

some of them are formed by rolling of the square ice fragments [4–7]. Also there were carried out some interesting works on computer simulation of the square ice [8–13]. Final “materialization” of this abstract model has recently been held [14]; it was found that a monolayer of ice between the layers of graphene takes the form of the square ice. Currently, a wide range of investigations are performed for so-called spin ice [15,16] and for artificial spin ice on a square lattice [17], its main feature is their similarity with the structure of ordinary water ice.

The reason of the square shape of water ice is the flexibility of the hydrogen (H-) bonds. A significant deviation from the tetrahedral coordination is compensated by a large number of H-bonds. However, some topologically possible configurations of the H-bond network are not implemented. Configurations with longitudinally arranged molecules are extremely unfavorable, because the hydrogen-bond angle 180° is far greater than the HOH angle [9], although such configurations do not violate the Bernal–Fowler ice rules [2]. The square ice model without longitudinally arranged molecules is considered in [18]. In this case, the structure is formed by unidirectional straight chains of H-bonds. The proton disorder is reduced to the arbitrariness in the directions of the individual chains (lines). Such arrangement has a large degeneracy, although sub-exponential in the size, thus leading to zero specific entropy in the thermodynamic limit. According to DFT calculations of square ice, the most energetically favorable structure is antiferroelectric with alternating directions of the H-bonded chains (i.e., ABAB) [19]. This model of directed lines is completely consistent with the intuitive idea of profitability of configurations with the opposite direction of the dipoles that are located in H-bonds. However, computer simulations show that there are other patterns of order. This applies to water clusters in the form of finite nanotubes [20], and also to the square ice monolayer with the other line ordering: AABB [9].

The paper presents a simple discrete model of square ice, which takes into account the interaction of the first, second and third neighbors (molecules). According to this model, the ground state combines a set of configurations that do not contain three neighboring unidirectional chains of hydrogen bonds. It was established that the new model is also applicable for corresponding system of point dipoles on the square lattice. For the new model, the degree of degeneracy of the ground state was calculated and the contributions of short-range and long range interactions were compared. The purpose of this article is to show that the structure of the ground state of square water ice is not just a result of the interaction between the nearest neighbors. In addition, the new model provides a basis for understanding the above-mentioned results of the computer simulation.

2. The effective pair interaction between nearest neighbors

In the construction of a discrete model for square ice the interaction of the second and third neighbors has been taken into account. That is why the approach, which had been developed for polyhedral water clusters, was used [21]. Different fragments of the structure of square ice are shown in Fig. 1. The arrows indicate the direction of the hydrogen bond: from the proton donor to the acceptor. The absence of longitudinally arranged molecules means that only four last configurations (Fig. 1b) are possible in each node. Let us consider the six molecule fragment in Fig. 1c as a basic one. Molecules 7 and 8 are supplementary (see lower). We now introduce the effective energy of pair interaction U_{eff} , which includes the interaction between the second and the third neighbors (U_2, U_3) as well as the interaction of the nearest H-bonded molecules:

$$U_{\text{eff}} = U_1 + U_2 + U_3, \quad U_1 = U_{12} \quad (1)$$

$$U_2 = (U_{15} + U_{16} + U_{23} + U_{24})/4 + (U_{34} + U_{56})/2, \quad U_3 = U_{36} + U_{45}$$

Summation U_{eff} for all H-bonds allows taking into account the interaction of the nearest, second and third neighbors for the lattice as a whole. Here, the coefficient $1/4$ for interaction U_{15} reflects the fact that this interaction is included in U_{eff} for H-bonded pairs 1–3, 2–5 and 3–5 as well as in the H-bonded pair 1–2. The situation is similar to the other diagonal interactions U_{16}, U_{23}, U_{24} . Interactions U_{34} and U_{56} are decreased by a factor 2, because they are repeated twice (the H-bonded pairs 1–7 and 2–8). The third neighbor interactions U_{36} and U_{45} are not repeated, because they refer to H-bonded pair 1–2 only. To simplify the model we do not consider the interaction of the third neighbors U_{78} . This allows restricting the analysis to simple 8-shaped fragments. The following two facts confirm the reasonability of that definition. Firstly, the orientations of molecules 7 and 8 differ only by the position of hydrogen atoms (protons) that take part in the forming of the vertical H-bonds. Secondly, the distance between them is much bigger than the distance between the pairs 3–6 and 4–5, since in the dipole approximation, the interaction decays as $1/r^3$.

All symmetrically distinct configurations for the basic 8-shaped fragment of square ice are shown schematically in Fig. 2d. In the first row, the vertical H-bonded chains are oppositely directed. In the second row, they are directed in the same way. In the first case, pairs of molecules that are disposed horizontally form energetically favorable trans-configurations. In the second case, they form less favorable cis-configurations (Fig. 1a, ovals). This separation into two types of H-bonds (*t*- and *c*-bonds) is valid for many of the ice structures. It is the basis of the discrete model of strong and weak H-bonds (model SWB) [21,22], which takes into account the interactions between the nearest molecules only. The ground state of the square ice in the SWB model is non-degenerate and is formed by only strong *t*-bonds (Fig. 1a, separated square of size 3×3). Note that this configuration is also the lowest energy configuration with account for all interactions including long-range ones (see above).

Fig. 2 shows the distribution of all bond types (8-shaped fragments) by the energy of the pair interaction U_1 and by the effective energy U_{eff} . The calculations were performed with the TIP4P water model [23] using the package TINKER [24]. These values correspond to the initial stage of geometric optimization (optimization accuracy in procedure Minrigid is 1.5).

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