

# Combinatorial entropy and phase diagram of partially ordered ice phases

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A close analytical estimate for the combinatorial entropy of partially ordered ice phases is presented. The expression obtained is very general, as it can be used for any ice phase obeying the Bernal-Fowler rules. The only input required is a number of crystallographic parameters, and the experimentally observed proton site occupancies. For fully disordered phases such as hexagonal ice, it recovers the result deduced by Pauling, while for fully ordered ice it is found to vanish. Although the space groups determined for ice I, VI, and VII require random proton site occupancies, it is found that such random allocation of protons does not necessarily imply random orientational disorder. The theoretical estimate for the combinatorial entropy is employed together with free energy calculations in order to obtain the phase diagram of ice from 0 to 10 GPa. Overall qualitative agreement with experiment is found for the TIP4P model of water. An accurate estimate of the combinatorial entropy is found to play an important role in determining the stability of partially ordered ice phases, such as ice III and ice V. © 2004 American Institute of Physics.

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## I. INTRODUCTION

The behavior and properties of ice have provided a constant challenge to our understanding of statistical mechanics and other related areas.<sup>1-3</sup> No other naturally abundant substance is known to show such a wide variety of solid phases, and the elucidation of their crystal structure has been a matter of research for many decades.<sup>4-6</sup>

Early attempts to determine the structure of ice I revealed a hexagonal arrangement of oxygen atoms.<sup>7</sup> Due to their low scattering intensity, the actual arrangement of hydrogen atoms could only be guessed, and different ordered structures were proposed.<sup>7,8</sup> At the same time, careful thermodynamic measurements revealed an absolute entropy for water molecules which could not be properly accounted by theoretical means.<sup>9</sup> This paradox was soon resolved by Pauling,<sup>10</sup> who suggested a random arrangement of protons consistent with the hydrogen bond network of Bernal and Fowler.<sup>8</sup> By means of a simple calculation, Pauling showed that the resulting disordered phase requires the addition of a combinatorial entropy per molecule of about  $k_B \ln 3/2$  to the theoretical estimate. This finding demonstrated that a crystal phase such as ice I could show full disorder at 0 K, against expectations from the third principle. Obviously, it is considered that this disagreement is due to kinetic reasons. It is interesting to point out, however, that conclusive evidence of an ordered low temperature phase at low pressures (ice XI) was only found many years later,<sup>11,12</sup> and requires doping with alkaline hydroxides.<sup>13</sup> At present a fully ordered crystalline structure has been proposed for ice XI,<sup>14</sup> but interpretation of results is quite difficult due to the presence of impurities.<sup>15,16</sup>

For a long time, most of the other ice phases which coexist with water were considered to be essentially disordered. However, the evidence for such belief was only indirect. It was based on the slope of the pressure-temperature

coexistence lines between ordered and disordered phases, or on dielectric response measurements.<sup>3</sup>

With the advent of neutron scattering technology for crystal structure determination, the actual hydrogen arrangements could be definitively settled for the first time. It was found that those structures believed to have random arrangement of protons (I, VI, VII) were indeed essentially disordered,<sup>3,17-19</sup> while the readily accessible low temperature phases (II, VIII) were found to be fully ordered.<sup>18,20</sup> Two other phases, however, presented an interesting behavior. Both ice III and ice V were found to show clear evidence of *partial ordering*: the hydrogen crystal sites in these structures are found to have a probability of being occupied which is neither 0 or 1 (fully ordered), nor 1/2 (random), but rather, take a value in between, which is known to depend on the thermodynamic state.<sup>21,22</sup> Similarly, the metastable phase ice IX, which is the ordered counterpart of ice III, was found to have some partial disorder.<sup>23</sup>

Under these conditions of partial ordering, an extension of the Pauling calculation for the combinatorial entropy is required. Some time ago, Minagawa applied a method apparently first proposed by Takagi in order to count the configurations in ice I.<sup>24</sup> This method is particularly suited for the problem of partial ordering, because it provides a parametric expression in terms of *occupancies*, the actual characterization of disorder which can be measured in neutron scattering experiments.<sup>21-23</sup> Howe and Whitworth applied this method in order to obtain a closed expression for the entropy in the special case where a single occupancy parameter describes the partial ordering of the crystal,<sup>25</sup> and argued that the entropy estimate so obtained is more accurate than that of Nagle, which has been applied to measure the entropy of ice IX.<sup>26</sup> In practice, however, the phases which show significant partial ordering over a wide region (ice III and V) have rather complex structures, the partial ordering is described by means of two or three occupancy parameters, respectively,

and the coupling of occupancies related to different water molecules needs to be accounted for.

An estimate for the combinatorial entropy of partially ordered phases is interesting for many reasons. It may allow one to reinterpret partial ordering from the pressure-temperature slope of phase diagrams. More importantly, it is a very important tool in order to calculate the phase diagram of water models by computer simulations.<sup>27–31</sup> Indeed, free energy determination of ice is typically performed for one or a few hydrogen bond arrangements, and at present there is no known computational scheme which would allow to count exactly the number of such arrangements. Therefore, an estimate for the combinatorial entropy is added *a posteriori* to the configurational free energy measured during the simulations, in order to account for all the hydrogen bond arrangements compatible with the considered crystal phase.<sup>27–31</sup> In this way, the success of the water model and the entropy calculation may be assessed by cross checking. Good agreement with experiment suggests that both the water model and entropy calculation are correct. Furthermore, splitting the entropy into two terms allows to assess what part of the latent entropy is related to the ordering of the hydrogen bond network, and which to the molecular vibrations within a given arrangement.

In this paper we extend the studies of Minagawa, Howe and Whitworth and propose a general expression for the combinatorial entropy of any partially ordered ice phase. This theoretical calculation is then employed in order to determine the phase boundaries of ice III and V by means of computer simulations. We employ the well known TIP4P model of water,<sup>32</sup> since it has been shown that it provides a qualitatively correct phase diagram over a very wide domain of temperatures and pressures.<sup>33,34</sup>

The paper is organized as follows. In the following section we present the theoretical calculation for the combinatorial entropy of ice phases. In Sec. III we describe the special techniques that are required in order to prepare partially disordered ice configurations, and provide a brief account of the techniques employed to determine the phase diagram. The results are presented in Sec. IV, and our conclusions are explained in Sec. V.

## II. COMBINATORIAL ENTROPY OF PARTIALLY ORDERED ICE

### A. Preliminary definitions

In this work we will consider solid phases obeying the Bernal-Fowler rules.<sup>8,10</sup> According to these rules, only ice configurations satisfying the following two conditions are allowed: (1) Each oxygen atom within the crystal network is covalently bonded to two hydrogen atoms. This rule simply implies that ice phases are molecular crystals formed by water molecules as in the vapor or liquid phase. (2) Every water molecule is tetrahedrally coordinated with other four molecules, forming hydrogen bonds. Geometrically speaking, this means that along the line joining two such oxygens there lies one and only one hydrogen atom.

Consider a crystal made of  $N$  water molecules. The crystal has a total of  $N_c$  unit cells, and each cell has a total of  $\nu_o$

nonequivalent oxygen atoms. Furthermore, each of the non-equivalent oxygen atoms has a multiplicity  $m_i$ , such that the total number of water molecules in the unit cell is  $m_i = \sum_{i=1}^{\nu_o} m_i$ .

An unspecified oxygen atom, say, atom  $i$ , is bonded to two hydrogen atoms. Each of these may occupy one out of four possible sites, which we call sites  $S_1^{(i)}$ ,  $S_2^{(i)}$ ,  $S_3^{(i)}$ , and  $S_4^{(i)}$ . Out of all six sites, only two are occupied at a time, however, such that the water molecule is allowed to have six possible rotational states. Let  $P^{(i)}$  be that rotational state with hydrogen sites  $S_1^{(i)}$  and  $S_2^{(i)}$  occupied. Let  $R^{(i)}$  be the “complementary” state, with neither  $S_1^{(i)}$  nor  $S_2^{(i)}$  sites occupied. Furthermore, let  $Q_j^{(i)}$  (with  $j=1,2,3,4$ ) be the four remaining rotational states, such that either  $S_1^{(i)}$  or  $S_2^{(i)}$  is occupied (cf. Fig. 1).

Let  $s_1^{(i)}$  denote the “occupancy” or probability of site  $S_1^{(i)}$  being occupied,  $s_2^{(i)}$  denote the occupancy of site  $S_2^{(i)}$ ,  $s_3^{(i)}$  denote the occupancy of site  $S_3^{(i)}$ , and so forth. Furthermore, let  $p^{(i)}$  denote the “orientation” or probability of rotational state  $P^{(i)}$  being occupied;  $q_1^{(i)}$  denote the orientation of rotational state  $Q_1^{(i)}$ , and so on.

