactions of the neighboring molecules in the first (see Fig. 6, *a*) and second (see Fig. 6, *b*) CS. The attraction energy of these pairs varies from the maximum $\varepsilon_{fg}^{ij}(1) = -2p - q$ (I CS), $\varepsilon_{fg}^{ij}(2) = -0.383p - 0.103q$ (II CS) (shown in Fig. 6 by continuous curve *1*) to the minimum $\varepsilon_{fg}^{ij}(1) = 2p - q$ (I CS), $\varepsilon_{fg}^{ij}(2) = 0.383p - 0.103q$ (II CS) (dashed line *4*). Curves *2* and *3* correspond to the intermediate energies $-2/3p - q$, $2/3p - q$ (I CS) and $-0.23p - 0.103q$ (II CS), respectively. The curves in Fig. 6 attest to the strong effect of the values of interaction parameters on the pattern of concentration dependences. As noted above, the general trend is the monotonic behavior of all curves. As the distance from the central molecule increases (*i.e.*, the intermolecular inter-

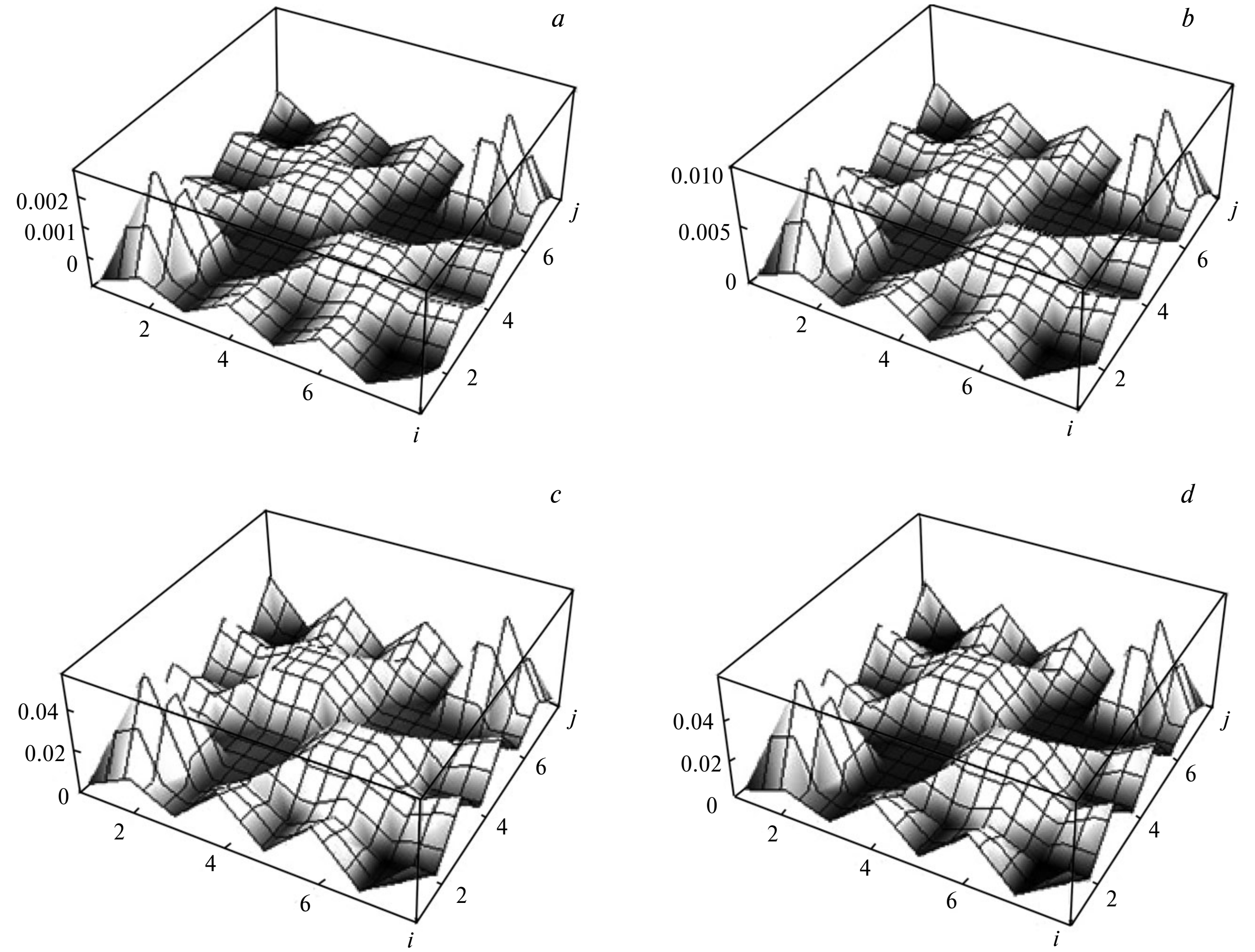

Fig. 5. The profiles of the functions θ_{f1}^{ij} for three concentrations of molecules $\theta = 0.1$ (*a*), 0.25 (*b*) and 0.85 (*c*, *d*), $T = 700$ (*a—c*) and 500 K (*d*). The values along *x* and *y* axes are *i* and *j*.

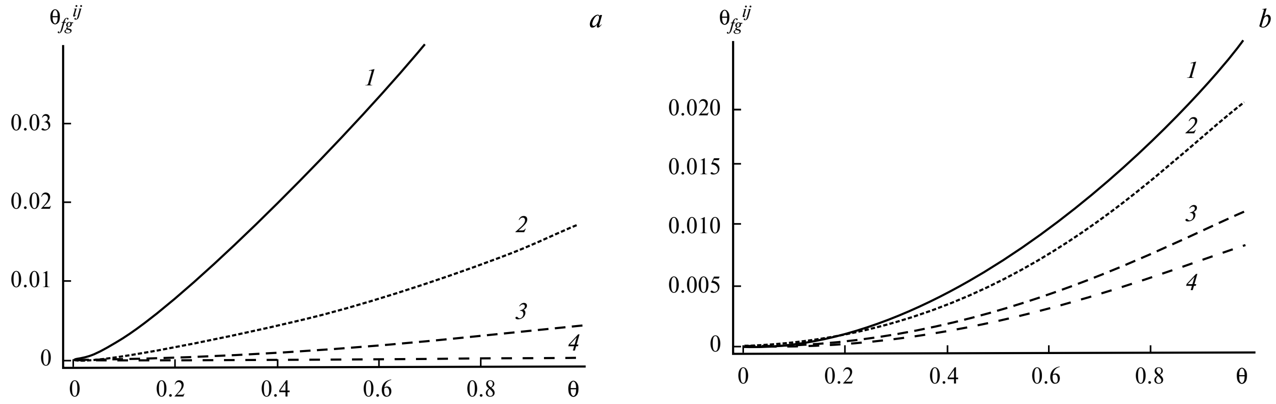

Fig. 6. Concentration dependences of the pair distribution functions θ_{f1}^{ij} for $r = 1$ (*a*) and 2 (*b*). For explanations, see the text.

action decreases (see Fig. 6, *a*, *b*)), the values considerably decrease in magnitude. The same effect is observed as the interaction is weakened, while the distance between the molecules is maintained constant, *i.e.*, on passing from curve *1* to curve *4* in each Figure.

The temperature dependence of the value of pair functions $\theta_{fg}^{ij}(1)$ is shown in Fig. 7 for water concentrations $\theta = 0.25$ (see Fig. 7, *a*) and 0.8 (see Fig. 7, *b*). The probability of detecting pairs whose interaction energy corresponds to attraction ($\varepsilon_{fg}^{ij} < 0$) diminishes (curve *1*) upon temperature rise, while the probability of detecting pairs whose interaction energy corresponds to repulsion ($\varepsilon_{fg}^{ij} > 0$) increases (curves *2—4*).

The considered trends of the pair correlation functions determine the behavior of an aqueous system over the whole range of density and temperature. This analysis explains the behaviors of the macroscopic characteristics such as isotherms and phase separation diagrams.

