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Properties of the H-bond network for two-dimensional lattice water model

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A microscopic Hamiltonian of the hydrogen-bond network in two-dimensional lattice water is proposed, which describes the formation and disruption of the H bonds, their bending, and which satisfies the Bernal–Fowler rules [J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933)]. The thermodynamic properties of the H-bond network are studied using the method of many-particle irreducible distribution functions, which is a generalization of the Kikuchi cluster approach [R. Kikuchi, Phys. Rev. **81**, 988 (1951)] and the Bethe–Peierls quasiactivities method [H. A. Bethe, Prog. R. Soc. A **150**, 552 (1935)]. The temperature dependencies of the average number of H bonds per molecules, the contribution of the H bonds into the heat capacity of the system, and the parameters describing the correlations between the states of molecules on the neighboring sites are investigated. It is shown that depending on the magnitude of the interaction between the H bonds in the H-bond subsystem either smooth or sharp first-order phase transition can occur. The role of different factors in the formation of the properties of the H-bond network is discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1940030]

I. INTRODUCTION

Due to the continual increase in the capabilities of both the laboratory experiments and computer simulations, a huge amount of data on the equilibrium and nonequilibrium characteristics of water has been accumulated. At that, the lag in the theoretical analysis of water properties is especially prominent against the background of the doubtless experimental successes.

Presently, it is undoubtable that the anomalies in the behavior of water are stipulated by the presence of the hydrogen-bond network. However, relatively small number of works are devoted to the study of the macroscopic properties of the network on the basis of the microscopic Hamiltonians.[1–4] In particular, the average number of H bonds per molecule and their contribution to the heat capacity and entropy have been studied.[3] It has been demonstrated that in the vicinity of a certain temperature these quantities undergo a sharp change, thus pointing out the possibility of a phase transition in the H-bond subsystem. Commonly, the attempts were undertaken to solve the more complicated problem of the simulation of the behavior of water itself, i.e., to take into account simultaneously the orientational and translational molecular degrees of freedom. This problem is extraordinarily complex due to the existence of more than 20 phases of gas, liquid, and solidified water.[5,6] Therefore, significant simplifications are employed for the description of the properties of certain phases of water. The models of normal and supercooled water and amorphous ice proposed in Refs. 7–10, which are the generalizations of the well-known lattice-gas model, can serve as examples. The introduction of the highly anisotropic (sharply directed) interparticle interaction is treated as a way to introduce the H bonds. Inherent to them, the effect of weakening of the H-bond energy at the increase of density has allowed the reproduction of the anomalous behavior of the latter. Models have been proposed[1,2,11–13] in which the location of the molecular centers of mass changes continuously, thus allowing to study the binary distribution function of the system. Contrary to Refs. 7–10, where the origin of the maximum is related to the three-particle interactions, in Refs. 1 and 2 this effect is stipulated by a specific form of pair interparticle potentials.

Note, however, that a number of drawbacks inherent in all the models listed above.

(1) Except in Refs. 1 and 2, the structure of the water molecule, namely, the presence of two donor and two acceptor ends and the tetrahedric coordination of the charge-density maxima, is not taken into account. Therefore, the H bond is introduced formally, and the Bernal–Fowler rules are not clearly represented.

(2) In Refs. 7–10 the formation of H bonds is modeled with the help of discrete "orientational" variables σ, $\sigma = 1, 2, \ldots, q$, that cannot reflect the tetrahedric coordination of the H bonds, which is characteristic for water. This feature is not satisfactorily reflected by other models of the water molecule.[3,11–13] Note that in molecular-dynamics simulations this difficulty is overcome by using more realistic pseudopotentials (e.g., Stillinger–David[14]).

(3) The equation of state is built in a one-particle mean-field approximation; the role of multiparticle correla-

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tions is in fact ignored (although, qualitatively, the authors in Refs. 7–10 admit to their key role in the system with strong H bonds). Multiparticle effects are taken into account only in Refs. 1 and 2 where the virial expansion is used.

As a consequence, the basic results of Refs. 7–13 require proper correction.

An attempt to improve the discussed models was undertaken in Ref. 15. The model of a water molecule with tetrahedrically coordinated two donor and two acceptor active ends that allows to take into account the Bernal–Fowler rules was considered there. It was assumed that the molecules can be only in discrete orientational states that allow formation and disruption of the H bonds. The dependence of the energy of the H bond upon the density of the system was introduced in the way similar to Refs. 7 and 8. The equation of state was built on the basis of the cluster approach to the calculation of the partition function in one- and nine-particle approximations. Since the one-particle approach is not applicable for the description of the systems with strong binary correlations,[16] it is not surprising that the solutions obtained in the two approximations were different even qualitatively. In the cluster method of the solution it is also important to account correctly for the fact that the molecules that are in the region of intersection of two clusters are in the same states. Therefore, the intersecting clusters are not statistically independent. This circumstance had been emphasized and analyzed in Ref. 17, but was not taken into account in Ref. 15.

In recent works[18,19] this error is partially corrected. However, analyzing the contributions from the four-particle clusters (irregular tetrahedra), the authors take into account only the overlap of their vertices. The overlap of the edges and faces is ignored, as before. The difference between donor and acceptor ends is also dropped out by not completely clear reasons. Moreover, varying the one-particle distribution function in Refs. 18 and 19 the principle of the equivalence of the lattice sites is violated, although the original expression, which relates the one-particle distribution function to the four-particle one, is correct and satisfies this requirement.

The consecutive study of the macroscopic properties of the H-bond network is of importance for the following reasons. Due to the substantial difference in the character of the angular and radial dependencies of the dispersion (van der Waals) forces and the forces corresponding to the H bonds, their contributions into the thermodynamical functions of the system should be additive. At that, the temperature dependence of the contribution of the dispersion forces into any thermodynamic function of water should be similar to its behavior in argon and other simple fluids. On the other hand, the temperature dependence of the contribution stipulated by the H bonds must be determined by the main thermodynamic characteristics of the H-bond network, referred to in Ref. 20 as structural functions. It was shown on the basis of the analysis of the temperature dependence of the specific volume and dielectric permittivity of water that among the structural functions the principal role is played by the average number of H bonds per molecule and the tetrahedricity parameter.[21] The role of the structural functions is also demonstrated in Ref. 22 where they determine the temperature dependence of the effective constant of the spin–spin interaction in the Ising-type Hamiltonian of the binary solutions. Therefore, the study of the structural functions of the H-bond network becomes one of the most important problems for the systems with strong hydrogen bonds.

The problems in the description of the thermodynamic properties of the systems with strong H bonds are in many respects similar to those arising in the physics of magnetics. The character of the magnetic ordering in the latter is determined by the interaction of not only spin variables but also of spins with the oscillations of the lattice, defects, etc. As the simultaneous account of all degrees of freedom is a complicated problem, only a spin subsystem is usually studied in zeroth approximation. Numerous model expressions for the spin Hamiltonians have been proposed.

In the presented work, as in Refs. 1–3, the main attention is focused on the study of the thermodynamic properties of the H-bond network in the two-dimensional water. It is assumed that the water molecules occupy the sites of the square lattice and are able to orient relative to the lattice in an arbitrary way. The condition for the formation of the H bond is defined; the possibility of its bending is embedded into the model. The Hamiltonian for the network of H bonds, which takes into account their interaction, is proposed. Therefore, the model under consideration is the natural extension of the Pauling ice model. The most important difference of the present work from the works cited above is that the analysis of the thermodynamic properties of the H-bond network is carried out in terms of the method of many-particle irreducible distribution functions, which is the generalization of the Kikuchi cluster approach[17] and the Bethe–Peierls quasiactivities method.[23] Special attention is paid to the reduction of the number of variational parameters, which is the typical difficulty of cluster approaches. The temperature dependence of the average number of H bonds formed by a molecule, the heat capacity of the system, and the correlation parameters that describe the degree of the correlation of states inside the compact clusters are studied in the present paper. The possibility of phase transition in the H-bond subsystem is investigated. The possible ways to generalize the obtained results are discussed in the Conclusion. The basic elements of the method and its applications to some problems of statistical physics can be found in Refs. 16 and 24–26.

II. HAMILTONIAN OF TWO-DIMENSIONAL WATER

The basic ideas for the construction of the model can be borrowed from the model of the two-dimensional Pauling ice.[27] According to it, the active ends of the molecule are located on the perpendicular line segments. Six possible variants of the location of two protons and two lone electron pairs on four lines of the density maxima are shown in Fig. 1. The Pauling model subjects the Bernal–Fowler[28] rules for the H bond: (1) the state of the pair in which the different active ends of the neighboring molecules lie on the lattice edge that connects the centers of molecules corresponds to

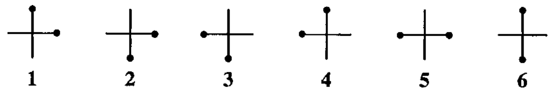

FIG. 1. Six ways ($\alpha=1\cdots 6$) of arranging the protons (solid circles) of a "flat" water molecule at fixed orientation of active ends.

the formation of the H bond, and (2) the state in which the neighboring molecules are turned to each other by the ends with the same charge is prohibited.