### B. Arrangements of water molecules

Given the definitions above, a glance at Fig. 1 readily shows that the occupancies must be related to the orientations in the following manner:

$$\begin{aligned} s_1^{(i)} &= p^{(i)} + q_1^{(i)} + q_2^{(i)}, \\ s_2^{(i)} &= p^{(i)} + q_3^{(i)} + q_4^{(i)}, \\ s_3^{(i)} &= r^{(i)} + q_1^{(i)} + q_3^{(i)}, \\ s_4^{(i)} &= r^{(i)} + q_2^{(i)} + q_4^{(i)}. \end{aligned} \quad (1)$$

However, this set of equations does not provide four independent constraints, because each oxygen is bonded to two hydrogen atoms. As a result, the occupancies must obey the following relation, which reflects the chemical identity of the water molecule (i.e., rule one of Bernal and Fowler):

$$s_1^{(i)} + s_2^{(i)} + s_3^{(i)} + s_4^{(i)} = 2. \quad (2)$$

The above equations result from the constraints imposed on the orientations by the geometry of the water molecule. They can be considered as a quantification of the first Bernal-Fowler rule. Notice that there are only four such constraints, so that we cannot express the six orientations in terms of occupancies only. We can nevertheless solve the above system of equations in terms of two selected orientations, which we choose to be  $q_1^{(i)}$  and  $q_2^{(i)}$ . After some simple algebraic rearrangements, we find that  $p^{(i)}$ ,  $q_3^{(i)}$ ,  $q_4^{(i)}$ , and  $r^{(i)}$  may be expressed in terms of  $q_1^{(i)}$ ,  $q_2^{(i)}$  and the occupancies as follows:

$$\begin{aligned} p^{(i)} &= s_1^{(i)} - q_1^{(i)} - q_2^{(i)}, \\ q_3^{(i)} &= s_2^{(i)} + s_3^{(i)} - 1 + q_2^{(i)}, \\ q_4^{(i)} &= 1 - s_1^{(i)} - s_3^{(i)} + q_1^{(i)}, \\ r^{(i)} &= 1 - s_2^{(i)} - q_1^{(i)} - q_2^{(i)}. \end{aligned} \quad (3)$$

This set of equations determine the possible orientations consistent with the imposed occupancies.

Since the crystal contains a total of  $m_i N_c$  water molecules of kind  $i$ , it will have on average  $p^{(i)} m_i N_c$  such molecules in rotational state  $P^{(i)}$ , and likewise for

the remaining rotational states. Accordingly, the number of ways that molecules of kind  $i$  may be arranged in the crystal such that there are  $p^{(i)} m_i N_c$  in state  $P^{(i)}$ ,  $q_1^{(i)} m_i N_c$  in state  $Q_1^{(i)}$ ,  $\dots$ , and so forth, is given by

$$W_i = \frac{(m_i N_c)!}{(p^{(i)} m_i N_c)! (q_1^{(i)} m_i N_c)! (q_2^{(i)} m_i N_c)! (q_3^{(i)} m_i N_c)! (q_4^{(i)} m_i N_c)! (r^{(i)} m_i N_c)!} \tag{4}$$

The above estimate explicitly takes into account that the orientation probabilities of equivalent water molecules are identical. In this way the symmetry is now imposed by force. We are no longer able to consider the possibility of symmetry degradation, as this would imply changing the assumed space group. Although this limitation could be avoided if necessary, it allows for a great simplification of the mathematical treatment.

The number of ways that each of the  $m_i N_c$  molecules may be arranged within the crystal will be given by

$$W = \prod_i^{v_o} W_i(s_1^{(i)}, s_2^{(i)}, s_3^{(i)}, s_4^{(i)}, q_1^{(i)}, q_2^{(i)}) \tag{5}$$

This equation quantifies the amount of disorder that is allowed by the first Bernal-Fowler rule. For the time being, the expression remains in terms of six parameters (only five of them are indeed independent), four occupancies and two orientations. There is, however, an important difference between occupancies and orientations: the occupancies are readily accessible by neutron scattering experiments,<sup>15,18,20-22</sup> while the orientations are not. Later on we will attempt to relate the orientations to the known occupancies.

### C. Account of hydrogen bonds

The above equation accounts for the total number of ways the water molecules may be arranged given that each of

them is found in one of six possible states. However, it does not account for constraints imposed on the rotational states by the neighboring molecules, i.e., according to the second Bernal-Fowler rule, only those arrangements are allowed such that each molecule simultaneously donates and accepts two hydrogen bonds. This constraint largely reduces the number of acceptable arrangements.

Let us now try to quantify the fraction of arrangements which fulfill the above condition.

Any oxygen atom has four possible hydrogen sites. Each of such sites is adjacent to similar sites pertaining to nearest neighbor oxygen atoms. Let us consider that one of the nearest neighbors of oxygen  $i$  is, say, oxygen  $j$ , such that site  $S_1^{(i)}$  is adjacent to, say, site  $S_2^{(j)}$ .

According to the ice rules, if  $S_1^{(i)}$  is occupied, site  $S_2^{(j)}$  must be empty, and vice versa. Therefore, the probability of  $S_2^{(j)}$  being occupied is  $1 - s_1^{(i)}$ , while the complementary probability of it being empty is  $s_1^{(i)}$ . Thus, the occupancy of both  $S_1^{(i)}$  and  $S_2^{(j)}$  is characterized by a single *occupancy parameter*, which we denote by a plain Greek letter, say,  $\alpha$  (i.e.,  $s_1^{(i)} = \alpha$ , and  $s_2^{(j)} = 1 - \alpha$ ). For the time being, we will refer to those bonds which involve site  $S_1^{(i)}$  and  $S_2^{(j)}$  as *alpha bonds*, for reason which will become clear afterwards. Let us also assume that the total number of such bonds per unit cell is  $n_\alpha$ . Overall, there must be  $\alpha n_\alpha N_c$  alpha bonds in the crystal, such that site  $S_1^{(i)}$  is occupied and site  $S_2^{(j)}$  is empty. Now, the probability that site  $S_1^{(i)}$  be occupied while site  $S_2^{(j)}$  is empty is  $\alpha^2$ . Therefore, the probability that a total of  $\alpha n_\alpha N_c$  alpha bonds are formed such that site  $S_1^{(i)}$  is occupied and site  $S_2^{(j)}$  is empty is given by  $P_{S_1^{(i)} \rightarrow, S_2^{(j)}} = \alpha^{2\alpha n_\alpha N_c}$ . Likewise, the total number of alpha bonds formed such that site  $S_2^{(j)}$  is occupied and  $S_1^{(i)}$  is empty is  $(1 - \alpha) n_\alpha N_c$ , and the probability of having one such bond is given by  $(1 - \alpha)^2$ . Hence, the probability that a total of  $(1 - \alpha) n_\alpha N_c$  alpha bonds are formed such that site  $S_2^{(j)}$  is occupied and  $S_1^{(i)}$  is empty is given by  $P_{S_2^{(j)} \rightarrow, S_1^{(i)}} = (1 - \alpha)^{2(1 - \alpha) n_\alpha N_c}$ . It follows that the probability of having one particular arrangement with  $\alpha n_\alpha N_c$  sites of kind  $S_1^{(i)}$  occupied and  $(1 - \alpha) n_\alpha N_c$  sites of kind  $S_2^{(j)}$  occupied, such that all the corresponding alpha bonds are properly formed is given by  $P_{S_1^{(i)} \rightarrow S_2^{(j)}} P_{S_2^{(j)} \rightarrow S_1^{(i)}}$ . However, the total number of such arrangements is given by all possible permutations between the bonds. As a result, the probability of having an arrangement

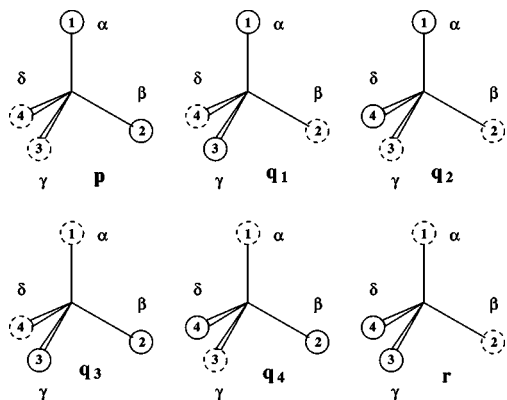


FIG. 1. Sketch of the six possible orientations a water molecule may take and the corresponding nomenclature for their orientations and proton sites. Full and dashed circles denote occupied and unoccupied hydrogen sites, respectively.

with all its alpha bonds properly formed, compatible with the imposed occupancy  $\alpha$  is

$$P_\alpha = \frac{(n_\alpha N_c)!}{(\alpha n_\alpha N_c)! [(1-\alpha)n_\alpha N_c]!} \times \alpha^{2\alpha n_\alpha N_c} (1-\alpha)^{2(1-\alpha)n_\alpha N_c}. \quad (6)$$

This equation quantifies the probability that a given arrangement of randomly oriented water molecules satisfies the second Bernal-Fowler rule.

We assume that similar arguments may be employed for the remaining bonds. In case of site  $S_2^{(i)}$ , for example, we consider that the adjacent site is, say,  $S_3^{(k)}$ , the corresponding occupancy number is denoted as, say,  $\beta$ , and the total number of *beta* bonds is  $n_\beta$ . Accordingly, the probability that one of the  $W$  arrangements fulfills the ice rules for all its bonds is given by

$$P = \prod_i^l P_{\lambda_i}, \quad (7)$$

where  $l$  is the total number of different bonds required to describe the crystal;  $\lambda_i$  stands for a ‘‘Greek letter,’’ such that  $\lambda_1 = \alpha$ ,  $\lambda_2 = \beta$ ,  $\lambda_3 = \gamma$ , etc.; and  $P_{\lambda_i}$  is given by Eq. (6), with  $\alpha$  substituted by  $\lambda_i$ .