Isotherms. The isotherm curves that show the relationship between the water pressure aP and density θ in the considered system at a constant temperature are presented in Fig. 8. The diamond structure ($z = 4$) and the simple cubic lattice ($z = 6$) were chosen as the lattices. In calculation of isotherms, only interactions between the nearest neighbors were taken into account. The isotherms were constructed for $T = 660$ (corresponds to the critical temperature of water) and 800 K (supercritical temperature). The curves were constructed taking into account the fact that LJ is constant ($q = 1000$ K), while the DD contribution (the parameter p in expression (4)) is 400, 500, and 600 K. All isotherm curves for $z = 6$ and the lower curve for $z = 4$ and $T = 660$ form van der Waals type loops. The loop means that the dependence of pressure on density is not monontonic and indicates the coexistence of the liquid and vapor phases at the same pressure over a certain range of densities, *i.e.*, separation of the system into two phases. The boundaries of this range θ_1, θ_2 and the corresponding pressure aP_{dis} can be found using the Maxwell rule according to which the areas of the figures formed by the horizontal line $aP = aP_{\text{dis}}$ and the corresponding convex and concave isotherm fragments should be equal. The disappearance of the loop for $z = 4$ upon temperature rise from 660 to 800 K implies transition of the system to the supercritical state where it is entirely gaseous. For $z = 6$, the loop does not disappear under these conditions. This is attributable to the fact that increase in the number of nearest neighbors from four to six enhances the interaction of the central particle with them.

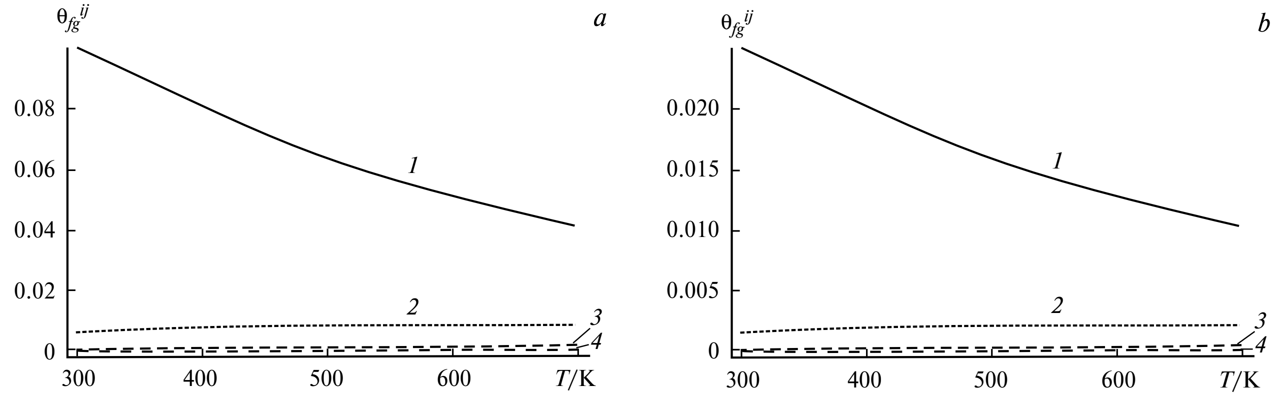

Fig. 7. Temperature dependences of the pair distribution functions $\theta_{f1}^{ij}(r)$; curves *1—4* correspond to the curves in Fig. 6, *a* for $\theta = 0.25$ (*a*) and 0.8 (*b*).