Contrary to ice, the water model should take into account the orientations of the molecules in which the active ends do not lie on the lattice edges. The state of a rigid molecule at the ith site is given by the variable α_i which takes the values $\alpha_i=1,2,\ldots,6$ and by the rotation angle φ_i which changes in the interval $-\pi/4 \leqslant \varphi_i \leqslant \pi/4$ (see Fig. 2). In order to reflect the high directionality of H bonds we assume that the formation of a H bond and a repulsion of the similar ends occur only if the rotation angles of both the neighboring molecules by modulus do not exceed some value Φ: $|\varphi_i|,|\varphi_j|<\Phi$. We will take the energy of the H bond for the angles $|\varphi_i|,|\varphi_j|<\Phi$ to be independent of the angles φ_i,φ_j and equal to $-\varepsilon_0$. The Bernal–Fowler rules imply the impossibility of the realization of the microstate because of the infinite interaction energy. If the absolute value of the rotation angle for any of the molecules in a pair exceeds Φ, the Bernal–Fowler rules are no longer valid and the energy of the pair in terms of the model can be taken to be equal to zero. Therefore,

$$\varepsilon_{\mathrm{H}}(\alpha_i,\varphi_i;\alpha_j,\varphi_j) = \begin{cases} +\infty \quad \text{if } \alpha_i,\ \alpha_j \text{ are incompatible}, \quad |\varphi_i|,|\varphi_j| < \Phi \\ -\varepsilon_0 \quad \text{if } \alpha_i,\ \alpha_j \text{ are compatible}, \quad |\varphi_i|,|\varphi_j| < \Phi \\ 0 \quad \text{if } |\varphi_i > \Phi| \text{ or (and) } |\varphi_j > \Phi|. \end{cases} \tag{1}$$

In the three-dimensional model the quantity Φ would qualitatively correspond to the amplitude of liberations of an ice molecule near its equilibrium position, thus implying the inequality $\Phi<(\ll)\pi/4$. Therefore, we choose the ratio of the angle Φ to the angular segment $(\pi/4)-\Phi$, in which the H bonds do not form,

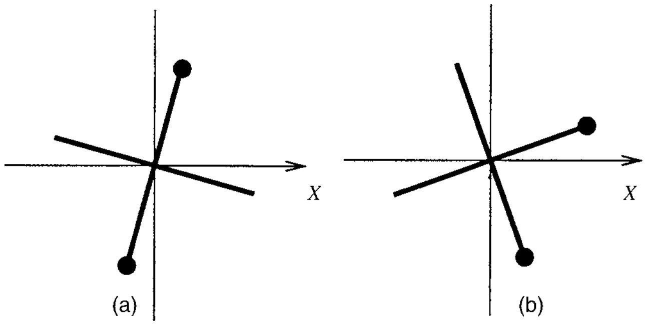

FIG. 2. Specification of the state of a molecule at the site: (a) $\alpha=6$, $\varphi=-15°$; (b) $\alpha=2$, $\varphi=20°$.

$$d^{-1} = \frac{\Phi}{\pi/4 - \Phi} \tag{2}$$

as one of the parameters of the model. The standard criteria of the H-bond formation[21] lead to an estimate $d\sim(10\text{–}15)$. In a two-dimensional model one should choose a slightly lesser value of d. We use the value $d=8$ for the numerical calculations in the present work. We consider the parameter ε_0 as the natural unit of energy: $\varepsilon_0=1$.

To model the interaction of the H bonds we use the following physical considerations. The most symmetric and energetically favorable configuration of the electron and proton density distribution occurs when a molecule forms four H bonds with its nearest neighbors. Hence we chose the interaction energy of the bonds in the form

$$\varepsilon_{\mathrm{HH}}(i) = \begin{cases} -\gamma \quad (\gamma<1) \quad \text{if } (n_{\mathrm{H}})_i = 4 \\ 0 \quad \text{otherwise}. \end{cases} \tag{3}$$

Note, that $\varepsilon_{\mathrm{HH}}(i)$ depends both on the states of the ith molecule and that of its nearest surrounding, so it is not a usual one-particle term, but a five-particle contribution.

As a result, the Hamiltonian of the system can be represented in the form

$$H = \sum_{\langle ij\rangle} \varepsilon_{\mathrm{H}}(ij) + \sum_i \varepsilon_{\mathrm{HH}}(i), \tag{4}$$

where $\langle ij\rangle$ denotes all pairs of the nearest neighbors.

III. METHOD OF IRREDUCIBLE MANY-PARTICLE DISTRIBUTION FUNCTIONS

The present work is mainly focused on the study of the peculiarities of the phase diagram and temperature dependencies of the following quantities, describing the H-bond network in the system: (1) the average number of the H bonds per molecule, (2) fraction of molecules that do not form H bonds, (3) heat capacity, and (4) the parameters which describe the correlation of the states of neighboring molecules. To achieve this target, we use the method of many-particle irreducible distribution functions (MMPIDF). The detailed presentation of its basic concepts in application to lattice and nonlattice systems is given in Refs. 16 and 24–26.

This method is the generalization of the Kikuchi cluster variational method,[17] and of the Bethe–Peierls quasichemical approach.[23] Although the cummulant expansion for the entropy was written by Ursel back in the 20s of the last century, the correct truncation of the series (being one of the three key points of the MMPIDF) for the lattice systems was accomplished only half a century afterwards. However, a rather formal presentation of the material in Refs. 29 and 30 has hampered its deserved acceptance, and the few works which employed the method (e.g., Refs. 15, 18, and 19) contained substantial errors. Moreover, two essential points of the MMPIDF, namely, nontrivial reduction rules[16,24] and methods for approximation of the highest correlation function, were neglected in the works cited above. Hence there are enough convincing arguments to provide the description of the MMPIDF in the present paper.

The energy E and the entropy S of the system, as well as its free energy $F=E-TS$, can be represented as the expansion in the many-particle distribution functions. In the case of two-particle intermolecular interaction the energy of the system is determined only by the binary distribution function:

$$E=\sum_{\langle i,j\rangle}\sum_{\zeta_i,\zeta_j}\varepsilon(\zeta_i,\zeta_j)\rho_2(\zeta_i,\zeta_j). \tag{5}$$

At the same time, the entropy is determined by the complete set of the distribution functions $\rho_k(\zeta_1,\dots,\zeta_k)$, $k=1,\dots,N$:

$$S=S_1+S_2+S_3+\cdots, \tag{6}$$

$$S_1=-\sum_i\sum_{\xi_i}\rho_1(\xi_i)\ln\rho_1(\xi_i)=-N\sum_{\xi_i}\rho_1(\xi_1)\ln\rho_1(\xi_1), \tag{7}$$

$$S_2=-\sum_{\langle ij\rangle}\sum_{\xi_i,\xi_j}\rho_2(\xi_i,\xi_j)\ln\frac{\rho_2(\xi_i,\xi_j)}{\rho_1(\xi_i)\rho_1(\xi_j)},$$

$$\cdots. \tag{8}$$

In these formulas the symbols $\langle ij\rangle$ denote all the possible pairs of particles. The series in (6) is the expansion of the entropy in the irreducible many-particle correlations.[16,29]

Next, we cut the series in (6) at the kth term. Let us discuss the character of the different contributions in the kth term of the series in (6). The graphs of the size k can be connected and disconnected. In a connected graph there is a path from any vertex to any other vertex. Further, in a set of connected graphs one can always choose the most compact graphs that have the least diameter.

From the physical point of view, the main contributions to the thermodynamic quantities are formed by the compact k-vertices graphs. For them the k-particle distribution function $\rho^{(k)}(\cdots)$ is determined mainly by the interactions between the particles inside the cluster and can be built *ab initio*. In particular, to determine $\rho^{(k)}(\cdots)$ for the Pauling ice the principle of equal probability for all allowed configurations of the k-cluster was used.[16] According to the above, the entropy in the k-particle approximation has the form

$$S^{(k)}=S_1^{(k)}+S_2^{(k)}+S_3^{(k)}+\cdots+S_k^{(k)}, \tag{9}$$

$S_m^{(k)}$ being the sum of the contributions of the types of (7) and (8) over all possible sets of m particles, $m=1,\dots,k$, belonging to the compact k cluster [in (9) and further the superscript denotes the order of approximation]. The entropy of the system is determined as a limit of $S^{(k)}$ at $k\to\infty$.

Consider the relation of the distribution function $\rho^{(k)}(\zeta_1,\zeta_2,\dots,\zeta_k)$ with the lower distribution functions $\rho_m^{(k)}$, $m=1,\dots,k-1$, of a k-particle cluster on the example of the two-particle nearest-neighbor distribution function on a simple square lattice.