#### D. Maximization of entropy

In the previous sections we have first calculated the total number of arrangements that result from placing the molecules in rotational states compatible with some prescribed occupancies. Then we have estimated the fraction of such arrangements which are compatible with the ice rules. It follows that the total number of arrangements consistent with the ice rules and the prescribed occupancy numbers  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc., are given by

$$\Omega = W \times P. \quad (8)$$

To this number of arrangements there corresponds an entropy:

$$S_C = k_B \ln \Omega \quad (9)$$

Note, however, that the above equation does not provide a close expression, because  $W$  is given in terms of individual contributions  $W_i$  and each of those depends on as yet unspecified orientations  $q_1^{(i)}$  and  $q_2^{(i)}$ . To obtain a closed result, we follow Howe and Whitworth,<sup>25</sup> and note that, in the absence of any other information,  $q_1^{(i)}$  and  $q_2^{(i)}$  should be obtained by maximizing the entropy, such that,<sup>25</sup>

$$\left( \frac{\partial S_C}{\partial q_1^{(i)}} \right) = 0 \quad \text{for } i = 1, \nu_o \quad (10)$$

$$\left( \frac{\partial S_C}{\partial q_2^{(i)}} \right) = 0.$$

Fortunately, the solution of this set of equations is very much simplified, because in the expression for the entropy the  $q_1^{(i)}$  and  $q_2^{(i)}$  are completely decoupled from  $q_1^{(j)}$  and

$q_2^{(j)}$  ( $j \neq i$ ). As a result, it is found that the  $q_1^{(i)}$  and  $q_2^{(i)}$  which maximize the entropy are given by the roots of the following equation:

$$\frac{q_1^{(i)}(q_1^{(i)} + 1 - s_1^{(i)} - s_3^{(i)})}{(s_1^{(i)} - q_1^{(i)} - q_2^{(i)})(1 - s_2^{(i)} - q_1^{(i)} - q_2^{(i)})} = 1, \quad (11)$$

$$\frac{q_2^{(i)}(q_2^{(i)} - 1 + s_2^{(i)} + s_3^{(i)})}{(s_1^{(i)} - q_1^{(i)} - q_2^{(i)})(1 - s_2^{(i)} - q_1^{(i)} - q_2^{(i)})} = 1.$$

After some rearrangements, the above set of equations may be converted into a fourth order polynomial, which may be solved either numerically or analytically. In principle, all positive roots resulting in meaningful orientations (i.e., such that all orientations are bound between 0 and 1) are acceptable. In practice, we found that only one out of the four possible roots yields physically meaningful results.

#### E. General solution

From the previous considerations, we can now write down the general solution for the combinatorial entropy of a partially ordered crystal phase of ice:

$$S_C = S_O - S_B. \quad (12)$$

The first term in the right-hand side,  $S_O = k_B \ln W$ , accounts for the entropy gained by the crystal due to the random allocation of molecules in one of six possible states, and reads,

$$\frac{S_O}{Nk_B} = \ln \prod_{i=1}^{\nu_o} [P^{(i)p^{(i)}} q_1^{(i)q_1^{(i)}} q_2^{(i)q_2^{(i)}} q_3^{(i)q_3^{(i)}} q_4^{(i)q_4^{(i)}} r^{(i)r^{(i)}}]^{-m_i/m_t}, \quad (13)$$

where  $\nu_o$  is the total number of nonequivalent oxygen atoms,  $m_i$  is the multiplicity of each of such atoms, and  $m_t$  is the total number of water molecules in a unit cell; while  $q_1^{(i)}$  and  $q_2^{(i)}$  are given by the roots of Eq. (11) and the remaining orientations by Eq. (3).

The second term  $S_B = k_B \ln P^{-1}$  accounts for the reduction of entropy due to the constraints imposed on the possible orientations by the second Bernal-Fowler rule:

$$\frac{S_B}{Nk_B} = \ln \prod_{i=1}^l [\lambda_i^{\lambda_i} (1 - \lambda_i)^{1 - \lambda_i}]^{-n_i/m_t}, \quad (14)$$

where the product runs over the different kinds of bonds, up to a total of  $l$ ;  $\lambda_i$  are the corresponding occupancy numbers ( $\lambda_1 = \alpha$ ,  $\lambda_2 = \beta$ ,  $\lambda_3 = \gamma$ , etc.), and  $n_j$  is the amount of such bonds per unit cell (note that  $\sum n_j = 2m_t$ , since there are two hydrogen bonds per molecule). At this point, we remark that Eq. (14) may be interpreted in either of two ways. We could assume that  $l$  stands for all different pairs of sites forming a bond, so that  $n_i$  stands for the number of such pairs per unit cell and  $\lambda_i$  characterizes the occupation of such bonds. Alternatively, we may note that due to crystallographic constraints, some occupation numbers are constraint to be identical. For this reason, we can sum up all bonds with equal occupation number. In that case,  $l$  is interpreted as the total number of different occupation numbers required and  $n_i$  is the sum of all bonds described by one such occupation number. We will henceforth adopt the latter interpretation.

TABLE I. Crystallographic parameters required to calculate the orientational contribution to the entropy, Eqs. (13) and (11) of the different ice phases. For each nonequivalent oxygen atom,  $i=1, i=2$ , etc., the table shows the multiplicity  $m_i$  and site occupancies of the related bonded protons. The latter are expressed in terms of the independent occupancy parameters, unless otherwise stated. The occupancy of site  $S_4^{(i)}$  follows from the remaining occupancies and Eq. (2).

| Ice  | $i$         | 1            | 2          | 3          | 4              |
|------|-------------|--------------|------------|------------|----------------|
| I    | $m_i$       | 4            |            |            |                |
|      | $s_1^{(i)}$ | $\alpha=1/2$ |            |            |                |
|      | $s_2^{(i)}$ | $\alpha=1/2$ |            |            |                |
|      | $s_3^{(i)}$ | $1-\alpha$   |            |            |                |
| II   | $m_i$       | 6            | 6          |            |                |
|      | $s_1^{(i)}$ | $\alpha$     | $\gamma$   |            |                |
|      | $s_2^{(i)}$ | $\beta$      | $\beta$    |            |                |
|      | $s_3^{(i)}$ | $1-\alpha$   | $1-\gamma$ |            |                |
| III  | $m_i$       | 8            | 4          |            |                |
|      | $s_1^{(i)}$ | $\alpha$     | $1-\alpha$ |            |                |
|      | $s_2^{(i)}$ | $\beta$      | $1-\alpha$ |            |                |
|      | $s_3^{(i)}$ | $1-\beta$    | $\alpha$   |            |                |
| V    | $m_i$       | 4            | 8          | 8          | 8              |
|      | $s_1^{(i)}$ | $1-\alpha$   | $\alpha$   | $1-\alpha$ | $1-\gamma$     |
|      | $s_2^{(i)}$ | $\alpha$     | $\beta$    | $1-\delta$ | $\epsilon=1/2$ |
|      | $s_3^{(i)}$ | $1-\alpha$   | $\gamma$   | $1-\gamma$ | $\gamma$       |
| VI   | $m_i$       | 8            | 2          |            |                |
|      | $s_1^{(i)}$ | $\alpha=1/2$ | $1-\beta$  |            |                |
|      | $s_2^{(i)}$ | $\beta=1/2$  | $1-\beta$  |            |                |
|      | $s_3^{(i)}$ | $\gamma=1/2$ | $1-\beta$  |            |                |
| VII  | $m_i$       | 2            |            |            |                |
|      | $s_1^{(i)}$ | $\alpha=1/2$ |            |            |                |
|      | $s_2^{(i)}$ | $\alpha=1/2$ |            |            |                |
|      | $s_3^{(i)}$ | $\alpha=1/2$ |            |            |                |
| VIII | $m_i$       | 8            |            |            |                |
|      | $s_1^{(i)}$ | $\alpha$     |            |            |                |
|      | $s_2^{(i)}$ | $\alpha$     |            |            |                |
|      | $s_3^{(i)}$ | $1-\alpha$   |            |            |                |

Equations (12), (13), and (14) provide a general expression for the combinatorial entropy of any water crystal phase obeying the ice rules. For a given crystal phase, the entropy is a function of the occupancy numbers,  $\alpha, \beta, \gamma$ , etc. For different crystal phases, the entropy will depend on the crystal geometry, as reflected by the number and multiplicity of the oxygens ( $\nu_o, m_i$ ), the corresponding occupancies,  $s_1^{(i)}, s_2^{(i)}$ , etc. and the arrangement of the hydrogen bonds ( $l$  and  $n_j$ ). The reader is referred to Tables I and II for details concerning the structure of the different crystal phases.

