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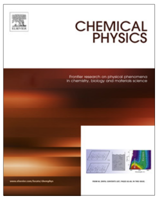

Structural characterization of ice polymorphs from self-avoiding walks

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ABSTRACT

Topological properties of crystalline ice structures are studied by means of self-avoiding walks on their H-bond networks. The number of self-avoiding walks, C_n, for eight ice polymorphs has been obtained by direct enumeration up to walk length $n = 27$. This has allowed us to determine the 'connective constant' or effective coordination number μ of these structures as the limit of the ratio C_n/C_{n-1} for large n. This structure-dependent parameter μ is related with other topological characteristics of ice polymorphs, such as the mean and minimum ring size, or the topological density of network sites. A correlation between the connective constant and the configurational entropy of hydrogen-disordered ice structures is discussed.

1. Introduction

Water exhibits a wide variety of solid phases, which are referred to as forms of 'ice'. Most of these phases are produced by the application of high pressures, which yields a denser packing of water molecules than in the usual hexagonal ice Ih. Thus, sixteen different crystalline ice phases have been identified so far [1–3], and their stability range in the temperature–pressure phase diagram has been investigated for several decades. Some of their properties lack, however, a complete understanding, mainly due to their peculiar structure, where hydrogen bonds between adjacent molecules give rise to the so-called 'water anomalies' [4,1,5].

In the known ice phases except ice X, water keeps its molecular character, building up a network connected by H-bonds. In this network each water molecule is surrounded by four others, in such a way that its orientation with respect to the neighboring ones fulfills the so-called Bernal–Fowler ice rules [6,1]. These rules allow for the presence of orientational disorder in the water molecules, which causes that in several ice phases hydrogen atoms present a disordered spatial distribution, as indicated by a fractional occupancy of their lattice sites. Thus, hexagonal ice Ih, the stable phase of solid water under normal conditions, displays hydrogen disorder compatible with the ice rules, whereas other phases such as ice II are H-ordered [7,8].

Given the number of ice structures, a unifying classification can help to deeper understanding of their specific properties [9,7]. For crystalline solids, classification schemes usually rest on the space symmetry, short-range atomic environments, or geometrical aspects of packing of structural units. These classification procedures have a geometrical nature, as their main criteria are geometrical characteristics of crystal structures [10–13]. These geometrical classification methods, however, can be hardly applicable to find relations between solids whose structures are somewhat distorted. A possible alternative consists in using classification schemes relying on topological criteria. This means centering attention mainly on the organization of interatomic bonds in a crystal structure as a basic criterion for a crystal-chemical analysis. In this line, topological properties of crystalline solids have been taken into account along the years to describe properties of different types of materials [10,12,11]. For the ice polymorphs, a discussion of different network topologies and the relation of ring sizes in the various phases with the crystal volume was presented by Salzmann et al. [7]. Topological studies of three-dimensional (3D) hydrogen-bonded frameworks in organic crystals have also helped to classify this kind of structures [14]. Moreover, graph theory has been used to study isotypism and order/disorder problems in crystal structures [13,8,15].

A direct and rather simple topological classification of ice structures can be based on structural rings, i.e., loops of water molecules characteristic of each polymorph [7]. A more elaborate procedure can be based on the so-called 'coordination sequence', defined as a series of numbers $\{N_k\}(k = 1, 2, \ldots)$, where N_k is the number of sites located at a topological distance k from a reference site [16–19]. The coordination sequence can be used to define a topological density, as a structural characteristic related to the increase in the number N_k of sites accessible through k links in a given structure [20,17,21]. Note that these concepts are based only on the topology of the considered network, and are not affected by lattice distortions or other structural factors. These concepts have been recently

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applied to ice polymorphs, allowing us to find a correlation between topological density and volume [22].

In this paper, a different way to characterize the ice polymorphs is introduced. Namely, it is based on self-avoiding walks in the corresponding structures. A self-avoiding walk (SAW) is a sequence of moves on a network that does not visit any node more than once. Contrary to unrestricted walks, SAWs contain implicit information on the topology of the considered network, as they are sensitive to characteristics such as the number and size of loops present in the structure. A particularly interesting parameter is the so-called connective constant or effective coordination number of the ice networks, which can be calculated from the long-distance behavior of the number of possible SAWs in the corresponding structures. These concepts are explained in detail in the following section.

The purpose of this paper is twofold. On one side, knowledge of the connective constants of ice structures is interesting from a basic point of view for their comparison with other crystal structures, for which this kind of statistical-mechanics questions have been analyzed in detail. On the other side, they are relevant for a topological and physico–chemical characterization of ice phases, allowing us to connect structural and thermodynamic properties of this type of solids. In particular, the configurational entropy associated to the hydrogen distribution on the available lattice sites is known to depend on the ice structure [23–25], so that a search for structural variables suitable to quantify in some way such a dependence is worthwhile in the context of ice thermodynamics.