In a square cluster, $k=m\times m$, the number of the pairs of the nearest neighbors is $2(m-1)m$. The contributions of all such pairs in $\rho_2^{(k)}(\zeta_1,\zeta_2)$ should be taken into account with the same weight, i.e.,

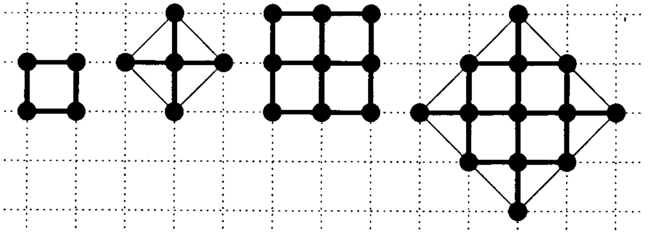

FIG. 3. 4-, 5-, 9- and 13-particle clusters on a square lattice.

$$\rho_2^{(k)}(\zeta_1,\zeta_2)=\frac{1}{2m(m-1)}\sum_{p=1}^{2m(m-1)}\sum_{\{\zeta_{i'}\}_{k-2}}\rho_2^{(k)}(\zeta_1,\zeta_2,\dots,\zeta_k). \tag{10}$$

Here, in addition to the summation over the pairs of the nearest neighbors, there is the summation over the states $\{\zeta_{i'}\}_{k-2}$ of all the molecules in a cluster except the selected pair. It is taken into account that the numbering of the molecules inside the k cluster is arbitrary, hence, generally, the sites (1, 2) in the left-hand side correspond to the molecules with different numbers in the right-hand side. Since the distribution function $\rho^{(k)}(\zeta_1,\zeta_2,\dots,\zeta_k)$ is normalized, so are the distribution functions $\rho_m^{(k)}$, constructed with the help of formulas of the type of (10):

$$\sum_{\{\zeta_i\}}\rho_m^{(k)}(\zeta_1,\dots,\zeta_m)=1,\quad m=1,\dots,k-1. \tag{11}$$

Using the properties of the logarithmic function and the reduction rules of type (10) results in the considerable simplification of $S^{(k)}$. In particular, on a simple square lattice in the approximations with $k=4$, 9, 5, and 13, for which the symmetry of the k cluster coincides with that of the lattice (see Fig. 3),

$$S^{(4)}=\tilde{S}_4^{(4)}-2\tilde{S}_2^{(4)}+\tilde{S}_1^{(4)}, \tag{12}$$

$$S^{(9)}=\tilde{S}_9^{(9)}-2\tilde{S}_6^{(9)}+\tilde{S}_4^{(9)}, \tag{13}$$

$$S^{(5)}=\tilde{S}_5^{(5)}-2\tilde{S}_{2,1}^{(5)}-2\tilde{S}_{2,2}^{(5)}+4\tilde{S}_1^{(5)}, \tag{14}$$

$$S^{(13)}=\tilde{S}_{13}^{(13)}-2\tilde{S}_{8,1}^{(13)}-2\tilde{S}_{8,2}^{(13)}+4\tilde{S}_6^{(13)}-\tilde{S}_4^{(13)}. \tag{15}$$

In the simplest cases of the three-dimensional lattice in the approximation of clusters-cube and clusters-irregular tetrahedra[19] (see Fig. 4) the entropy per molecule is

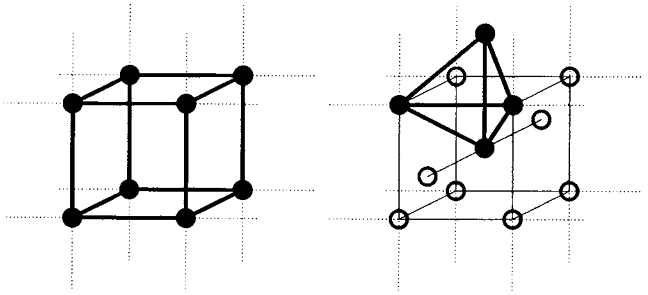

FIG. 4. Clusters–cube ($k=8$) and clusters–irregular tetrahedra on a simple cubic and bcc lattice, correspondingly.

$$S^{(8)} = S_8^{(8)} - 3S_4^{(8)} + 3S_2^{(8)} - S_1^{(8)}, \tag{16}$$

$$S_{\mathrm{tetr}}^{(4)} = 6S_4^{(4)} - 12S_3^{(4)} + 4S_{2,1}^{(4)} + 3S_{2,2}^{(4)} - S_1^{(4)}. \tag{17}$$

As it is seen from (12)–(17), the expression for $S^{(k)}$ is simpler the higher the symmetry of the cluster is. In the approximation of the two-particle cluster, which has the symmetry lower than that of the square (simple cubic) lattice,

$$S_{\mathrm{square}}^{(2)} = 2\widetilde{S}_2^{(2)} - 3\widetilde{S}_1^{(2)}, \tag{18}$$

$$S_{\mathrm{cubic}}^{(2)} = 3\widetilde{S}_2^{(2)} - 5\widetilde{S}_1^{(2)}. \tag{19}$$

In formulas (12)–(18) the designation

$$\widetilde{S}_p^{(k)} = -\sum_{\{\zeta\}} \rho_p^{(k)}(\{\zeta\}) \ln \rho_p^{(k)}(\{\zeta\}), \tag{20}$$

with $\{\zeta\} \equiv \zeta_1, \ldots, \zeta_p$, is used.

The double numeration in formulas (14), (15), and (17) has the following meaning. The contributions $\widetilde{S}_{2,1}^{(5)}$ and $\widetilde{S}_{2,2}^{(5)}$ arise from the pairs of nearest (2, 1) and next to nearest (2, 2) neighbors, correspondingly. Both contributions are calculated by the formulas of type (20). The contributions into $S^{(5)}$ from the pairs of the most distant neighbors, as well as from the triples and quadruples of particles, are absent.

Note that in terms of the MMPIDF the values of the distribution functions for the prohibited microstates are taken to be equal to zero. Hence the prohibited states do not contribute directly neither to the entropy nor to the energy of the system, and manifest themselves only through the normalization conditions.

The following methods can be used to construct the distribution function $\rho^{(k)}(\zeta_1, \zeta_2, \ldots, \zeta_k)$ and the equation of state of the system: (1) the direct variational method (DVM), (2) the method of correlated quasiactivities of the links (CQLs), and (3) the method of noncorrelated quasiactivities of the links (NCQLs).

In the DVM the values of the distribution function $\rho^{(k)}(\zeta_1, \zeta_2, \ldots, \zeta_k)$ that are physically different and linearly independent, i.e., not related by means of symmetry properties and normalization condition, are considered as a set of independent variational parameters $\{z_i\} = z_1, \ldots, z_t$. The number t of the parameters depends on the order of approximation k. The values of z_i are determined directly from the requirements of the minimum of the free energy $F = E(\{z_i\}) - TS(\{z_i\})$:

$$\frac{\partial F(\{z_i\})}{\partial z_j} = 0, \quad 1 \leqslant j \leqslant t(k). \tag{21}$$

In the method of quasiactivities the Boltzmann factor $\exp(E(\{z_i\})/T)$ that corresponds to the interaction energy $E(\{z_i\})$ of the molecules inside the cluster is written explicitly:

$$\rho^{(k)}(\zeta_1, \zeta_2, \ldots, \zeta_k) = A(\{\zeta_i\}) \exp\left(-\frac{E(\{\zeta_i\})}{T} \right), \tag{22}$$

T being the absolute temperature. The factor $A(\{\zeta_i\})$ describes the interaction of the k cluster with the other molecules of the system. In the NCQL method the "quasiactivity" $\mu(\zeta)$ is assigned to each link that connects the cluster molecule in the state ζ with the nearest molecule of the surrounding of the cluster (the quasiactivity of one of the states can be assigned as unity). Therefore, the factor $A(\{\zeta\})$ is represented as a product:

$$A(\{\zeta\}) = A \prod_i \mu(\zeta_i), \tag{23}$$

the value of A being determined for the normalization condition [Eq. (11)] for the distribution function. The number of the variational parameters is less than the number of the different states on a site by one and does not depend on k. The decrease in the number of the variational parameters in comparison with the DVM results in some loss of accuracy. However, the discrepancies in the determination of the distribution function $\rho^{(k)}(\zeta_1, \zeta_2, \ldots, \zeta_k)$ are smoothed due to the summation operations [Eq. (12)] used to determine the lower distribution functions $\rho_m^{(k)}(\zeta_1, \ldots, \zeta_m)$, which results in substantially lesser errors in the thermodynamic potentials.

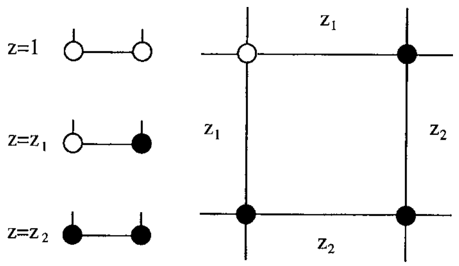

FIG. 5. The choice of the quasiactivities of the links in the CQL method (k=4). The black circles correspond to the states with $|\varphi_i| < \Phi$, the white to $|\varphi_i| \geqslant \Phi$.

Contrary to the NCQLs, in the CQLs, the quasiactivity is assigned not to each external link separately but to a set of most strongly correlated links. For example, in the case of four-particle approximation on a simple square lattice (see Fig. 5), the most strongly correlated pairs of the external links are those perpendicular to the same edge of the square. The quasiactivity of the one arbitrary chosen state of the pair, for example $(\zeta_1 = 1, \zeta_2 = 1)$, can be put equal to unit $z(\zeta_1 = 1, \zeta_2 = 1) = 1$.