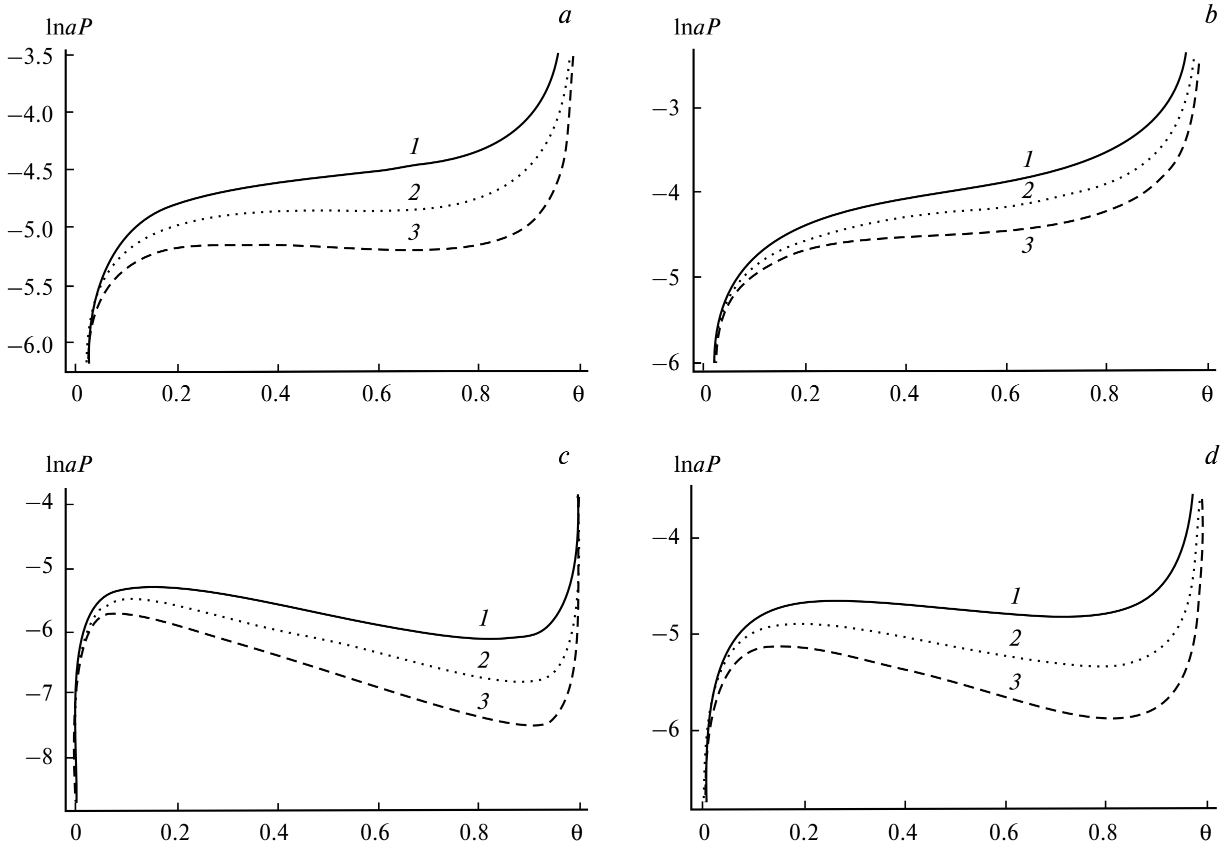

Fig. 8. Isotherms relating the density of the bulk liquid to its chemical potential fir two lattice structures and two temperatures calculated for different ratios of DD and LJ interactions: $z = 4$ (*a*, *b*) and 6 (*c*, *d*), $T = 660$ (*a*, c) and 800 K (*b*, *d*). Only the first neighbors were taken into account ($r = 1$). Energy parameters: $q = 1000$ K, $p = 400$ (*1*), 500 (*2*), 600 K (*3*).

Phase separation curves. Numerous isotherms having van der Waals type loops form phase separation curves that interrelate the densities of the coexisting vapor and liquid. Figure 9 shows the calculated separation curve of a vapor—liquid aqueous system. The theoretical curve that we obtained is in good agreement with the experimental curve[10] but has a more symmetric shape. This is caused by the limitations of the used model: inclusion of only several nearest interactions, the lattice rigidity, and fixation of the molecules in its units. The elimination of these assumptions results in better quantitative agreement with experimental data for a very broad range of molecules.[12]

The necessity of inclusion of the LJ contribution. Usually, dipole systems are considered taking into account only the electrostatic energy.[13—15] However, for interaction with the nearest neighbors, the LJ contribution to the energy exceeds in magnitude the electrostatic contribution for most orientations, while for the parallel arrangement of dipoles optimal from the electrostatic standpoint, this contribution is only half that of the electrostatic component. To verify the adequacy of this approach, calculations without taking into account the LJ interactions of particles ($q = 0$) were carried out and the effective dipole moment (*i.e.*, the parameter p), which reproduces the critical temperature and phase separation curve in considering I CS was found (Fig. 9, curve *3*). It can be seen that

