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Residual entropy of ice nanotubes and ice layers

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ABSTRACT

A relatively simple algorithm is presented for the complete enumeration of all H-bond networks in finite fragments of ice nanotubes and ice layers with periodic boundary conditions. This algorithm is based on the well-known transfer matrix method and it includes a convenient procedure for calculation of the elements of transfer matrices themselves. To facilitate this, it is necessary to specify only very small local matrices of sizes 2×2 or 4×4. We present exhaustive statistics of H-bonds arrangements for finite-size zigzag- and armchair-like ice nanotubes, for the fragments of hexagonal monolayer and bilayer and also for ice nanotubes consisting of stacked n-membered rings. Using the new algorithm, we have also calculated the specific residual entropy for the infinite two-dimensional lattices. The agreement with the well-known solution for a square ice model demonstrates the reliability of the obtained results.

1. Introduction

The importance of water for living and nonliving matter is well-known. Water as a host also into plays a role in modern nanotechnology. For example, water layers can be formed on a graphene surface. At present water on its own account has become an important subject in nanotechnology. For instance, recent reports have highlighted the technique of ice lithography [1]. Modern nano- and bio-technologies can benefit from a better understanding of water and ice properties, especially at the nano level.

A characteristic feature of ice and other systems consisting of water molecules is the residual entropy. The crystal lattice allows a substantial amount of disorder manifested by the positions of the hydrogen atoms (protons) that are localized into a specific arrangement at low temperatures. At the same time there exist certain restrictions that determine the underlying structure. According to well-known Bernal–Fowler ice rules [2], (i) each oxygen atom has only two nearest neighboring hydrogen atoms and (ii) only one hydrogen atom is present on each O–O linkage. The first condition preserves the water molecule structure while the second one excludes very disadvantageous relative orientations of neighboring molecules.

The first approximate formula for residual entropy of ice was supported by Pauling in 1935 [3]. He has shown that the number of H-bond arrangements is very large and grows exponentially with the number of molecules (N) as $(3/2)^N$. The predicted value of the residual entropy coincides with the experimental data for ice near 0 K. However, it was soon found that an exact calculation of the number of possible configurations is a very difficult problem. For this reason, it has taken more than thirty years in order to produce trustworthy results [4]. As it has turned out, the actual result is currently only slightly different than Pauling's original estimation.

The exact value of residual entropy was obtained for a two-dimensional ice model known as "square ice" by Lieb [5] using the transfer-matrix method [6]. This method has been used very effectively for finding the exact solution of many classical models, including the two-dimensional Ising model [7]. The transfer-matrix method has also been applied to the

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calculation of the number of proton configurations in polyhedral water clusters [8,9]. In order to represent the polyhedra as quasi one-dimensional systems, we carried out a topological evolution for the side surface of the polyhedra. For a number of polyhedral water clusters from a cube up to a fullerene, the exact numbers of Bernal–Fowler configurations were obtained. However, the most suitable systems for the application of the transfer-matrix method are nanotubes and layers of ice. Two recent articles of Tokmachev and Dronskowskii are devoted to this subject [10,11].

The main drawback of the transfer-matrix method, when it is applied to quasi one-dimensional systems is the calculation of the transfer-matrix itself. The size of the matrix is determined by the number of states of the separate system elements, which is usually rather large. In this article, the transfer-matrices of all ice-like systems under consideration are calculated using auxiliary small transfer-matrices of sizes 2×2 and 4×4. The developed algorithm is very simple and descriptive. The overwhelming majority of calculations up to matrices of sizes 1024×1024 has been carried using Mathcad and can be easily checked. Along with ice monolayers and single-walled nanotubes, we also considered rather stable ice bilayers [12,13].