The optimal value of k depends on the details of interparticle interactions. For the Pauling ice and other systems with the strict selection rules[16,27] k should be greater than 1. This follows from the impossibility of taking into account the constraint rules in the one-particle, i.e., mean field, approximation. The analysis shows that the distribution function and entropy are best approximated when k corresponds to the clusters of the symmetry, which coincides with that of the lattice.[16] For the square lattice this requirement is satisfied for the clusters with k=4,5,9,13,... that have the square shape for k=4,9,16,... and the rhombus shape for k=5 and 13 (see Fig. 3). Moreover, in the systems with H bonds the accuracy of the calculations depends on the presence of the closed loops of H bonds in the cluster.[16] In particular, in the compact 4-, 9-, 16-particle clusters all loops are closed, while in the five-particle cluster the closed loops are absent. The clusters with the closed loops of the H bonds play the leading role because in them the multiparticle interactions are considered in the most comprehensive way.

In the systems with the strong anisotropic interactions, where the microinhomogeneous structures can form, the value of k should be chosen in accordance with the size of the microinhomogeneity regions.

IV. EQUATION OF STATE

A. Two-particle approximation, $k=2$

Due to the piecewise character of the functions that define the Hamiltonian [Eq. (4)] of the system, the distribution function $g^{(2)}(\alpha_1,\varphi_1;\alpha_2,\varphi_2)$ is discontinuous at $|\varphi_1|,|\varphi_1|=\Phi$:

$$g^{(2)}(\alpha_1,\varphi_1;\alpha_2,\varphi_2) = \begin{cases} 0 & \text{if } |\varphi_1|,|\varphi_1|<\Phi, \quad \alpha_1,\ \alpha_2 \text{ are noncompatible} \\ g(2) & \text{if } |\varphi_1|,|\varphi_1|<\Phi, \quad \alpha_1,\ \alpha_2 \text{ are compatible} \\ g(0) & \text{if } |\varphi_1|,|\varphi_1|\geqslant\Phi \\ g(1) & \text{if } \varphi_1<\Phi, \quad \varphi_2\geqslant\Phi \text{ or } \varphi_1\geqslant\Phi, \quad \varphi_2<\Phi. \end{cases} \tag{24}$$

The parameter $p=0$, 1, and 2 which enters $g^{(2)}(p)$ denotes the number of the molecules in the pair for which $|\varphi_i|\leqslant\Phi$. The quantities $g(p)$ do not depend on the states of the molecules $\alpha_{1(2)}=1,\ldots,6$. Consider the procedure for the determination of the values $g(p)$ in terms of the method described above. The simplest of them is the approximation of NCQLs.

1. Approximation of noncorrelated quasiactivities of the links

We define the quasiactivity of the external link that connects the molecule i of a cluster with one of the surrounding molecules as

$$z(\varphi_i) = \begin{cases} 1 & \text{if } |\varphi_i|<\Phi \\ z & \text{if } \Phi\leqslant|\varphi_i|\leqslant\pi/4. \end{cases} \tag{25}$$

According to Eqs. (22) and (23) and the Hamiltonian of the system [Eq. (4)], the quantities $g^{(2)}(p)$ satisfy the relation

$$g^{(2)}(2):g^{(2)}(1):g^{(2)}(0)=\exp(1/T):z^3:z^6. \tag{26}$$

As it follows from (24), the degeneracies of the states of the two-particle cluster with $p=0$, 1, and 2 are

$$\nu(2)=18, \quad \nu(1)=72, \quad \nu(0)=36. \tag{27}$$

The distribution function $g^{(2)}(\alpha_1,\varphi_1;\alpha_2,\varphi_2)$ satisfies the normalization condition

$$\sum_{\alpha_1\alpha_2=1}^{6}\int_{-\pi/4}^{\pi/4}d\varphi_1\int_{-\pi/4}^{\pi/4}d\varphi_2 g^{(2)}(\alpha_1,\varphi_1;\alpha_2,\varphi_2)=1 \tag{28}$$

which in conjunction with (26) and (27) yields

$$g(2)=\frac{1}{\Omega}\exp(1/T), \quad g(1)=\frac{z^3}{\Omega}, \quad g(0)=\frac{z^6}{\Omega}, \tag{29}$$

with the normalization factor $\Omega=\Omega(z,T)$ being equal to

$$\Omega(z,T)=(2\Phi)^2[18\exp(1/T)+72(z^3d)+36(z^3d)^2]. \tag{30}$$

The one-particle distribution function $g_1^{(2)}(\alpha,\varphi)$ determined from the reduction relations [Eq. (11)] does not depend on the discrete state variable α:

$$g_1^{(2)}(\alpha,\varphi) = \begin{cases} g_1^{(2)}(1), & \text{if } |\varphi|<\Phi \\ g_1^{(2)}(0) & \text{if } \Phi\leqslant|\varphi|\leqslant\pi/4, \end{cases} \tag{31}$$

where

$$g_1^{(2)}(1)=2\Phi[3g^{(2)}(2)+6g^{(2)}(1)d], \tag{32}$$

$$g_1^{(2)}(0)=2\Phi[6g^{(2)}(1)+6g^{(2)}(0)d]. \tag{33}$$

After the summation over α_1 and the integration over the angles φ_i the formulas for the energy and entropy per molecule take form

$$E^{(2)}=-2G^{(2)}(2)-\gamma\frac{(G^{(2)}(2))^4}{(G_1^{(2)}(1))^3}, \tag{34}$$

$$\begin{aligned} S^{(2)} &= 2S_2^{(2)}-3S_1^{(2)}+G_1^{(2)}(0)\ln d \\ &= -2\left[G^{(2)}(2)\ln\frac{G^{(2)}(2)}{18}\right. \\ &\quad \left.+G^{(2)}(1)\ln\frac{G^{(2)}(1)}{72}+G^{(2)}(0)\ln\frac{G^{(2)}(0)}{36}\right] \\ &\quad +3\left\{G_1^{(2)}(1)\ln\frac{G_1^{(2)}(1)}{6}+G_1^{(2)}(0)\ln\frac{G_1^{(2)}(0)}{6}\right\} \\ &\quad +G_1^{(2)}(0)\ln d, \end{aligned} \tag{35}$$

where

$$G^{(2)}(2)=18(2\Phi)^2g^{(2)}(2), \tag{36}$$

$$G^{(2)}(1)=72(2\Phi)^2g^{(2)}(1), \tag{37}$$

$$G^{(2)}(0)=36(2\Phi)^2g^{(2)}(0). \tag{38}$$

The quantity $G^{(2)}(p)$, $p=0$, 1, and 2, has the meaning of the probability for the p molecules of a pair to be deviated by the angles not greater than Φ. Similarly, $G_1^{(2)}(1)$ and $G_1^{(2)}(0)$ are the one-particle probabilities of the states for which $|\varphi|<\Phi$ or $\Phi\leqslant|\varphi|$, correspondingly,

$$G_1^{(2)}(1)=6(2\Phi)g_1^{(2)}(1), \tag{39}$$

$$G_1^{(2)}(0)=6(2\Phi)dg_1^{(2)}(0). \tag{40}$$

The factor 2 in Eq. (34) accounts for the fact that the number of the pairs of the nearest neighbors is two times greater that the number of sites.

The quantities defined above allow to investigate the temperature dependence of the average number $\bar{n}_{\mathrm{H}}$ of the H bonds per molecule, the simplest correlation parameters, and the heat capacity of the system.

The average number of H bonds $\bar{n}_{\mathrm{H}}$ per molecule is given by the formula

$$\bar{n}_{\mathrm{H}} = \sum_{n_{\mathrm{H}}=1}^{4} n_{\mathrm{H}} W(n_{\mathrm{H}}), \tag{41}$$

$W(n_{\mathrm{H}})$ being the probability of the formation by a molecule of n_{H} H bonds with its nearest neighbors.

Let us consider the algorithm for the construction of $W^{(2)}(3)$. The probability of a formation by a molecule of three H bonds is $G_1^{(2)}(1)\ (G^{(2)}(2)/G_1^{(2)}(1))^3$, where the first multiplier denotes the probability of the molecule to be in a state that favors the formation of H bonds ($|\varphi| < \Phi$), and the expression in the brackets is the conditional probability of the formation of the H bond with the nearest neighbor. The factor $4(1/2)(G^{(2)}(1)/G_1^{(2)}(1))$ corresponds to the fourth neighbor that can be found on any of four neighboring sites. The factor $1/2$ is present because the absence of the H bond is stipulated by only one of two allowed states of the pair. Therefore,

$$W^{(2)}(3) = 2G_1^{(2)}(1)\left(\frac{G^{(2)}(2)}{G_1^{(2)}(1)}\right)^3. \tag{42}$$

As a result, formula (41) takes form

$$\bar{n}_{\mathrm{H}}^{(2)} = 4G^{(2)}(2)\left(\frac{G^{(2)}(2)}{G_1^{(2)}(1)}\right)^3 + 6G^{(2)}(1)\left(\frac{G^{(2)}(2)}{G_1^{(2)}(1)}\right)^3 + 3\frac{(G^{(2)}(1))^2}{G_1^{(2)}(1)}\left(\frac{G^{(2)}(2)}{G_1^{(2)}(1)}\right)^2 + \frac{1}{2}G^{(2)}(2)\left(\frac{G^{(2)}(1)}{G_1^{(2)}(1)}\right)^3. \tag{43}$$

We define the simplest correlation parameters $K(1)$ and $K(0)$, that describe the tendency for aggregation of molecules that are able (or unable) to form H bond, by the equations

$$K^{(2)}(1) = \frac{G^{(2)}(2)}{(G_1^{(2)}(1))^2}, \quad K^{(2)}(0) = \frac{G^{(2)}(0)}{(G_1^{(2)}(0))^2}. \tag{44}$$

We will use the standard expression for the heat capacity:

$$C^{(2)} = T\frac{dS^{(2)}}{dT}, \tag{45}$$

$S^{(2)}$ being given by formula (35).