**F. Special cases**

**1. One independent occupancy parameter**

The simplest possible case which allows partial ordering is sketched in Fig. 2. There is only one nonequivalent oxygen, with multiplicity  $m_i$  and two nonequivalent hydrogen sites. Every oxygen atom has four bonds between 2-3 hydrogens, but since each bond is shared between two identical oxygens, there are overall two 2-3 bonds per oxygen, whose occupancy is described by a single independent occupancy parameter,  $\alpha$  ( $n_\alpha=2m_i$ ). Let  $s_1^{(1)}$  and  $s_2^{(1)}$  stand for the oc-

cupancies of two hydrogens labeled as 2 in Fig. 2, and  $s_3^{(1)}$  and  $s_4^{(1)}$  stand for the occupancies of the two hydrogens labeled as 3, respectively. In our treatment we assume that all equivalent crystallographic sites with a unit cell are identical, so that, from the outset  $s_1^{(1)}=s_2^{(1)}$  and  $s_3^{(1)}=s_4^{(1)}$ . Since, according to the ice rules, each pair of adjacent 2-3 sites must contain one and only one hydrogen, the following relation among the occupations must also hold:

$$s_1^{(1)} + s_3^{(1)} = 1,$$

$$s_2^{(1)} + s_4^{(1)} = 1. \tag{15}$$

As a result, two of the hydrogen sites have  $s_1^{(1)}=s_2^{(1)}=\alpha$ , while the remaining hydrogen sites must obey  $s_3^{(1)}=s_4^{(1)}=1-\alpha$ . Upon substitution of these relations into Eq. (11), we find

$$q_1^{(1)} = q_2^{(1)}$$

$$q_2^{(1)} = \frac{1}{3} - [\frac{1}{9} - \frac{1}{3}(\alpha - \alpha^2)]^{1/2}. \tag{16}$$

Further substitution of the above relations into Eq. (3), yields,

$$p^{(1)} = \alpha - \frac{2}{3}[1 - (3\alpha^2 - 3\alpha + 1)^{1/2}]. \tag{17}$$

So that our approach recovers the result suggested by Howe and Whitworth for partially ordered phases described by a single independent occupancy parameter, as expected.<sup>25</sup> In the particular case of full proton disorder we have  $\alpha=1/2$ , whereby Eqs. (2) and (3) show that  $p^{(1)}=q_i^{(1)}=r^{(1)}=1/6$  ( $i=1,2,3,4$ ). Accordingly, one finds  $S_C=Nk_B \ln 3/2$ . Hence, Eqs. (12)–(14) reproduce the Pauling estimate for the combinatorial entropy of fully disordered ice.<sup>10</sup>

**2. Ice I**

In ice I there is also only one nonequivalent oxygen atom ( $m_1=m_i$ ) and two nonequivalent hydrogen atoms.<sup>3</sup> As shown in Fig. 3, each oxygen has three 2-2 bonds and just one 3-3 bond. In principle, this would require two independent occupancy parameters. However, in this case the adjacent hydrogen sites along a bond are both of the same crystallographic kind, and the ice rules adopt the most simple form possible:

$$s_1^{(1)} + s_1^{(1)} = 1,$$

$$s_2^{(1)} + s_2^{(1)} = 1. \tag{18}$$

This means that both occupancies are the same,  $s_1^{(1)}=s_2^{(1)}=\alpha$ , but moreover, that  $\alpha$  is *not* an independent parameter, but on the contrary, bound to have  $\alpha=1/2$ . Therefore, only one occupancy parameter is required and  $n_\alpha=2m_i$ . Thus, the case of ice I is the same as that of a single independent occupancy parameter discussed before, but with full proton disorder.

There is, however, an important conceptual difference. In this case, it is predicted that Ice I is an intrinsically proton-disordered phase: the disorder is imposed by the crystallographic structure itself and there is no room for partial proton ordering upon cooling. In this case, any deviation away from  $\alpha=1/2$  would necessitate a departure from the considered

TABLE II. Crystal parameters required to calculate the bond contribution to the entropy, Eq. (14) of the different ice phases. The entries in columns labeled 1 to 5 show the multiplicity and occupancy parameter of each possible bond in the crystal.

| Ice  | $i$         | 1         | 2         | 3           | 4                              | 5            |
|------|-------------|-----------|-----------|-------------|--------------------------------|--------------|
|      | bond/s      | 2-2, 3-3  |           |             |                                |              |
| I    | $n_i$       | 8         |           |             |                                |              |
|      | $\lambda_i$ | $\alpha$  |           |             |                                |              |
|      | bond/s      | 3-5       | 4-10, 6-8 | 7-9         |                                |              |
| II   | $n_i$       | 6         | 12        | 6           |                                |              |
|      | $\lambda_i$ | $\alpha$  | $\beta$   | $\gamma$    |                                |              |
|      | bond/s      | 3-7, 6-8  | 4-5       |             |                                |              |
| III  | $n_i$       | 16        | 8         |             |                                |              |
|      | $\lambda_i$ | $\alpha$  | $\beta$   |             |                                |              |
|      | bond/s      | 5-7, 6-11 | 8-14      | 9-15, 13-17 | 10-12                          | 18-18, 16-16 |
| V    | $n_i$       | 16        | 8         | 16          | 8                              | 8            |
|      | $\lambda_i$ | $\alpha$  | $\beta$   | $\gamma$    | $\delta=2-\alpha-\beta-\gamma$ | $\epsilon$   |
|      | bond/s      | 3-3       | 4-6       | 5-5         |                                |              |
| VI   | $n_i$       | 8         | 8         | 4           |                                |              |
|      | $\lambda_i$ | $\alpha$  | $\beta$   | $\gamma$    |                                |              |
|      | bond/s      | 2-2       |           |             |                                |              |
| VII  | $n_i$       | 4         |           |             |                                |              |
|      | $\lambda_i$ | $\alpha$  |           |             |                                |              |
|      | bond/s      | 2-3       |           |             |                                |              |
| VIII | $n_i$       | 16        |           |             |                                |              |
|      | $\lambda_i$ | $\alpha$  |           |             |                                |              |

space group.<sup>35</sup> This is not in conflict with experiments, which suggest a significant loss of entropy before the I–XI transition is attained.<sup>11,12</sup> According to our model, strong orientational ordering is compatible with full proton disorder. Indeed, in the more general case, the values taken by  $q_1^{(1)}$  and  $q_2^{(1)}$  should be obtained by extremalising the free energy, rather than just the entropy. In such a case, we could envisage a situation where the extremalisation yields  $\alpha=1/2$  and

$q_1^{(1)}=q_2^{(1)}=q$ , but  $q$  deviates from the fully random value of  $1/6$ , as a result of specific interactions among the molecules. For this particular case, substitution into Eq. (3) shows that the remaining orientations are given by

$$p^{(i)} = \frac{1}{2} - 2q,$$

$$q_3^{(i)} = q,$$

$$q_4^{(i)} = q,$$

$$r^{(i)} = \frac{1}{2} - 2q.$$

(19)

Clearly, any value from  $q=1/4$  to  $q=0$  is possible. In the former case, only four out of six orientational states would be visited, while in the latter case the water molecules would be allowed to choose between just two states.

Actually, this apparent freedom between two states is illusory. There is only one possible crystal configuration in which half the molecules are found in state  $P^{(1)}$  and half the remaining molecules in state  $R^{(1')}$ . It corresponds to a case where the symmetry is broken, the water molecules in the  $P$  and  $R$  state become nonequivalent, and the symmetry changes from  $P6_3/mmc$  to  $Cmc2_1$ , i.e., it corresponds to the actual ordering transition thought to occur between ice I and ice XI.<sup>14-16</sup> The illusory orientational freedom between the  $P$  and  $R$  states is a result of averaging over nonequivalent sites and may be remedied by considering explicitly the four water molecules inside the unit cell of ice I.<sup>36</sup>

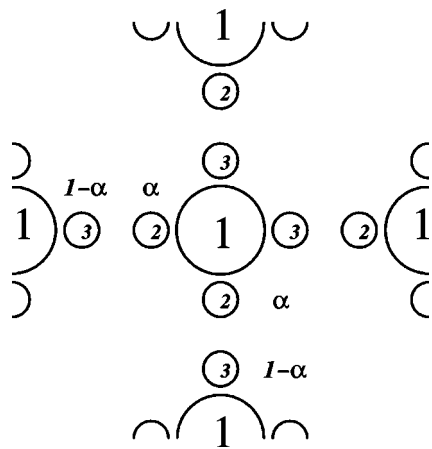


FIG. 2. Hypothetical local environment for a crystal with a single non-equivalent water molecule and two nonequivalent hydrogen atoms. The arrangement is such that a single occupancy parameter, denoted as  $\alpha$  is required to describe proton ordering in this phase. The large and small circles denote oxygen and hydrogen atoms, respectively and the numbers represent nonequivalent atoms. This structure corresponds to that found in ice VIII. In the special case where hydrogen sites 2 and 3 become equivalent, the local environment becomes that found for ice VII.

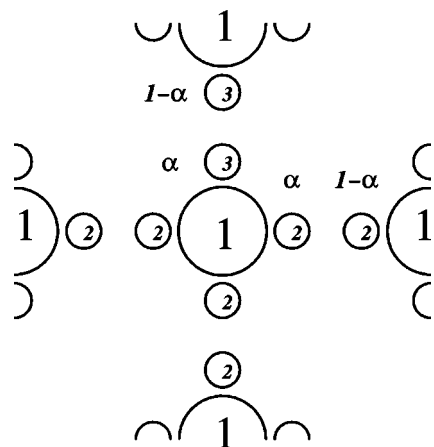


FIG. 3. Local environment of the nonequivalent water molecules in ice I. The large and small circles denote oxygen and hydrogen atoms, respectively; the numbers represent nonequivalent atoms and the Greek letters denote the corresponding hydrogen occupancy parameters.