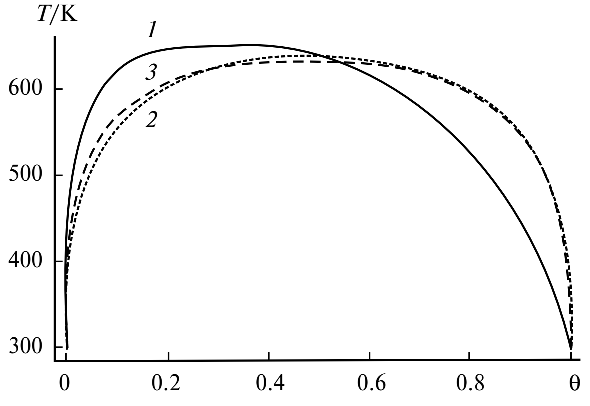

Fig. 9. Separation curves for water taking into account only nearest neighboring interactions ($r = 1$) with different interaction energy parameters for a tetragonal lattice ($z = 4$): (*1*) experimental results,[10] (*2*) model calculations ($p = 1000$ K and $q = 500$ K), (*3*) model calculation without the van der Waals contribution ($p = 1750$ K and $q = 0$ K).

this parameter differs by 75% from the value found previously (for $q > 0$). This means that an attempt to reproduce the experiment using the electrostatic energy alone results in pronounced overestimation of the corresponding parameters, distorts the long-range interactions, and, hence, can lead to substantial errors in the calculation of properties such as the dielectric constant. Considering the charge field at large distances shows that the dipole interactions become prevailing for the far CS, whereas for small intermolecular distances, more complete description of the field is required with inclusion of the non-electrostatic contribution and taking account of the inaccuracy caused by the fact that the interacting particles are not points.

The started study of the dipole liquids over the whole range of densities based on the discrete description of the solvent extends the traditional use of the LGM. The model describes satisfactorily the behavior of an aqueous system, which means that the phase diagram of water may be interpreted by assuming the existence of a tetrahedral molecular structure arising as a result of formation of directed hydrogen bonds.

In the future this will allow successful modeling of a large number of physicochemical processes, in particular, various reactions on homogeneous and heterogeneous surfaces, absorption and adsorption of gases and gas mixtures on a solid with allowance for the dipole character of the potential. The replacement of the continuous set of particle coordinates by their discrete positions simplifies the equations of the theory and provides considerable progress in their analytical or numerical solution.

The development of the discrete model is necessary due to detailing of the microscopic nature of processes in the reaction systems. For calculating any characteristics of the condensed phase, it is necessary to properly take into account all types of interactions from short-range exchange and dispersion interactions to long-range dipole and Coulomb forces. For these calculations, it is important to take into account the polarization contributions to energy, which depend on the instantaneous distributions of the local electric fields. Owing to the presence of electronic polarizability, these fields depend on the local spatial distributions of molecules and charged particles and on the orientation and displacements (oscillations) of molecules. Thus, all system components become interrelated, which results in their interdependence.

Thus, it is necessary to take into account the orientation of the hydrogen bonds in "pure" water and in aqueous solutions. The use of this approach ensures the construction of effective potential functions, which are suitable for correct account of the key characteristics of the interaction of solute molecules with one another and with solvent molecules.

According to the constructed model, a dipole liquid demonstrates qualitatively the same behavior as regards thermodynamic properties as any other simple liquid. However, the use of the DD potential changes the pattern of local distributions of molecules (since the interactions become orientation-dependent) and imparts additional flexibility to the model. Therefore, adjustment of lattice models to dipole systems may become the basic method for description of the properties of non-electrolyte solutions and a broad range of surface systems.

The foundations for the lattice model for an aqueous vapor—liquid system were developed. The model allows varying the level of detailing the description of the potential of the water molecule: point LJ potential, point dipole, dipole + LJ potentials, triatomic molecule with Coulombic and LJ potentials on each atom. Even the early stages of model verification demonstrated the importance of LJ contribution and revealed the inadequacy of analysis of only electrostatic interaction. When both effects are included, some thermodynamic properties of water can be reproduced with quantitative accuracy. The same possibility may be suggested for other dipole liquids as the model does not require macroscopic characteristics such as the dielectric constant.

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