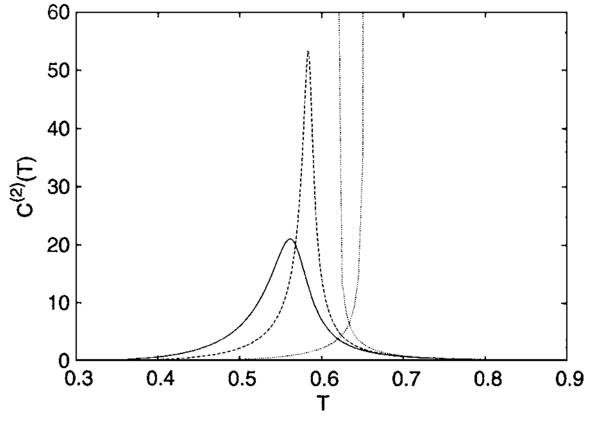

FIG. 6. The temperature dependence of the heat capacity $C^{(2)}(T)$ in the approximation of the noncorrelated quasiactivities of the links for $\gamma=0$ (solid line), $\gamma=0.1$ (dashed line), and $\gamma=0.3$ (dotted line).

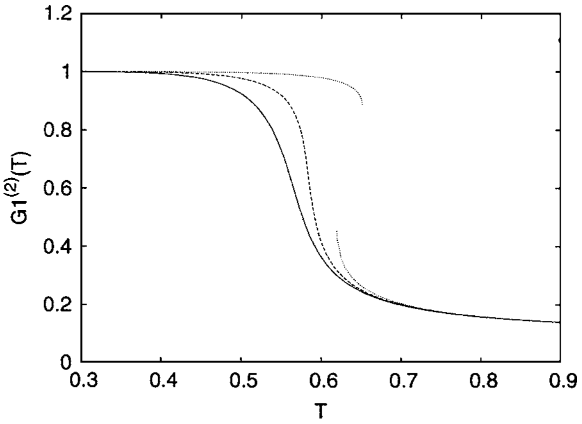

FIG. 7. The temperature dependence of the fraction of molecules $G_1^{(2)}(T)$ [see (39)] that are deviated on small angles in the approximation of the noncorrelated quasiactivities of the links for $\gamma=0$ (solid line), $\gamma=0.1$ (dashed line), and $\gamma=0.3$ (dotted line).

All the thermodynamic quantities listed above depend on the quasiactivity $z^{(2)}(T)$ which is determined from the equation $\partial F^{(2)}(z^{(2)},T)/\partial z^{(2)}=0$.

The analysis of this equation shows that for $0 \leqslant \gamma \leqslant 0.17$ and $d=8$ it has only one root $z^{(2)}(T)$. The temperature dependencies of $G_1^{(2)}(1)$, $K^{(2)}(1)$, and $K^{(2)}(0)$, as well as of $C^{(2)}(T)$ and $\bar{n}_{\mathrm{H}}^{(2)}(T)$, at $\gamma=0$, 0.1, and 0.3 are presented in Figs. 6–10. One can see that the majority of H bonds break in the narrow temperature interval ΔT, which can be interpreted as a "smoothed" first-order phase transition. The width of the region essentially depends on γ: the greater is γ the lesser is ΔT. The value of the maximum of the heat capacity $C_{\max}$ is also sensitive to the parameter γ: on change of γ from zero to 0.2 it changes by an order of magnitude. At the same time, the area under the curve $C^{(2)}(T)$ in the interval ΔT depends on γ weakly. Note that the average number of the H bonds $\bar{n}_{\mathrm{H}}^{(2)}$ does not exceed 1 above the temperature of the smoothed phase transition, while it is close to 4 below it.

At $\gamma > 0.17$ in the narrow temperature interval $[T_1^{(2)}(\gamma), T_2^{(2)}(\gamma)]$ two solutions of the variational equation exist, one corresponding to the stable, another to the metastable

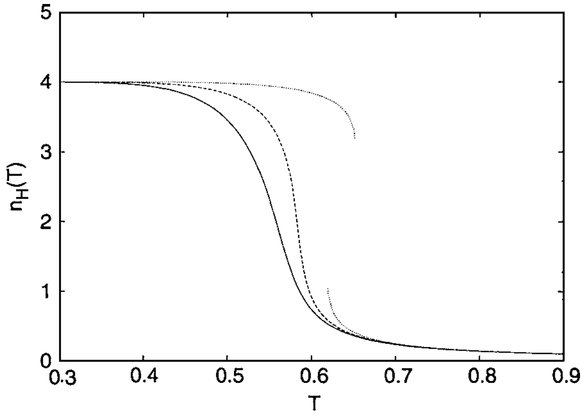

FIG. 8. The temperature dependence of the average number of H bonds per molecule $\bar{n}_{\mathrm{H}}^{(2)}$ [see (43)] in the approximation of the noncorrelated quasiactlivites of the links for $\gamma=0$ (solid line), $\gamma=0.1$ (dashed line), and $\gamma=0.3$ (dotted line).

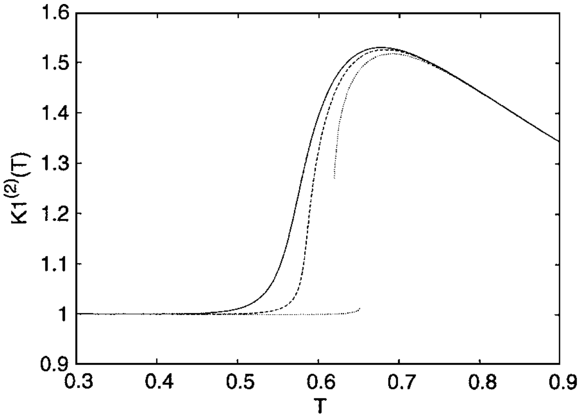

FIG. 9. The temperature dependence of the parameter $K^{(2)}(1)$ in the approximation of the noncorrelated quasiactivities of the links for $\gamma=0$ (solid line), $\gamma=0.1$ (dashed line), and $\gamma=0.3$ (dotted line).

state. The equilibrium transition point T_* and the hidden heat of the phase transition per molecule are determined in the standard way:

$$F_1^{(2)}(T_*) = F_2^{(2)}(T_*), \tag{46}$$

$$\Delta Q = T_*(S_2(T_*) - S_1(T_*)), \tag{47}$$

in which $F_i^{(2)}(T)=F_i^{(2)}(z_i(T),T)$ are the free energies of the concurrent phases; here, as above, the superscripts denote the different phases of the system. At approaching the end points $T_1(\gamma)$ and $T_2(\gamma)$ from the side of the metastable states, heat capacity diverges, thus leading to the assumption that $T_1(\gamma)$ and $T_2(\gamma)$ are the spinodal points in the model of two-dimensional water.

The correlation parameter $K^{(2)}(0)$ in the region where $\bar{n}_{\mathrm{H}}^{(2)} \approx 4$ is much greater than unity. This suggests that the break of the H bonds of two adjacent molecules is much more favorable than the break of the H bonds of two remote molecules. On the contrary, the parameter $K^{(2)}(1)$ is greater than 1 in the region where $\bar{n}_{\mathrm{H}}^{(2)} \leqslant 1$, so the molecules with unbroken H bonds also form compact samples. Similar strong correlations are typical for the Pauling ice and the Flory–Huggins polymer solution[25]

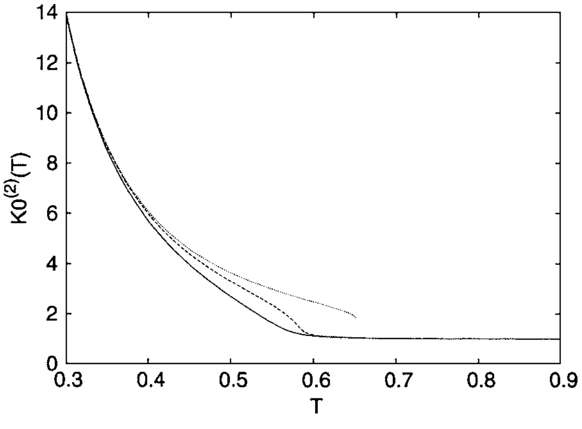

FIG. 10. The temperature dependence of the parameter $K^{(2)}(0)$ in the approximation of the noncorrelated quasiactivities of the links for $\gamma=0$ (solid line), $\gamma=0.1$ (dashed line), and $\gamma=0.3$ (dotted line).

2. The direct variational approximation

In the two-particle approximation there are two independent variational parameters, z_1 and z_2, which can be chosen in the following way:

$$G^{(2)}(0) = 36z_1/\Omega(z_1,z_2,T), \tag{48}$$

$$G^{(2)}(1) = 72z_2/\Omega(z_1,z_2,T), \tag{49}$$

$$G^{(2)}(2) = 18/\Omega(z_1,z_2,T). \tag{50}$$

The normalization factor

$$\Omega(z_1,z_2,T) = 18 + 72z_1 + 36z_2 \tag{51}$$

is chosen to meet the normalization condition $\Sigma_{p=0}^{2} G^{(2)}(p) = 1$. The behavior of thermodynamic functions listed in Figs. 6–10 obtained within the DVA is qualitatively similar to that obtained in the NQL approximation. It is important to note that the results coincide for $\gamma=0$, i.e., in the case when only two-particle interaction of the nearest neighbors is presented in Hamiltonian. However, for the $\gamma<0.3$ the deviation is small enough.