### 3. Ice III

In the case of ice III there are two nonequivalent oxygen atoms in each unit cell ( $\nu_o=2$ ), oxygen 1 has a multiplicity of eight ( $m_1=8$ ) and oxygen 2 a multiplicity of four ( $m_2=4$ ). By taking into account the coordinates of all nonequivalent oxygen and hydrogen atoms as determined by neutron diffraction,<sup>22</sup> one finds that the local environment is as shown in Fig. 4. For every oxygen of type 1 there is one bond between 3-7 hydrogens, other between 4-5 hydrogens (since one 4-5 bond is shared by two type 1 oxygens) and other between 6-8 hydrogens. Let  $s_1^{(1)}$ ,  $s_2^{(1)}$ ,  $s_3^{(1)}$ , and  $s_4^{(1)}$  stand for the occupancies of hydrogen sites 3, 4, 5, and 6, respectively; and  $s_1^{(2)}$ ,  $s_2^{(2)}$  stand for the occupancies of hydrogens 7 and 8, respectively. From the ice rules, the following constraints between the occupancies must hold:

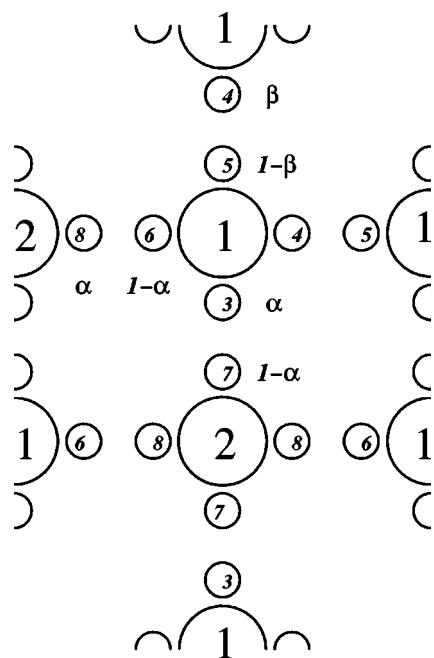


FIG. 4. As in Fig. 3 but for ice III.

$$\begin{aligned}
 s_1^{(1)} + s_1^{(2)} &= 1, \\
 s_2^{(1)} + s_3^{(1)} &= 1, \\
 s_4^{(1)} + s_2^{(2)} &= 1.
 \end{aligned}
 \tag{20}$$

The fact that each oxygen atom must be chemically bonded to two hydrogen atoms poses two other constraints:

$$\begin{aligned}
 s_1^{(1)} + s_2^{(1)} + s_3^{(1)} + s_4^{(1)} &= 2 \\
 2s_1^{(2)} + 2s_2^{(2)} &= 2.
 \end{aligned}
 \tag{21}$$

Solving for the occupancies (cf. Table I), it is found that bonds between 3-7 and 6-8 hydrogens are characterized by a single occupancy parameter, which we call  $\alpha$ , while the remaining bond between 4-5 hydrogens is characterized by a parameter which we denote  $\beta$ . As a result, the number of alpha bonds is  $n_\alpha=2m_1$ , while that of beta bonds is  $n_\beta=m_1$ , and the total number of occupancy parameters required is  $l=2$ .

### 4. Ice V

This is the most complex crystallographic structure of the solid water phases.<sup>22</sup> It has a total of four nonequivalent oxygen atoms per unit cell, with multiplicities as shown in Table I. As many as 14 nonequivalent hydrogen atoms may be found, and the crystallographic environment as determined from neutron diffraction is shown in Fig. 5. We denote  $s_1^{(1)}$  and  $s_2^{(1)}$  the occupancies of sites 5 and 6 and  $s_1^{(i)}$ ,  $s_2^{(i)}$ ,  $s_3^{(i)}$ ,  $s_4^{(i)}$  the occupancies of the four sites of each of the remaining oxygen atoms ( $i=2,3,4$ ). The ice rules impose the following constraints on these occupancies:

$$\begin{aligned}
 s_1^{(1)} + s_1^{(2)} &= 1, \\
 s_2^{(1)} + s_1^{(3)} &= 1, \\
 s_2^{(2)} + s_4^{(3)} &= 1, \\
 s_3^{(2)} + s_1^{(4)} &= 1, \\
 s_4^{(2)} + s_2^{(3)} &= 1, \\
 s_3^{(3)} + s_3^{(4)} &= 1, \\
 s_2^{(4)} + s_2^{(4)} &= 1, \\
 s_4^{(4)} + s_4^{(4)} &= 1.
 \end{aligned}
 \tag{22}$$

Additionally, the chemical identity of the water molecule further imposes the following constraints:

$$\begin{aligned}
 2s_1^{(1)} + 2s_2^{(1)} &= 2, \\
 s_1^{(i)} + s_2^{(i)} + s_3^{(i)} + s_4^{(i)} &= 2, \quad i=2,3,4.
 \end{aligned}
 \tag{23}$$

Solving for the occupancies, it is found that bonds 5-7 and 6-11 are characterized by the same occupancy parameter, which we denote  $\alpha$ ; bond 8-14 is characterized by a single parameter, which we denote  $\beta$ ; bonds 9-15 and 13-17 are characterized by the same occupancy parameter, denoted as  $\gamma$ ; the occupancy of bonds 10-12 is denoted as  $\delta$ ; while the occupancy of bonds 16-16 and 18-18 may be formally denoted as  $\epsilon$ , although the ice rules provide the requirement  $\epsilon=1/2$ . Further note that  $\delta$  is not truly an independent param-

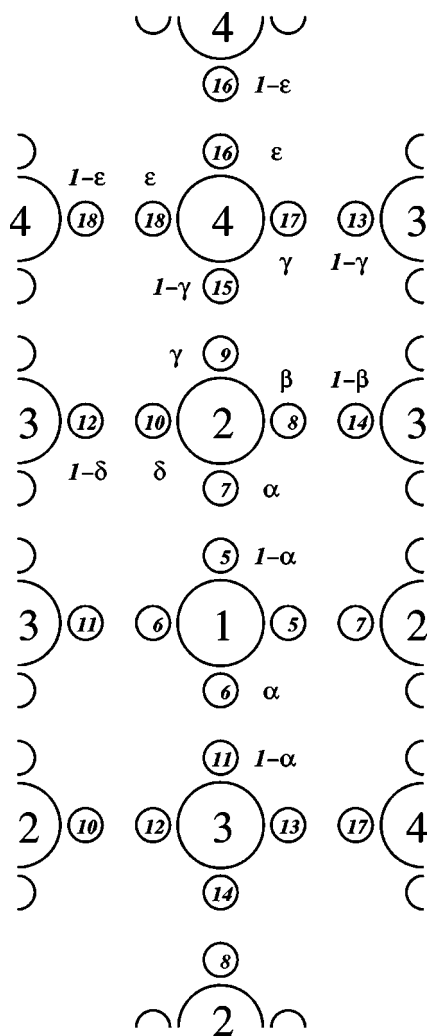


FIG. 5. As in Fig. 3 but for ice V.

eter, but rather bound by the constraint  $\alpha + \beta + \gamma + \delta = 2$ . On the basis of the considerations above, we find that the number of occupancy parameters required to estimate the entropy is  $l=5$ , the corresponding number of bonds is  $n_\alpha=16$  ( $4m_1=m_2+m_3$ ),  $n_\beta=8$  ( $2m_1=m_3$ ),  $n_\gamma=16$  ( $m_2$ ),  $n_\delta=8$  ( $m_2$ ), and  $n_\epsilon=8$  ( $m_4=8$ ).

### 5. Other structures

The remaining structures may be divided into two categories, ordered and disordered. Ice II and ice VIII belong to the former category, while ice VI and ice VII belong to the latter.

The asymmetric unit of ice II contains two water molecules, with four nonequivalent hydrogen sites each. The coordination among the molecules is depicted in Fig. 6, and the constraints imposed on the occupations may be found in Table I. Although three independent occupancy parameters are required to describe the proton arrangements, ice II is thought to be fully ordered, and no evidence of partial ordering has been observed within its stability domain. A first-order transformation is encountered upon heating before any significant disordering is observed.<sup>20,37</sup> Accordingly, the three occupancy parameters may be considered equal to

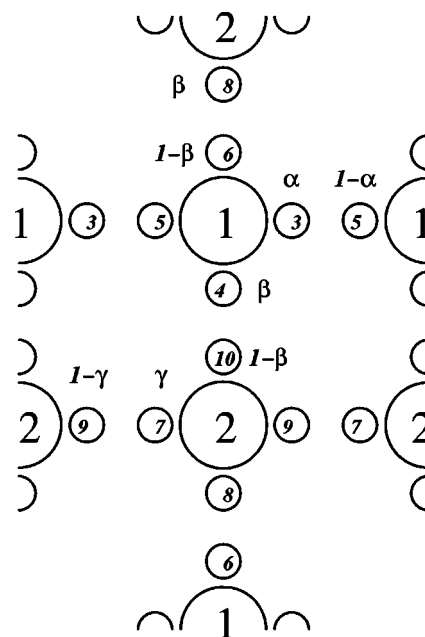


FIG. 6. As in Fig. 3 but for ice II.

unity and the combinatorial entropy is zero. The structure of ice VIII is somewhat simpler. The unit cell contains only one nonequivalent water molecule, with two different hydrogen sites each. The Bernal-Fowler rules allow for a single occupancy parameter (cf. Table I), so that the local environment about a water molecule is as depicted in Fig. 2. Note that ice VIII is formed by two unconnected hydrogen bond networks. The figure shows only one such network, both presenting identical connectivity. Despite the possibility of partial ordering in ice VIII, neutron scattering experiments suggest no appreciable disordering within its stability region,<sup>18</sup> so that its combinatorial entropy is zero.

