RESIDUAL ENTROPY OF POLYHEDRAL WATER CLUSTERS. EXACT RELATIONS

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Earlier, for polyhedral water clusters, the relation

\[ s_0 = Nk \ln(3/\sqrt{2}) = 0.7520Nk \]  

was derived [1] as an analog of Pauling's approximate formula [2] defining residual entropy of hexagonal and cubic ice. The relation was verified for clusters with \( N = 8-14 \) molecules by calculating the precise number of isomers due to proton disorder. It was found that the error is 1% and tends to decrease with growth of \( N \).

In this communication we give exact formulas specifying the number of such isomers for two groups of polyhedral clusters. The first group is a series of clusters in the form of \( n \)-angular prisms. The second group represents clusters in the form of polyhedra also having the \( n \)th order rotation symmetry, with a convex side surface consisting of pentagons (see Fig. 1). The two groups together cover the majority of possible stable polyhedral configurations of water molecules [1]. These also include the most stable configuration in the form of pentagonal dodecahedron with all pentagonal faces.

The desired number of isomers is obtained using a system of recurrent relations on a regular cyclic closed two-dimensional net. This approach was first used by Leeb to calculate residual entropy of "square ice." All phase transition models having exact solutions (the one- and two-dimensional Ising problems and the two-dimensional ferroelectric model) were essentially derived from this method [2]. While in those models cyclic closure is introduced artificially, in our case this an intrinsic property of the system.

The prism-shaped cluster, composed of water molecules with tetrahedrally oriented bonds, is topologically equivalent to the closed band of "square ice." The free bonds not depicted in the figure have the same direction. The problem, therefore, is reduced to finding the number of oriented graphs satisfying the "ice condition" [2] as follows: in each node either one or two arrows should be converging.

Consider first an open side surface (see Fig. 1a). Let us introduce a four-component vector \( A_n \), whose \( i \)th component equals the number of permitted configurations obeying an additional condition: the direction of the bonds at the free end is the same as in the \( i \)th row of the scheme (Fig. 1b). This state vector satisfies the recurrent relation

\[ A_n = \hat{B} \cdot A_{n-1} = \hat{B}^{n-1} \cdot A_1. \]  

Figure 1b shows the scheme for deriving the coefficients of the transfer matrix \( \hat{B} \). The figures in the scheme correspond to the number of methods for joining two sequential links permitted by the "ice condition."

It is easily verified that the number of permitted configurations closed by the first method (the direction of bonds in the last link is the same as in the first row in Fig. 1b) equals the first vector element \( B^{n-1}b_1 \). Here the \( b_1 \) vector is composed of the elements of the first column of the \( \hat{B} \) matrix. Consequently, the total number of the desired configurations is

\[ X_n = \text{Tr} \hat{B}^n = \sum_{i=1}^{4} \lambda_i^n. \]  

In this case, the eigenvalues of the transfer matrix are readily found and we get the following formula:
Fig. 1. Scheme of transfer matrix arrangement: a) the "square ice" band; b) the diagram for prisms; c) the diagram for the clusters of the second group (see text).

\[ X_n = \frac{1}{2^n} \left( (5 + \sqrt{17})^n + (5 - \sqrt{17})^n \right) + 2^n + 1. \]  

(4)

Although \( X_n \), as well as the residual entropy of the corresponding clusters, may be found using only the first equality in (3), the latter relation has the advantage of readily giving an asymptotic formula for residual entropy

\[ S_0 = \frac{1}{2} N \ln \left( \frac{5 + \sqrt{17}}{2} \right) = 0.7588 N k. \]  

(5)

Here \( N = 2 \cdot n \).

For clusters of the second group, the number of isomers is found in just the same way. In this case, the state vector is 8-dimensional, according to the number of arrow arrangement variants on the free bonds (Fig. 1c). From the figure it follows, e.g., that the transfer matrix element \( B_{11} = 5 \). Then \( \hat{B} \) is of the form

\[
\begin{pmatrix}
5 & 4 & 1 & 2 & 1 & 1 & 0 \\
2 & 5 & 3 & 4 & 1 & 2 & 1 \\
4 & 3 & 5 & 2 & 3 & 2 & 1 \\
1 & 4 & 3 & 5 & 1 & 3 & 2 \\
3 & 2 & 3 & 1 & 5 & 3 & 4 \\
1 & 3 & 2 & 3 & 2 & 5 & 3 \\
1 & 1 & 2 & 1 & 4 & 3 & 5 \\
0 & 1 & 1 & 2 & 1 & 4 & 3 \\
\end{pmatrix}
\]

(6)

Just as for prism-shaped clusters, the desired number of permitted configurations \( Y_n \) is found from (3), from which we can also use only the first equality.

Here again we can obtain exact relations in radicals for eigenvalues of the transfer matrix. For that we need not solve the eighth-order secular equation. We can do it in a different way. Among the approximately calculated eigenvalues are pairs of numbers which add up to integers. This points to a rational way of factorizing the secular equation to multipliers \((\lambda - \lambda_i) (\lambda - \lambda_j)\). As a result, to find all \( \lambda_i \) it is sufficient to solve a few quadratic equations accurately. The final relations for the eigenvalues are of the form

\[
\lambda_{1,2,3,4} = 6 \pm 2\sqrt{5} \pm \sqrt{50 \pm 22\sqrt{5}}, \\
\lambda_{5,6,7,8} = 4 \pm \sqrt{10 \pm 2\sqrt{5}}.
\]  

(7)

The circle before the radical implies that the sign here is given separately; in other places the signs are specified