B. Four-particle approximation, *k*=4

The four-particle cluster is formed by four molecules lying at the vertices of the unit square. If the rotation angles of all four molecules are small, the Bernal–Fowler rules allow only 82 of the 6^4 discrete states of the cluster. The similar situation is also typical for the Pauling ice.[16] As in the two-particle approximation, the expressions for the entropy and energy become simpler after summation over the discrete variables α_i and the integration over the angles φ_i:

$$S^{(4)} = \tilde{S}_4^{(4)} - 2\tilde{S}_2^{(4)} + \tilde{S}_1^{(4)} + G_1^{(4)}(0)\ln d. \tag{52}$$

Here,

$$\begin{aligned}\tilde{S}_4^{(4)} = -\Bigg[& G^{(4)}(4)\ln\left(\frac{G^{(4)}(4)}{82}\right) \\ & + G^{(4)}(3)\ln\left(\frac{G^{(4)}(3)}{6^4}\right) + G^{(4)}(2,1)\ln\left(\frac{G^{(4)}(2,1)}{2(6^4)}\right) \\ & + G^{(4)}(2,2)\ln\left(\frac{G^{(4)}(2,2)}{2(6^4)}\right) + G^{(4)}(1)\ln\left(\frac{G^{(4)}(1)}{4(6^4)}\right) \\ & + G^{(4)}(0)\ln\left(\frac{G^{(4)}(0)}{6^4}\right)\Bigg]\end{aligned} \tag{53}$$

The following designations are used in Eqs. (52) and (53) and below. (1) $G^{(4)}(p)$, $p=0$, 1, 3, and 4, is the probability that only p molecules of the four-particle cluster are deviated on the angles that by the absolute value do not exceed Φ (2) At $p=2$ there are two options: $G^{(4)}(2,1)$ and $G^{(4)}(2,2)$ correspond to the situations when two molecules with small rotation angles lie in the neighboring and opposite vertices of the square, correspondingly. The quantity $G_1^{(4)}(1)$ has the same meaning as $G_2^{(2)}(1)$ and differs only in the order of approximation. The same applies to the other cases.

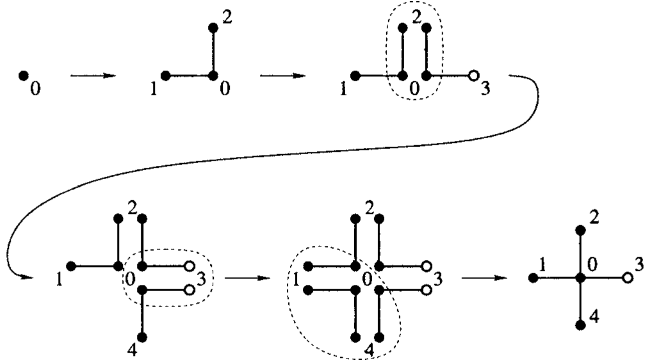

FIG. 11. The illustration to the calculation of the probability $W^{(4)}(3)$. The black (a) and white (b) circles denote molecules, in which angles of rotation by the absolute value do not (a) or do (b) exceed the quantity Φ, correspondingly.

To calculate the energy of the system [see (4)] and the average number of H bonds per molecule requires, as before, the knowledge of the probabilities $W^{(4)}(p)$ of the formation of p H bonds by a molecule. Let us demonstrate the details of the derivation of $W^{(4)}(p)$ on the example of $W^{(4)}(3)$.

One of four physically equivalent states contributing to $W^{(4)}(3)$ is presented in Fig. 11. The molecule "0" is, with the probability $G_1^{(4)}(1)$, in a state in which it is able to form a H bond. In the four-particle approximation the states of the molecules in each of the four triplets ("1,0,2," "2,0,3," "3,0,4," and "4,0,1") are correlated. The conditional probability $P(1,0,2)$ for the triplet of the molecules "1,0,2" to be in the state shown in Fig. 11 is equal to

$$P(1,0,2) = \frac{G^{(4)}(4) + G^{(4)}(3)/4}{G_1^{(4)}(1)}. \tag{54}$$

The two terms in the numerator correspond to two ways to complement the triplet of particles "1,0,2" to the four-particle cluster: $G^{(4)}(4)$, by the molecule, deviated on a small angle, and $G^{(4)}(3)/4$, by the molecule, deviated on a large angle ($|\varphi| \geqslant \Phi$).

Since the state of the pair "0,2" is already fixed, the conditional probability $P(2,0,3)$ for the triplet "2,0,3" differs from (54) by the change from the one-particle probability $G_1^{(4)}(1)$ to the two-particle one $G_2^{(4)}(2)$:

$$P(2,0,3) = \frac{G^{(4)}(4) + G^{(4)}(3)/4}{G_2^{(4)}(2)}. \tag{55}$$

For the triplet "3,0,4" the conditional probability $P(3,0,4)$ can be determined in a similar way:

$$P(3,0,4) = \frac{G^{(4)}(3)/4 + G^{(4)}(2,1)/4}{G_2^{(4)}(2)}. \tag{56}$$

For the last triplet, "4,0,1," one should take into account that the states of both pairs, "0,1" and "0,4," are fixed; therefore,

$$P(4,0,1) = \frac{(G^{(4)}(3)/4 + G^{(4)}(2,1)/4)G_1^{(4)}(1)}{(G_2^{(4)}(1)/2)^2}. \tag{57}$$

The factor $G_1^{(4)}(1)$ appears in the numerator because the molecule "0" is taken into account twice: in pair with the molecule "1" and molecule "4."

As a result, $W^{(4)}(3)$ is equal to

$$W^{(4)}(3) = 4\left[4\frac{\left(G^{(4)}(4) + \dfrac{G^{(4)}(3)}{4}\right)^2\left(\dfrac{G^{(4)}(3)}{4} + \dfrac{G^{(4)}(2,1)}{4}\right)^2 G_1^{(4)}(1)}{(G_2^{(4)}(2))^2(G_2^{(4)}(1))^2}\right]. \tag{58}$$

The expressions for the three other probabilities $W^{(4)}(p)$, $p=1$, 2, and 4, are derived in a similar way:

$$W^{(4)}(1) = 4\frac{\left(\dfrac{G^{(4)}(3)}{4} + \dfrac{G^{(4)}(2,1)}{4}\right)^2\left(\dfrac{G^{(4)}(2,2)}{2} + \dfrac{G^{(4)}(1)}{4}\right)G_1^{(4)}(1)}{\left(\dfrac{G_2^{(4)}(1)}{2}\right)^3 G_2^{(4)}(2)}, \tag{59}$$

$$\begin{aligned} W^{(4)}(2) = \frac{G_1^{(4)}(1)}{2(G_2^{(4)})^2(G_2^{(4)}(1))^2}\Bigg[&\left(G^{(4)}(4) + \frac{G^{(4)}(3)}{4}\right) \\ &\times(G^{(4)}(3) + G^{(4)}(2,1))^2\left(G^{(4)}(2,2) + \frac{G^{(4)}(1)}{2}\right) \\ &+ \frac{1}{4^2}(G^{(4)}(3) + G^{(4)}(2,1))^4\Bigg], \end{aligned} \tag{60}$$

$$W^{(4)}(4) = \frac{\left(G^{(4)}(4) + \dfrac{G_3^{(4)}}{4}\right)^4 G_1^{(4)}(1)}{(G_1^{(4)}(2))^4}. \tag{61}$$

Two- and one-particle probabilities are found with help of the reduction rules:

$$G_2^{(4)}(2) = \frac{4G^{(4)}(4) + 2G^{(4)}(3) + G^{(4)}(2,1)}{4}, \qquad (62)$$

$$G_2^{(4)}(1) = \frac{2G^{(4)}(3) + 2G^{(4)}(2,1) + 4G^{(4)}(2,2) + 2G^{(4)}(1)}{4}, \qquad (63)$$

$$G_2^{(4)}(0) = \frac{4G^{(4)}(0) + 2G^{(4)}(1) + G^{(4)}(2,1)}{4}, \qquad (64)$$

$$G_1^{(4)}(1) = \frac{4G^{(4)}(4) + 3G^{(4)}(3) + 2G^{(4)}(2,1) + 2G^{(4)}(2,2) + G^{(4)}(1)}{4}, \qquad (65)$$

$$G_1^{(4)}(0) = \frac{4G^{(4)}(0) + 3G^{(4)}(1) + 2G^{(4)}(2,1) + 2G^{(4)}(2,2) + G^{(4)}(3)}{4}. \qquad (66)$$

With help of formulas (58)–(64), it is not difficult to obtain in the four-particle approximation the explicit expressions for the energy $E^{(4)} = -2G_2^{(4)}(2) - \gamma W^{(4)}(4)$ and for the average number of the H bonds $[n^{(4)} = \Sigma_{p=1}^{4} p W^{(4)}(p)]$ per molecule.