Upon heating, ice VIII undergoes a first-order transition into ice VII. The tetragonal oxygen lattice is rearranged, evolving into a cubic structure. The gain in symmetry results in a degeneracy of the hydrogen sites. Referring to Fig. 2, sites  $S_1^{(1)}$  and  $S_2^{(1)}$  become identical and a single occupancy parameter  $\alpha$  is needed. The Bernal-Fowler rules require  $\alpha = 1/2$ , however. As a result, full disorder is imposed in ice VII by the crystal structure, in a manner similar to that discussed previously for ice I (cf. Table I).

Proton disorder of this kind may also appear in crystal structures with a much more complex asymmetric unit than that of ice I and ice VII. Ice VI (cf. Fig. 7) and the recently discovered ice XII are an example. Particularly, in ice VI there are two identical hydrogen bond networks, with two nonequivalent water molecules and four nonequivalent proton sites each. However, the occupancy parameters required to describe proton sites 3 and 5 take the value  $1/2$ , due to the constraint imposed by Bernal-Fowler rules. The remaining degree of freedom, required to describe the 4-6 is only illusory. The constraint which imposes chemical identity of water molecule 2 [Eq. (2)] also imposes random proton arrangement in this bond. As a result, ice VI also exhibits full proton disorder of the kind imposed by symmetry requirements. The occupancy of the different hydrogen sites is described in



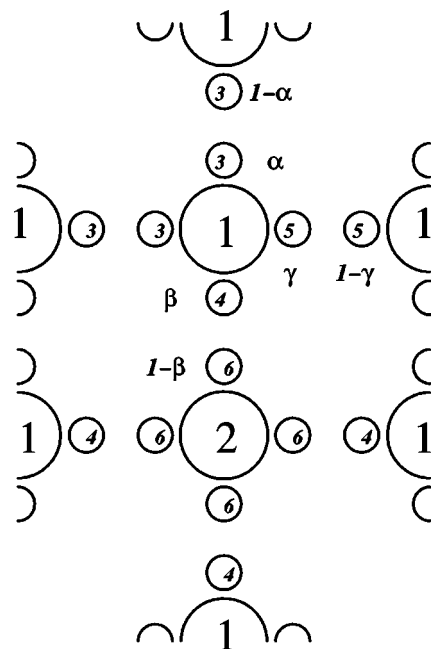


FIG. 7. As in Fig. 3 but for ice VI.

Table I. Interestingly, no convincing evidence of either partial or complete ordering at low temperatures has yet been found.<sup>3</sup>

### G. Comments

It is advisable to summarize the approximations that have been made in order to understand the limitations of the entropy estimate presented in this work.

From the outset, we have assumed that equivalent water molecules (within the considered space group) within a unit cell are identical, such that their orientations may be characterized by a single set of parameters ( $p$ ,  $q_i$  and  $r$ ). Similarly, we also assumed that all equivalent hydrogen sites within a unit cell are identical, such that their occupancies may be described by a single occupancy parameter ( $\alpha, \beta, \dots$ ). This is the case as long as the system remains in the assumed space group. Unfortunately, imposing the symmetry this way does not allow us to predict a possible symmetry degradation, which could result if the occupancies of equivalent hydrogen sites become different.

Secondly, we calculated the constraints imposed by the hydrogen bonds in a mean field way, in the sense that we made no explicit account of correlations between neighbor water molecules. Obviously, if the ice rules are considered to hold, the location of a water molecule in one particular rotational state largely reduces the possible rotational states of the four neighbor molecules. Moreover, the constraints over the different kinds of bonds were imposed independently, even when such bonds involved the same molecule. Finally, since nearest neighbor correlations are ignored, it is clear that no account can be made of “ring correlations,” which are inherent in the water crystal structure.<sup>3</sup>

Clearly, a large number of approximations are involved, but the hope is that the effect is small, at least for phases with high disorder, where strong correlations are expected to be less apparent and can be averaged out. Indeed, our expres-

sion reduces to the Pauling estimate, which is known to be rather accurate, even though it suffers from the same approximations. Also, one must bear in mind that this treatment is valid within a limited range of temperatures. At very high temperatures it would fail, because the ice rules are not necessarily obeyed. At low temperatures, it would also fail, because then, the energy differences among the bonds will be “felt” by the molecules, and so bias the orientations accordingly. Obviously, this energy effect is ignored altogether when we estimate  $q_1^{(i)}$  and  $q_2^{(i)}$  from Eq. (10). A more general treatment would imply extremalisation of the free energy, instead of just the combinatorial entropy. This would have significant consequences in the mathematical tractability of our approach. We expect that a simple mean field approximation for the lattice energy should depend on the orientations of all the nonequivalent water molecules. Therefore, explicit account of this effect would couple the orientations of different molecules, so that finding the values of  $q_1^{(i)}$  and  $q_2^{(i)}$  which extremalise the free energy would involve solving for a system of coupled nonlinear equations. The rather involved problem of explicitly considering energy interactions for each water molecule within the unit cell has been considered for the particular case of ice I. The solution requires extremalisation of 13 nonindependent variables.<sup>24,36</sup> Minagawa showed that right above an ordering transition at rather low temperatures, the system becomes completely disordered. In that case, considering the nonequivalent water molecules only, and ignoring the coupling effect discussed above provides the same solution as the full treatment.

An alternative approach for the enumeration of all possible arrangements compatible with the ice rules has been employed to estimate the combinatorial entropy of ice IX.<sup>26</sup> The number of arrangements obeying the second Bernal-Fowler rule is counted exactly, and then multiplied by the approximate fraction of configurations obeying the first Bernal-Fowler rule. In this work the calculation is done in the reverse order. First we count exactly the number of ways the molecules may be arranged into six possible rotational states, and then multiply by the approximate fraction of configurations obeying the second Bernal-Fowler rule. Since both methods include an approximation in one of the steps they are not equivalent, although they yield equal results in the limiting case of full order and full disorder. It is not evident why one method should be superior to the other, but Howe and Whitworth argue that the enumeration scheme employed here is more accurate.<sup>25</sup>

### III. SIMULATION OF PARTIALLY ORDERED ICE

Predicting the phase diagram of partially ordered phases is a complicated problem. Apart from the difficulties involved in the calculation of free energies of molecular solids,<sup>38–40</sup> the fact is that ice III and V show phase boundaries with four other phases each and a total of six different phases must be considered. A full explanation of the different methodologies employed is lengthy. In this section we will present only a brief description of the strategy employed, as

well as full details of specific methodologies required for the simulation of partially ordered phases (further details may be found elsewhere<sup>33,34,41</sup>).

### A. Model potential

In order to study the effect of the combinatorial entropy of partially ordered phases of water, we employed the well known TIP4P model.<sup>32</sup> This model is based on a simple point charge description, similar to that proposed by Bernal and Fowler long time ago.<sup>8</sup>

The molecular core is described by a single Lennard-Jones interaction site placed on the center of the oxygen atom, with LJ range and force parameters of  $\sigma=3.154 \text{ \AA}$  and  $\epsilon=78.02 k_B$ . One positive partial charge  $q=0.52e$  is placed at each hydrogen site, while a negative charge is placed along the H–O–H bisector, displaced in the direction of the hydrogen atoms at a distance of  $0.15 \text{ \AA}$  away from the oxygen site. This small shift of the negative partial charge is thought to be crucial in order to properly describe ice polymorphs.<sup>33</sup> The model is rigid, with an assumed bond length of  $0.975 \text{ \AA}$  and an assumed bond angle of  $104.5^\circ$ .

The choice of this model is based on recent studies, which have shown that TIP4P provides a qualitatively correct phase diagram for the solid phases of water.<sup>33,34</sup>

### B. Initial configurations

In order to simulate ice III and V, we need to generate initial configurations with partial ordering of hydrogen atoms. Buch *et al.* have developed an algorithm which allows the generation of fully disordered ice I in two stages.<sup>42</sup> In stage one, a perfect oxygen lattice is generated, and the two allowed hydrogen sites between each nearest neighbor oxygen pair are identified. A single hydrogen atom is then placed at random on one of the two allowed sites of each such pair. In this way, one ensures that there will be only one hydrogen between every two nearest neighbor oxygens. However, the oxygen atoms will be coordinated by anything between zero and four hydrogen atoms, while only those configurations with two hydrogens per oxygen are acceptable. This problem is remedied in stage two. A hydrogen atom chosen at random is displaced to an adjacent hydrogen site along the hydrogen bond. If the effect of this displacement is to reduce the coordination difference between the two oxygen atoms involved, the change is accepted right away, and a new hydrogen atom is selected. If the coordination difference remains the same, the change is accepted with probability 1/2, while if the change increases the coordination difference between the oxygen atoms, it is rejected right away. The procedure is repeated until the coordination of each oxygen atom becomes equal to two.