Before proceeding it is necessary to make the following point: the aim of the present article is not only the estimation of the residual entropy but also the exact proton configuration statistics for finite fragments of ice nanotubes and ice layers with different periodicity, the latter being of interest to nanoscience and nanotechnology. This is because the configurations of ice-like nanostructures with different hydrogen bond arrangements are distinguished essentially by energy and other characteristics [14–17]. Therefore the exact proton configuration statistics for a set of increasing fragments under periodic boundary conditions can be the first step to the detailed classification and detail investigation of the multitude of all proton configurations in ice nanotubes and ice layers using computer simulation methods.

2. Ice monolayer and nanotubes

The residual entropy of a hexagonal ice monolayer is essentially greater than the entropy of bulk ice Ih. In this case each molecule participates in only three hydrogen bonds. In earlier studies, by analogy with the well-known Pauling formula [3] we have obtained the following expression for the residual entropy (in dimensionless form) of polyhedral water clusters [18]:

$$S = \frac{\ln(M)}{N} = \ln\left[2^{1,5N} \cdot \left(\frac{6}{8}\right)^{N}\right] = \ln\left(\frac{3}{\sqrt{2}}\right) = 0.7520, \tag{1}$$

where M is the total number of configurations satisfying the Bernal–Fowler rules and N is the number of molecules. This expression applies equally to the ice monolayer [19,20]. It differs from the Pauling formula in having 1.5 bonds per molecule. In addition, there are only 8 independent arrangements of three hydrogen bonds near each molecule instead of 2^4 in the bulk. Hydrogen bond arrangements when all three bonds near one molecule are either acceptors (incoming) or donors (outcoming) are forbidden. That is only 6 variants are allowed; in this sense, the ice monolayer is one of 6-vertex ice models [21].

The model for the ice monolayer is shown in Fig. 1(a). The straight lines indicate the rectangular unit cells of the lattice. Characteristic fragments corresponding to vertical and horizontal directions are shown in Fig. 1(b), (c). The corresponding nanotubes obtained by folding of the ice layer are known as zigzag- and armchair-like (Fig. 1(d), (e)). Hydrogen bonds, shown as dotted lines (Fig. 1(b), (c)), are replications of the lowest bonds. These fragments can be simultaneously considered as parts of the plane hexagonal layer with periodic boundary conditions in the vertical direction. In order to calculate the number of Bernal–Fowler configurations via the transfer-matrix method it is necessary to determine the transfer matrix itself. The size of the matrix is $2^k \times 2^k$, where k is the number of free bonds from one side of the fragment. For the zigzag form we consider two somewhat different fragments and calculate the two transfer-matrices. Periodic closure along the tube is possible only for an even number of such fragments (pairs). By using only one transfer matrix for the nanotube and joining the first and third fragments with shifting, see Fig. 1(b), under toroidal boundary conditions results in a strong deformation of all hexagons. On the other hand, this corresponds to the calculation of characteristics of an oblique-angled strip of a hexagonal layer under periodic boundary conditions.

The transfer-matrix from one fragment to another describes the increasing of the total number of allowed configurations in the tube (or strip). The elements of the transfer-matrix are determined by the number of allowed configurations in the zigzag chain, see Fig. 1(b), for all fixed directions of the hydrogen bonds on the left and right. It is easily seen that the separate tube fragment is also a quasi one-dimensional system. For this fragment, the number of allowed configurations can be also calculated using the transfer-matrix method. In Fig. 2 one can see all possible directions of two adjacent H-bonds of the zigzag chain for the two directions of the outer H-bonds (dotted lines): towards and away from the zigzag fragment. The elements of transfer-matrices $B1$ and $B2$ (0 and 1 in Fig. 2) are equal to the numbers of allowed directions of ingoing and outgoing H-bonds determined by the zigzag chain. In this case, "0" corresponds to the configuration that is forbidden by the Bernal–Fowler ice rules. Thus we have

$$B1 = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix} \qquad B2 = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}. \tag{2}$$

For the outer horizontal H-bonds, see Fig. 1(b), the direction from left to right along the tube axis will be considered as the reference. Then, it is convenient to enter two transfer-matrices $A1$ and $A2$ separately for the transfers near odd bonds