In this approximation, besides the simplest parameters $K(1)$ and $K(0)$, it is possible to introduce the parameters that describe the irreducible correlations in the states of the quadruplets of particles. The parameter $Q(1)$ defined as

$$Q(1) = \frac{G^{(4)}(4)(G_1^{(4)}(1))^2}{(G_2^{(4)}(2))^4} \qquad (67)$$

is of special interest. It characterizes the tendency for the formation of a closed loop by four H bonds. This loop is minimal on the two-dimensional lattice.

1. Approximation of noncorrelated quasiactivities of the links

As in the two-particle approximation, we assign the quasiactivity z to each link of a molecule with rotation angle in the interval $\Phi \leqslant |\varphi| \leqslant \pi/4$. Then it is not difficult to obtain

$$G^{(4)}(4) = \frac{82\exp(4/T)}{\Omega^{(4)}},$$

$$G^{(4)}(3) = \frac{4(18^2)(z^2 d)\exp(2/T)}{\Omega^{(4)}},$$

$$\cdots . \qquad (69)$$

The normalization factor $\Omega^{(4)}$ is equal to

$$\Omega^{(4)} = 80e^{4/T} + 4(18^2)(z^2 d)e^{2/T} + 2(6^4)e^{1/T}(z^2 d)^2 + 2(6^4) \times (z^2 d)^2 + 4(6^4)(z^2 d)^3 + 6^4 (z^2 d)^4. \qquad (70)$$

The solution of the variational equation is qualitatively the same with those obtained in the two-particle approximation. This is not surprisingly because 2- and 4-particle clusters do not contain any molecule with its complete surrounding, so in both approximations the energy of the H-bond interaction is accounted quite roughly.

The parameter $Q(1)$ slightly differs from the unit far from the temperature of phase transition $(|T - T_*| > 0.15)$, but in the transition region has very sharp minima. This indicates the breakage of closed loops of H bonds in the corresponding temperature interval.

2. Approximation of correlated quasiactivities of the links

Let us divide eight external links of the four-particle cluster into four pairs so that the links of each pair are perpendicular to the same edge of the square (see Fig. 5).

Evidently, the correlations of the states of links of the same pair are stronger than the correlations of links of different pairs. We define the quasiactivities of the pair of links from the neighboring molecules of the square i and j in the following way:

$$z = \begin{cases} 1 & \text{if } |\varphi_i| < \Phi, \quad |\varphi_j| < \Phi \\ z_1 & \text{if } |\varphi_i| < \Phi, \quad |\varphi_j| \geqslant \Phi \quad \text{or } |\varphi_j| < \Phi, \quad |\varphi_i| \geqslant \Phi \\ z_2 & \text{if } |\varphi_i| \geqslant \Phi, \quad |\varphi_j| \geqslant \Phi. \end{cases} \qquad (71)$$

It is not difficult to cast the expressions for the functions $G^{(4)}(p)$ equal to the probabilities that p of four molecules of a cluster are rotated by a small angle, e.g.,

$$G^{(4)}(3) = \frac{4(18^2)(z_1^2 d)\exp(1/T)}{\Omega^{(4)}}, \qquad (72)$$

$$G^{(4)}(2,1) = \frac{2(36^2)(z_1^2 z_2 d)\exp(1/T)}{\Omega^{(4)}},$$

$$\cdots . \qquad (73)$$

3. Direct variational approximation

In the four-particle approximation there are five independent variational parameters. We define them in the following way:

$$P^{(4)}(4) = \frac{1}{\Omega^{(4)}} 82\exp(4/T), \qquad (74)$$

$$P^{(4)}(3) = \frac{1}{\Omega^{(4)}} 6^4 d z_1' \exp(2/T), \qquad (75)$$

$$P^{(4)}(2,1) = \frac{1}{\Omega^{(4)}} 2(6^4) d^2 z_2' \exp(1/T), \qquad (76)$$

$$P^{(4)}(2,2) = \frac{1}{\Omega^{(4)}} 2(6^4) d^2 z_3', \qquad (77)$$

$$P^{(4)}(1) = \frac{1}{\Omega^{(4)}} 4(6^4) d^3 z_4', \qquad (78)$$

TABLE I. The dependence of the temperatures of the instability (spinodal) T_1 and T_2, equilibrium phase transition T_*, and the heat of transition Q on the interaction parameter γ. $(2-1)-k=2$, NCQL; $(2-2)-k=2$, DVA; $(4-1)-k=4$, NCQL; $(4-2)-k=4$, CQL; $(4-5)-k=4$, DVA.

		$\gamma=0.15$	$\gamma=0.20$	$\gamma=0.25$	$\gamma=0.30$	$\gamma=0.35$
T_1	(2–1)	⋯	0.6057	0.6132	0.6196	0.6252
	(2–2)	⋯	0.608	0.616	0.623	0.629
	(4–1)	⋯	0.6076	0.6171	0.6248	0.6314
	(4–2)	⋯	⋯	⋯	0.6378	0.6480
	(4–5)	⋯	⋯	⋯	⋯	0.6525
T_*	(2–1)	⋯	0.6078	0.6212	0.6351	0.6491
	(2–2)	⋯	0.609	0.622	0.634	0.648
	(4–1)	⋯	0.6081	0.6224	0.6367	0.6509
	(4–2)	⋯	⋯	⋯	0.6384	0.6521
	(4–5)	⋯	⋯	⋯	⋯	0.6526
T_2	(2–1)	⋯	0.6100	0.6296	0.6516	0.6749
	(2–2)	⋯	0.610	0.628	0.647	0.667
	(4–1)	⋯	0.6087	0.6287	0.6512	0.6752
	(4–2)	⋯	⋯	⋯	0.6388	0.6548
	(4–5)	⋯	⋯	⋯	⋯	0.6526
Q	(2–1)	⋯	1.0947	1.5399	1.7812	1.9450
	(2–2)	⋯	0.9386	1.4383	1.7066	1.877
	(4–1)	⋯	0.7727	1.4532	1.7436	1.9256
	(4–2)	⋯	⋯	⋯	0.9943	1.6126
	(4–5)	⋯	⋯	⋯	⋯	0.1799

$$P^{(4)}(0) = \frac{1}{\Omega^{(4)}} 6^4 d^4 z_5', \tag{79}$$

where

$$\Omega^{(4)} = 82e^{4/T} + 6^4 d z_1' e^{2/T} + 2(6^4) d^2 z_2' e^{1/T} + 2(6^4) d^2 z_3' + 4(6^4) d^3 z_4' + 6^4 d^4 z_5'. \tag{80}$$

The comparison of the thermodynamic functions, such as $\bar{n}_{\mathrm{H}}(T)$, $C(T)$, etc., obtained in the above described approximations at $k=4$ leads to the following conclusion:

(1) The typical behavior of the phase diagram of the system in the T, γ space is qualitatively the same.
(2) At $\gamma=0$ the results obtained in the CQL and DVA coincide. It is the rigorous result for the systems with the two-particle interaction of nearest-neighbor molecules.

In Table I the temperatures of instability $T_1(\gamma)$ and $T_2(\gamma)$, and also the temperatures of equilibrium phase transition $T_*(\gamma)$ calculated in different approximations are presented. We see that the more precise is the approximation the higher is $T_1(\gamma)$ and the lesser is $T_2(\gamma)$. This means that more correct account of H-bond correlations results effectively in the stabilization of both phases.

Another possibility for quantitative comparison of the results obtained is due to that the values z, z_1, $\sqrt{z_2}$, and $\sqrt{z_1'}$ [see (71)–(80)] have close physical meaning. The differences between these values are caused by the correlation effects, which are accounted to different extents in each approximation. The corresponding results are collected in Table II.

Note that the inequality $z_1^2 < z_2$ holds at all temperatures (the equality $z_1^2 = z_2$ would correspond to NCQLs). This inequality together with the inequality $K^{(4)}(i) > 1$, $i=0,1$, points out the tendency to the grouping of the molecules that are in the states of the same type.

C. Nine-particle approximation, $k=9$

The molecules of the nine-particle cluster are located on the edges and in the center of a square with a side length $a=2$. In this approximation there are 102 different states of the cluster, each of them being realized with the probability $G^{(9)}(t,s)$, where t is the number of the molecules able to form H bonds, and t denotes the configurations formed by these molecules. The parameter t can have the values $t=0,\dots,9$, and s changes from 1 to some value $s(t)$. For example, $s(9)=1$, $s(8)=3$, $s(7)=8$, etc., so that $\Sigma_{t=0}^{9} s(t) = 102$.

TABLE II. The comparison of the quasiactivities of links and the variational parameter $\sqrt{z_1'}$ at $k=4$ and $\gamma=0.3$.