Whereas this method produces fully random order, what we need is a procedure to allocate hydrogens in each non-equivalent hydrogen site according to some prescribed probability. In order to do so, we modify the algorithm of Buch *et al.* in two ways. In the first stage of the algorithm, we do not allocate the hydrogen atoms at random in one of the two sites, but rather, place them with probability equal to their occupancy: we choose one hydrogen site at random. We gen-

erate a number between 0 and 1 with uniform probability. If that number is smaller than the occupancy of the chosen site, we place the hydrogen there. Otherwise, we place the hydrogen in the opposite site. In the second stage of the algorithm, we do not attempt hydrogen displacements at random. Instead, the displacements are chosen from a biased distribution, such that those attempts which will drift the population of occupied hydrogen sites towards the desired occupancies are favored. This is performed in the following way. First, a hydrogen is selected at random. Let the actual occupancy of that kind of hydrogen site in the crystal be  $s_{\text{real}}$ , and let  $s'_{\text{real}}$  be the actual occupancy of the adjacent hydrogen site ( $s'_{\text{real}}=1-s_{\text{real}}$ ). We define an actual occupation shift as

$$\Delta s_{\text{real}} = s'_{\text{real}} - s_{\text{real}}. \quad (24)$$

Now, let  $s_{\text{ideal}}$  be the desired occupancy of the chosen site, and let  $s'_{\text{ideal}}$  be the desired occupancy of the adjacent hydrogen site. We define an ideal occupation shift as

$$\Delta s_{\text{ideal}} = s'_{\text{ideal}} - s_{\text{ideal}}. \quad (25)$$

A displacement from the chosen to the adjacent hydrogen site is selected with probability  $\min[1, \exp\{-w(\Delta s_{\text{real}} - \Delta s_{\text{ideal}})\}]$ , where  $w$  is an arbitrary parameter which determines the broadness of the distribution. Once a displacement is selected according to the proposed underlying matrix, the algorithm proceeds as explained before, accepting or rejecting the proposed displacement depending on the coordination difference that results.

We found that a choice of  $w$  between 1 and 1/2 produced configurations which deviated but little from the prescribed occupancies. Out of all such configurations, only those with zero dipole moment were chosen. We found that producing partially ordered configurations with zero dipole moment for both ice III and ice V was considerably more difficult than for ice I. Several thousand configurations had to be produced in order to find one with negligible net dipole moment.

### C. Free energy calculations

The configurational free energy of the solid phases was calculated using the extension of the Einstein crystal method<sup>43</sup> to molecular fluids, as suggested by Vega *et al.*<sup>38–40</sup> This method provides the free energy of a configuration with a specified hydrogen bond network. In this work we assume that this configurational free energy so obtained does not depend significantly with the chosen hydrogen bond network, as long as the hydrogen site occupancies remain the same. With this assumption, the total free energy of a crystal with some chosen occupation parameters,  $\alpha, \beta$ , etc., may be approximated as

$$G_{\text{crystal}}(\alpha, \beta, \dots) = G_{\text{conf}} - TS_C(\alpha, \beta, \dots), \quad (26)$$

where  $S_C$  is calculated as explained previously.

The free energy of the liquid phase was determined by integrating along a path which switched the Hamiltonian from that of the water model considered to that of the Lennard-Jones fluid. The free energy of the Lennard-Jones fluid may be readily determined from a parametric fit to Molecular Dynamics simulations.<sup>44</sup>

Once the free energy of the different phases is known, the coexistence point may be determined by thermodynamic integration along isotherms and isobars, as required. This was achieved by employing NpT Monte Carlo simulations, using the Rahman-Parrinello method in order to account for nonorthogonal box geometries consistent with the crystal phase considered.<sup>45,46</sup>

The full phase diagram was then obtained by tracing the coexistence boundaries by means of the Gibbs-Duhem method,<sup>47</sup> using a fourth-order predictor-corrector Runge-Kuta method for the integration of Clapeyron's equation.

#### IV. RESULTS

In order to calculate the combinatorial entropy of a crystal, we must first estimate somehow the proton site occupancies.

In those phases with random proton order imposed by the crystal symmetry, ice I, VI and VII, the occupancies must take the value 1/2. Furthermore, experimental evidence suggests that in the neighborhood of phase transformations of these phases, the thermal energy is significantly higher than the energy differences resulting from partial orientational ordering. The orientations are then also random, and we can assume a Pauling like value for the combinatorial entropy  $S/Nk_B = \ln(3/2)$ .

Other phases, such as ice II and ice VIII have at least one degree of freedom for partial proton ordering, but experimental evidence suggests that these phases may be considered as fully ordered at the phase transition. We therefore assumed a value of 1 for the involved occupancy parameters, leading to zero combinatorial entropy.

Finally, ice III and V are known to show some degree of partial proton ordering. The occupancy parameters take non-trivial values which must be obtained from experiment. The problem in this case is that the occupancies depend to some extent on temperature and pressure, and the experimental data is somewhat limited. With the available data from Lobban *et al.*,<sup>22</sup> however, we can infer approximate occupations at the experimental triple points, which allow a comparison with measured entropies of transition.

Table III shows a comparison between the measured entropies of transition and the estimated combinatorial entropy changes at some selected triple points. The assumed occupancies are indicated in the caption as estimated from Ref. 22. Obviously, one cannot expect full agreement, because the experimental entropies of transition include not only a combinatorial entropy change, but also the corresponding configurational contribution. However, since volume changes in solid/solid transitions are relatively small, it is assumed that the combinatorial entropy change will play an important role. Indeed, it is observed that the entropy of transition between a fully ordered and a disordered phase is much bigger than that found between disordered phases, and this trend is captured by simply considering the combinatorial entropy as predicted from our simple theoretical model. If we assumed that the combinatorial entropy estimate is exact, it is difficult to provide a simple thumb rule for the relative contribution of the configurational entropy change. For transitions between an ordered and a disordered phase (I-II, II-III, II-V), the combi-

TABLE III. Estimated combinatorial entropy change for several solid/solid coexistence lines at the triple points, compared with the corresponding experimental entropy change (taken from Ref. 2). For ice V we assumed the experimental occupancies found at 254.0 K and 5.0 GPa,  $\alpha=0.47$ ,  $\beta=0.299$ ,  $\gamma=0.485$ . For ice III we assumed occupancies as measured experimentally at 250.0 K and 0.25 GPa,  $\alpha=0.35$  and  $\beta=0.5$  [occupancies as determined by Lobban *et al.* (Ref. 22)].

| Triple point | Transition |     | $\Delta S / (\text{J mol}^{-1} \text{K}^{-1})$ |               |
|--------------|------------|-----|------------------------------------------------|---------------|
|              | from       | to  | Total                                          | Combinatorial |
| L-I-III      | I          | III | 1.6                                            | -0.25         |
| L-III-V      | III        | V   | -0.3                                           | -0.01         |
| I-II-III     | I          | II  | -3.2                                           | -3.37         |
|              | I          | III | 0.7                                            | -0.25         |
| II-III-V     | II         | III | 3.9                                            | 3.12          |
|              | II         | III | 5.1                                            | 3.12          |
|              | II         | V   | 4.8                                            | 3.11          |
|              | III        | V   | -0.3                                           | -0.01         |

natorial contribution is large, and may vary between as much as 90%, to about 60% of the total change. For transitions between two disordered phases, the comparison is difficult, because the changes are small and the relative error could become too large. Comparing the combinatorial entropy changes of Table III with the total entropy changes as estimated from computer simulation,<sup>34</sup> where the configurational entropy change may be measured explicitly, we find that the combinatorial contribution varies between 0 and  $3.5 \text{ J mol}^{-1} \text{K}^{-1}$ , while the configurational change lays between roughly 0 and  $1.5 \text{ J mol}^{-1} \text{K}^{-1}$  for transitions among solid phases.

In order to assess the role of combinatorial entropy in a more direct manner, we calculated the phase diagram of water using computer simulations as described previously. For ice III and V, the Gibbs free energy of the model is calculated in an approximate manner, by assuming prescribed occupancies consistent with experimental measurements. As noted previously, the problem is that the occupancies depend to some extent on the temperature, so that the choice is somewhat arbitrary. Fortunately, ice III is stable only in a rather narrow range of temperatures, and we do not expect major rearrangements within its stability domain. From inspection of experimental data,<sup>22</sup> we assumed  $\alpha=1/3$  and  $\beta=1/2$ , which results in an entropy estimate of  $S/Nk_B=0.3686$ . This was the value of the combinatorial entropy used to compute the phase diagram of the TIP4P model.<sup>33,34</sup> Notice that this value amounts to a 9% reduction with respect to the Pauling entropy. Using the Nagle enumeration scheme for the same degree of disorder, Nishibata and Whalley predict a value which is closer to the Pauling estimate  $S/Nk_B=0.3818$ .<sup>26</sup> For ice V, the situation is somewhat more complicated, because it is stable within a temperature range of several decades, and the occupancies change to a larger extent within this range.<sup>22</sup> As a compromise, we assumed  $\alpha=1/2$ ,  $\beta=3/10$ , and  $\gamma=1/2$  (with  $\delta=2-\alpha-\beta-\gamma$ ). This yields an entropy of  $S/Nk_B=0.3817$ , only 6% smaller than the Pauling estimate for fully disordered ice. This was the value of the combinatorial entropy used to compute the phase dia-