2. Computational method

In order to study SAWs for the different ice polymorphs, we consider each structure as defined by the positions of the oxygen atoms. One has thus a network, where the nodes are O sites, and the links are H-bonds between nearest neighbors. The network coordination is four ($z = 4$), which gives a total of $2N$ links, N being the number of nodes. We implicitly assume that on each link there is one H atom.

A self-avoiding walk on an ice network is defined as a walk in the simplified structure which can never intersect itself. On a given network, the walk is restricted to move to a nearest neighbor site during each step, and the self-avoiding condition constrains the walk to occupy only sites which have not been previously visited in the same walk [26–28]. We illustrate the application of this definition to ice Ih in Fig. 1, where an eight-step SAW is shown. Note that the link indicated with a cross is not available for step $n = 8$, as the walk would reach a node already visited in an earlier step.

SAWs have been used in condensed-matter science for several purposes. For instance, they were employed for modeling the large-scale properties of long-flexible macromolecules in solution and adsorbed on surfaces [27,29–31], as well as for the study of polymers trapped in confined regions, gel electrophoresis, and size exclusion chromatography, which deal with the transport of polymers through membranes with very small pores [32–34]. They have been also employed in the analysis of critical phenomena in lattice models [26,35–38], and to study complex networks [39–41]. Moreover, SAWs with multiple site weightings and restrictions have been discussed in the literature [42,43].

Given a network and a site i in it, we will call C_n^i the number of different SAWs of length n starting from this site. For networks where all sites are topologically equivalent, the sequence $\{C_n^i\}_{n=1}^{\infty}$ will coincide for all nodes, but in general, sequences corresponding to different nodes in a network may be different. (Note that for all sequences mentioned in the following n is understood to run from 1 to ∞, although not explicitly indicated.) It is important to recall that crystallographically equivalent sites are always topologically equivalent, but sites non-equivalent crystallographically may be topologically equivalent or not [22]. Then, we define an average sequence $\{C_n\}$ for each network, where for a given n, C_n is obtained by averaging the C_n^i values for the oxygen sites in the unit cell:

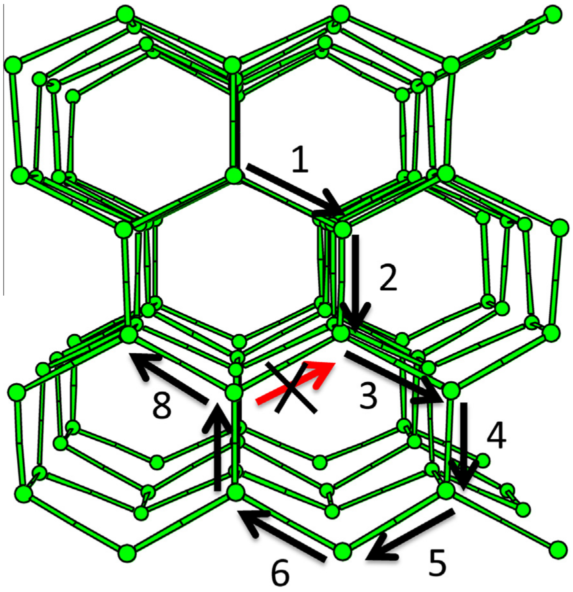

Fig. 1. Sketch of the ice Ih structure with an eight-step self-avoiding walk. A cross indicates a non-allowed step.

$$C_n = \frac{1}{M} \sum_i m_i C_n^i. \tag{1}$$

Here m_i is the multiplicity of site i in the unit cell and $M = \sum_i m_i$. For ice structures including oxygen sites topologically non-equivalent (e.g., ices III, IV, V, VI, and XII; see Ref. [22]), relative differences between C_n^i values corresponding to different sites in a given structure decrease fast with the walk length n. In fact, the relative difference is about 1% for $n = 25$, and becomes negligible in the large-n limit.

It is remarkable that universal constants are known to describe some properties of self-avoiding walks. These constants depend on the network dimension, and have been discussed in detail in the literature [44,45]. Other parameters controlling the long-distance behavior of SAWs are network-dependent, and can be used to characterize different networks with the same dimension. Analytical expressions describing the asymptotic behavior of SAWs for large n are significantly different from those of unrestricted walks. It is particularly interesting the dependence of C_n on the number of steps n for long walks. Its asymptotic behavior for large n is known to be given by [44–46]

$$C_n \sim n^{\gamma-1} \mu^n, \tag{2}$$

where γ is a critical exponent which takes a value $\approx 7/6$ for 3D structures [45,47,48], and μ is the so-called 'connective constant' or effective coordination number of the corresponding structure [27,45,46].

Defining the ratio

$$x_n = \frac{C_n}{C_{n-1}} \tag{3}$$

one has

$$x_n \approx \mu \left(1 + \frac{1}{n-1}\right)^{\gamma-1} \xrightarrow{n\to\infty} \mu \tag{4}$$