T	z	z_1	$\sqrt{z_2}$	$\sqrt{z_1'}$
0.20	0.0003	0.0003	0.0014	0.0003
0.30	0.0056	0.0056	0.0157	0.0057
0.40	0.0248	0.0248	0.0531	0.0249
0.50	0.0613	0.0614	0.1157	0.0615
0.55	0.0882	0.0883	0.1613	0.0890
0.60	0.1268	0.1287	0.2300	0.1310
0.65	0.7392	0.6229	0.6961	0.5276
0.70	0.8261	0.7838	0.8115	0.7389
0.75	0.8701	0.8477	0.8620	0.8176
0.80	0.8985	0.8851	0.8935	0.8630
0.90	0.9344	0.9285	0.9320	0.9148

In the nine-particle approximation the probability $W^{(9)}(p)$ of the formation by a molecule of four bonds is related to the functions $G^{(9)}(t,s)$ by the linear relationships of the type

$$W^{(9)}(4) = G^{(9)}(9,1) + G^{(9)}(8,1) + \sum_{s=1}^{2} G^{(9)}(7,s) + G^{(9)} \times (6,1) + G^{(9)}(5,1). \tag{81}$$

The origin of each term becomes more evident after imagining the five-particle crosslike configuration (see Fig. 3), in which the central molecule is connected to four other molecules by the H bonds, being augmented to the nine-particle cluster.

According to the above, the energy of the system is

$$E^{(9)} = -2G_2^{(9)}(2) - \gamma\left(G^{(9)}(9,1) + G^{(9)}(8,1) + \sum_{s=1}^{2} G^{(9)} \times (7,s) + G^{(9)}(6,1) + G^{(9)}(5,1)\right). \tag{82}$$

We skip the explicit expressions for the average number of the H bonds $\bar{n}_{\mathrm{H}}$ and the functions $G_6^{(9)}(p,s)$ and $G_6^{(9)}(p,s)$ determining the entropy because of their complexity.

In the nine-particle approximation the molecules of a cluster are in the physically nonequivalent locations: only the central molecule is surrounded by the neighbors that belong to the same cluster. Therefore, the NCQL method allows two options:

(1) The quasiactivity of each external link of the boundary molecule of the cluster is introduced in the same way as in the two- and four-particle approximations; and

(2) The states of the boundary molecule of the cluster under the constraint that the molecule is rotated on a small angle $|\varphi| < \Phi$ fall into one of the two groups, the first containing the states in which the molecule is able to form four bonds with its neighbors, the second containing the states with three or less H bonds. We take the quasiactivities of the external links to be equal to 1 in the first case, and z_1 in the second case.

Note the following qualitative differences in the character of the obtained solutions from those found in the two- and four-particle approximations:

(1) The first version of the NCQL method (number of variational parameters is $m=1$). At all values of γ ($0 \leqslant \gamma \leqslant 0.3$) the free energy $F^{(9,1)}(z,T)$ as a function of the quasiactivity has at $z=0$ an additional minimum corresponding to the "ideal ice." This minimum is present only in the interval $0 < T < \tilde{T}^{(9,1)}(\gamma)$ $[\tilde{T}^{(9,1)}(0) \approx 0.91, \tilde{T}^{(9,1)}(0.2) \approx 1.00]$. It can be either absolute or local minimum depending on the magnitude of γ and temperature. If the interaction between the H bonds is small ($\gamma < 0.2$), the ideal ice exists only as a metastable state. At $\gamma = 0.30$ in the range $0.54 < T < 0.60$ the ideal ice becomes stable. Another phase, which corresponds to the minimum of $F^{(9,1)}(z,T)$ at nonzero quasiactivity $z(T)$, is reentrant. At the boundaries of the given range the values of $\bar{n}_{\mathrm{H}}$ are essentially different, $\bar{n}_{\mathrm{H}}(0.54) \approx 4$ and $\bar{n}_{\mathrm{H}}(0.6) \approx 1.7$. At $\gamma \leqslant 0.3$ the first-order phase transition from the "nonideal ice" state ($z \neq 0, \bar{n}_{\mathrm{H}} \approx 4$) into the orientationally disordered state ($\bar{n}_{\mathrm{H}} < 1$) is not observed in this approximation.

(2) The second version of the NCQL method ($m=2$). For $\gamma=0$ there is the first-order phase transition at $T_*^{(9,2)}(0) \approx 0.58$ from the nonideal ice to the orientationally disordered state. The ideal ice ($z = z_1 = 0$) exists as a metastable state up to approximately the same temperature. At $\gamma = 0.1$ the same phase transition takes place at $T_*^{(9,2)}(0.1) \approx 0.60$. In the interval $0.59 < T < 0.61$ one of the phases exists as metastable. At $T < 0.61$ $[\tilde{T}^{(9,2)}(0.1) = 0.61]$ there is also the solution that corresponds to the metastable ideal ice. At $\gamma = 0.3$ the metastable ideal ice phase exists up to $\tilde{T}^{(9,2)} = 0.70$. The equilibrium phase transition takes place at $T_*^{(9,2)}(0.3) \approx 0.65$. The temperatures corresponding to the spinodals are $T_1^{(9,2)}(0.3) = 0.62$ and $T_2^{(9,2)}(0.3) = 0.66$.

Since the appearance of the ideal ice phase ($z=0$) in the NCQL approximations casts doubts, the phase diagram of the system has been also analyzed by the CQL method. The case was considered when different quasiactivities are assigned to the three links perpendicular to the edge of the square depending on the rotation angle of the molecules. Five variational parameters, z_1–z_5, appear in this approximation. The analysis of the free energy shows that the ideal ice phase indeed does not appear. Moreover, in this approximation the sharp first-order phase transition exists starting from $\gamma = 0$. Other features of the phase diagram remain the same.

The DVM which employs 101 variational parameters was not considered in the present work.

V. CONCLUSION

The most important thermodynamic properties of the H-bond network of the two-dimensional water, namely, the average number of the H bonds per molecule, the heat capacity of the system, and the correlation parameters describing the degree of mutual influence of the H bonds formed by a molecule with its neighbors, have been studied in the present paper. The important problem on the possibility of phase transition in the H-bond subsystem has been investigated. The study is based on the microscopic Hamiltonian of the H-bond network proposed in the present work which adequately reflects the Bernal–Fowler rules and allows the bending of the H bonds. The results have been obtained with help of the method of many-particle irreducible distribution functions, substantially enhanced compared to the previous works.[16,24–26]

It has been shown that in the low-order approximations in the case of weakly interacting H bonds ($\gamma \leqslant 0.2$) only a smooth first-order phase transition is possible. At $\gamma \geqslant 0.2$ there is the first-order phase transition between the ordered and disordered states of the H-bond subsystem. In the ordered phase the average number of the H bonds per molecule $\bar{n}_{\mathrm{H}}$ is slightly less than 4, which allows to interpret this phase as the nonideal two-dimensional ice. In the disordered phase $\bar{n}_{\mathrm{H}} \ll 1$. The nonideal ice phase in the temperature interval $[T_m, T_s^{(I)}]$, $T_m < T_s^{(I)}$, T_m being the temperature of the equilibrium phase transition and $T_s^{(I)}$ being the spinodal temperature, can exist in the superheated state. Similarly, the existence of the disordered phase is limited from below by the spinodal $T_s^{(\mathrm{dis})} < T_m$. In the nine-particle approximation with five variational parameters the sharp first-order transition appears even at $\gamma=0$. At the same time, the analysis of the free energy of the system in the nine-particle approximation, method of noncorrelated quasiactivities, displays that in the narrow vicinity of T_m a more stable phase of the ideal ice ($\bar{n}_{\mathrm{H}}=4$) appears. However, it is not excluded that at the account of the higher-order contributions the free energies of the nonideal ice and disordered phase decrease relative to the free energy of the ideal ice.

Therefore, the small interaction between the H bonds can substantially alter the thermodynamic properties of the system. It should be carefully chosen on the basis of the physical considerations or quantum-chemical calculations. The necessity to take into account this interaction is confirmed by the analysis of the spectroscopic data,[31] as well as by the specifics of the behavior of the supercooled water at approaching the water–hexagonal ice spinodal.[32] The possibility of the formation of the bifurcate bonds should be embedded in more detailed models because the computer simulation data explicitly confirm their noticeable relative number. We finally note that the account of the multipole interaction in addition to the interaction of the H bonds and the isotropic van der Waals interaction can allow to include into consideration the effects of the proton ordering in ice.

We should note that the influence of the lattice type and fine details of the Hamiltonian on the thermodynamic properties of the system remains not completely clear. Indeed, the temperature dependencies of the average number of H bonds per molecule and the heat capacity of the system, obtained in the present work, and using the Monte Carlo method on a triangular lattice,[3] are qualitatively similar. However, in Ref. 3, in the region of the "smooth" phase transition, strong dependence of the considered thermodynamic quantities upon the system size was found. This could possibly indicate that the system is close to spinodal which separates the ordered and disordered states of the H-bond network.

The possibility of the phase transitions in the H-bond subsystem requires further analysis. The distinct separation of the formation and disruption of the H bonds and their bending seems to be of special importance. This circumstance is directly pointed out by the existence of the amorphous phases of low- and high-density water[33] and the analysis of the dielectric permeability of the normal water.

The methods of construction of the thermodynamic potentials also require further development. While being exact, the direct variational method in the higher-order approximations, unfortunately, involves a rather large number of variational variables. To reduce this number, one has to use the approximate methods of correlated and noncorrelated quasiactivities, that may result in some artifacts. The existence of many phases of the solidified water stresses the importance of the many-particle correlation effects and, as a consequence, rises higher demands to the accuracy in the determination of the correlation functions.

In addition to the analytical calculations, the selection of the most probable configurations has been carried out by the Monte Carlo method. The results obtained in this way are in good agreement with the numerical calculations in terms of the method we used.

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