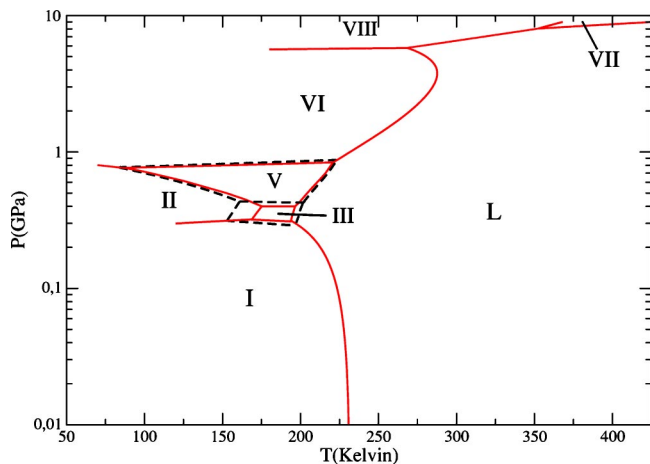


FIG. 8. Calculated phase diagram for the TIP4P model of water. The full line represent estimates obtained with allowance for partial disorder in ice III and V. The dashed line results from considering the combinatorial entropy of ice III and V to be that of a fully disordered ice.

gram of the TIP4P model.<sup>33,34</sup> Notice, however, that the combinatorial entropy of ice V changes somewhat within its thermodynamic stability range. For instance close to the experimental II-V-VI triple point of water, at about 200 K, the measured occupancies resemble more  $\alpha=0.45$ ,  $\beta=0.28$ ,  $\gamma=1/2$ , which yields  $S/Nk_B=0.3671$ .

The phase diagram of the TIP4P model, with combinatorial entropies estimated as described above is shown in Fig. 8 (full lines). As can be seen, the qualitative agreement with the experimental phase diagram is remarkable, although quantitative agreement is not achieved. Most noticeable, the TIP4P model predicts melting temperatures which are about 40 to 60 K low. A more detailed comparison with experimental results was reported elsewhere,<sup>33,34</sup> and we will not pursue this issue here, but rather, discuss the effect of the combinatorial entropy.

As the Einstein crystal simulations are rather expensive, we estimated the role of the combinatorial entropy by adding the Pauling value [i.e.,  $k_B \ln(3/2)$ ] to the configurational free energy of ice III and V (instead of using the value of the combinatorial entropy obtained from the treatment of this work). The goal was to analyze the effect of such change on the phase diagram. Replacing the combinatorial entropy of this work by the Pauling value increases the combinatorial entropy of these phases by 9% and 6% in  $k_B$  units, respectively. From the estimated free energies, coexistence points were obtained, and the full diagram was then calculated by using the Gibbs-Duhem method. The resulting phase diagram is shown in Fig. 8 (dashed lines).

As expected, increasing the entropy of ice III and ice V has the effect of increasing their stability. In order to see the extent of this effect, Fig. 9 shows the calculated phase diagrams at higher resolution. On the one hand, the melting temperatures increase, while on the other hand, the coexistence temperatures with ice II decrease. A striking feature is the extent of stabilization with respect to ice II, which is much more apparent than the corresponding stabilization with respect to water. In the latter case, the melting temperature changes by a few Kelvin, while in the former the coex-

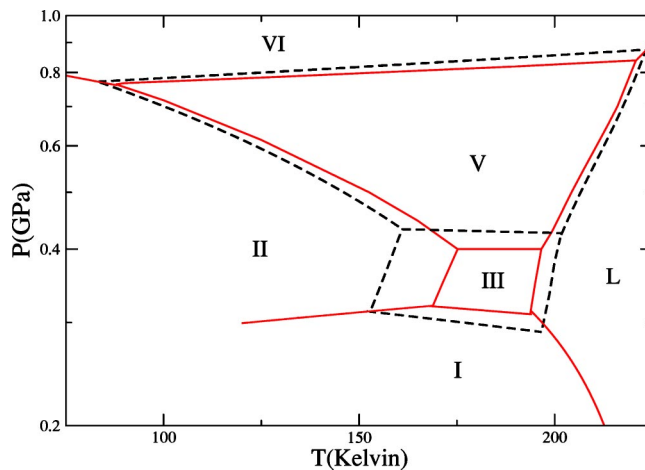


FIG. 9. Calculated phase diagram of the TIP4P model of water in the neighborhood of the partially disordered ice phases III and V. Rest of caption as in Fig. 8.

istence temperature changes as much as 25 K or so. This shows clearly the importance of combinatorial entropy in determining the stability of partially ordered phases. Experimentally, ice III is stable over a very small temperature range, of only 13 K. The TIP4P model already predicts too large a temperature range for ice III when partial order is considered, i.e., 23 K. If, however, full disorder were assumed, this range would increase up to 43 K, approximately. On the other hand, by employing the entropy estimate of Nishibata and Whalley, the temperature range where ice III is stable would lie somewhere in between 23 K and 43 K. The simulation results therefore argue in favor of our own estimate, although this evidence is obviously indirect and could result from a cancellation of errors.

The large stabilization that occurs against ice II may be rationalized as follows. When we assume partial disorder, the phase diagram is calculated by assuming equal chemical potentials for each phase:

$$\mu_a(p, T) = \mu_b(p, T), \quad (27)$$

where  $a$  stands for either ice II or liquid water, and  $b$  denotes a partially ordered phase (ice III or V). If we now assume full disorder for phase  $b$ , its entropy is changed by a positive  $\Delta S_C$ . At constant pressure, the coexistence condition now becomes

$$\mu_a(p, T') = \mu_b(p, T') - T' \Delta S_C, \quad (28)$$

where  $T'$  is the new coexistence temperature at the imposed pressure. If we now make a Taylor expansion about  $T$ , in the spirit of Clapeyron's equation, we obtain

$$T' = T \frac{S_b - S_a}{S_b - S_a + \Delta S_C}. \quad (29)$$

For the II-III transition,  $S_{III} - S_{II} = 3.1 \text{ J mol}^{-1} \text{ K}^{-1}$  is small and positive,<sup>34</sup> the entropy ratio of Eq. (29) is smaller than one and the coexistence temperature decreases. For the L-III transition, on the other hand,  $S_{III} - S_L = -16.4 \text{ J mol}^{-1} \text{ K}^{-1}$  is large and negative,<sup>34</sup> the entropy ratio is greater than one, and the melting temperature increases. For the II-III transition, however,  $\Delta S_C$  is a larger fraction of the total entropy

than it is for the L-III transition. Hence, the change is much more apparent in the former than in the latter. Analogous arguments apply for the II-V and L-V transitions.

## V. CONCLUSIONS

In this paper we have presented a general expression in order to estimate the combinatorial entropy of partially ordered ice phases. The equation requires knowledge of the crystal structure, and depends on occupancy parameters which may be measured by neutron scattering techniques.<sup>22</sup> Rather simple symmetry arguments allow to assess the degree of disorder that may be expected. Particularly, ice I, VI, and VII are likely to show full proton disorder as a result of constraints on the crystal structure. However, such a proton disorder is not incompatible with partial orientational ordering, because the occupancies do not completely determine the fraction of molecules with a given orientation. This fact could help reconciling apparently conflicting experimental measurements of disorder in ice VI and VII. Calorimetric and dielectric relaxation experiments have suggested significant orientational rearrangements,<sup>3,48</sup> while neutron scattering techniques support full proton disorder.<sup>18</sup> Both observations seem to be possible on the basis of our study. A careful assessment of the energy gained on ordering would be required to properly estimate the extent of orientational ordering compatible with random proton allocation.

Some improvement of the expression presented is desirable. For example, higher correlations could be incorporated. A systematic method in this direction was proposed recently for fully disordered ice,<sup>49</sup> but an extension to partially ordered phases is still required. Another route for improvement which is important at low temperatures is to assess the biasing effect of hydrogen bond energy on the orientations. This could be done on the lines of density functional theory, which was used with promising results by Woo and Monson in order to study the stability of ordered counterparts of ice III and V.<sup>50</sup>

Estimates for the combinatorial entropy were combined with direct free energy calculations from simulations in order to study the effect of partial ordering on the stability of ice. From our study, which employed the TIP4P model of water, it was found that partial ordering plays an important role in the stability of ice III and V, particularly in the former phase. A change from 0.35 to 0.5 in the occupancy of 2/3 of all the hydrogen sites of ice III may change the combinatorial entropy by about 9%, and thereby shifting the triple point temperature significantly. These findings have some experimental implications. The observed phase behavior could be very sensitive to changes in the occupancies of the crystal samples studied. At low temperatures, for example, it is not unexpected to find some dependence of the occupancies on sample preparation, and one should test carefully whether proton ordering is reversible in such cases.

Finally, the approximate nature of our calculations should be mentioned, at least to highlight the difficulties that may be encountered in calculating the phase diagram of water. Actually, the occupancies employed in order to estimate the combinatorial entropy should be obtained self-consistently for a given water potential. At this moment,

however, this seems a difficult task beyond our computer power capabilities. Presumably, one would have to allow for hydrogen bond network rearrangements, and devise some method in order to calculate the free energy of such a crystal. Whereas the former issue could be tackled by employing a method recently developed by Rick and Haymet,<sup>51</sup> the latter possess problems which still need to be solved.

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