The configurational entropy of ice is calculated by thermodynamic integration from high to low temperatures. We use Monte Carlo simulations with a simple energy model which reproduces the Bernal-Fowler ice rules. This procedure is found to be precise enough to give reliable values for the residual entropy $s_{th}$ of different ice phases in the thermodynamic limit. First, we check it for a two-dimensional ice model. Second, we calculate $s_{th}$ for ice Ih, and compare our result with those previously given in the literature. Third, we obtain $s_{th}$ for ice VI, for which we find a value clearly higher than for ice Ih.

II. COMPUTATIONAL METHOD

To calculate the configurational entropy of the different ice structures, we consider a simple model. The only requirement for this model is that it has to reproduce the ice rules at low temperature. Thus, irrespective of its simplicity, it can give the actual entropy if an adequate thermodynamic integration is carried out.

For concreteness, we summarize the ice rules:

1. There is one hydrogen atom between each pair of neighboring oxygen atoms, forming a hydrogen bond.
2. Each oxygen atom is surrounded by four $H$ atoms, and that there must be exactly one proton between two contiguous oxygen atoms.
3. The entropy of a crystal of contiguous oxygen atoms.

The presence of orientational disorder in the water molecules is a property of several ice phases. While the oxygen atoms show a full occupancy ($f$) of their crystallographic positions, the hydrogen atoms may display a disordered spatial distribution as indicated by a fractional occupancy of their lattice sites. Thus, ice Ih, the stable phase of solid water under normal conditions, presents full proton disorder compatible with the ice rules, i.e., occupancies of H-sites of $f = 0.5$. However, other phases such as ice II are $H$-ordered, while others as ice III are characterized by a partial proton ordering, i.e., some fractional occupancies of H-sites are different from 0.5.

Configurational disorder of protons in ice was first studied by Pauling who estimated its contribution to the entropy of a crystal of $N$ molecules to be $S = Nk_B \ln(3/2)$. This combinatorial estimate turned out to be in good agreement with the “residual” entropy deduced from the experimental heat capacity of ice Ih, although the calculation did not take into account the actual structure of ice Ih. Nagle calculated later the residual entropy of hexagonal ice Ih and cubic ice Ic by a series method, and found in both cases very similar values, which turned out to be close to but slightly higher than the Pauling’s estimate. More recently, Berg et al. have used multicanonical simulations to calculate the configurational entropy of ice Ih, assuming a disordered proton distribution compatible with the ice rules. Moreover, several authors have calculated the configurational entropy of partially ordered ice phases, a question that will not be addressed here.

Ice-type models are important not only for condensed phases of water, but also for other kinds of materials showing atomic disorder as well as in the statistical mechanics of lattice models. Although exact analytical solutions for the ice model in the actual three-dimensional ice structures are not known at present, an exact solution was found by Lieb for the two-dimensional square lattice. In this case, the configurational entropy results to be $S = Nk_B \ln W$, with $W = (4/3)^{3/2} = 1.5396$, somewhat higher than the Pauling value $W_P = 1.5$.

In this paper, we present a simple, but “formally exact” method, to obtain the configurational entropy of $H$-disordered ice structures. It is based on a thermodynamic integration from high to low temperatures, for an ice model which reproduces the ice rules at low temperatures.
network coordination is four, which gives a total of 2
the links are H-bonds between nearest neighbors. The
defines a network, where the nodes are the O sites, and
so that each O atom has four nearest O atoms. This
to it.
two of them covalently bonded and two other H-bonded
to it.
Our model is defined as follows. We consider an ice
structure as defined by the positions of the oxygen atoms,
so that each O atom has four nearest O atoms. This
defines a network, where the nodes are the O sites, and
the links are H-bonds between nearest neighbors. The
network coordination is four, which gives a total of 2\(N\)
links, \(N\) being the number of nodes. We assume that
on each link there is one (and only one) H atom, which
can move between two positions on the link (close to one
oxygen or close to the other).

Given a configuration of H atoms on an ice network,
the energy \(U\) is defined as:
\[
U = \sum_{n=1}^{N} E(i_n)
\]  
where the sum runs over the \(N\) nodes in the network, and
\(i_n\) is the number of hydrogen atoms covalently bonded
to the oxygen on site \(n\), which can take the values 0,
1, 2, 3, or 4. The energy associated to site \(n\) is then
\(E(i_n) = |i_n - 2|\) (see Fig. 1), having a minimum for \(i_n = 2\),
which imposes the fulfillment of the ice rules at low
temperature. In this way, all hydrogen configurations
compatible with the ice rules on a given structure are
equally probable in the low-temperature limit, i.e., it is
implicit in the model that all configurations obeying
the ice rules have the same energy.

We note that this simple model, although it is a con-
venient tool for our present purposes, does not represent
any realistic interatomic interaction, in the sense that
we are not dealing with a real ordering process, but with
a numerical approach to “count” H-disordered config-
urations of ice. Since the entropy is a state function, one can
obtain the number of configurations compatible with the
ice rules by a kind of thermodynamic integration from a
reference state \((T \to \infty)\) for which the H configuration
is random (does not respect the ice rules), to a state in
which these rules are strictly fulfilled \((T \to 0)\). We note
that in our calculations we use reduced variables, so that
all quantities such as the energy \(U\) and the temperature \(T
\) are dimensionless. The entropy per site \(s\) that we cal-
culate is therefore related with the physical configurational
entropy \(S\) as \(S = Nk_B s\).

The heat capacity per site,
\[
c_v(T) = \frac{1}{N} \frac{d\langle U \rangle}{dT}
\]  
has been obtained from the energy fluctuations at tem-
perature \(T\), by using the expression
\[
c_v(T) = \frac{(\Delta U)^2}{N T^2},
\]
where \((\Delta U)^2 = \langle U^2 \rangle - \langle U \rangle^2\). The configurational
entropy per site can be obtained from the heat capacity by
thermodynamic integration as
\[
s(T) = s(\infty) + \int_{\infty}^{T} \frac{c_v(T')}{T'} dT'
\]
In our case, the entropy per site for \(T \to \infty\) is given by
\[
s(\infty) = \frac{1}{N} \ln(2^{2N}) = 2 \ln 2
\]
where \(2N\) in the exponent indicates the number of links
in the network under consideration (Note that \(2^{2N}\) is
the total number of possible configurations in our model,
since each of the \(2N\) links admits two different positions
for an H atom).

A practical problem with Eq. (1) in a thermodynamic
integration is that the limit \(T \to \infty\) cannot be reached,
and any cutoff in the temperature, even if this is taken
at large \(T\), can introduce systematic errors in the cal-
culated entropies. To overcome this problem we use the
fact that an analytical model can approximate very well
the high-temperature thermodynamic variables, with an
error smaller than the error bars associated to the sim-
ulation procedure. Such an analytical model can be ob-
tained by considering the nodes as “independent”, as in
Pauling’s original calculation for a hypothetical network
including no loops. In this case, the partition function is
given by
\[
Z = \frac{z^N}{2^{2N}}
\]
where \(z\) is the one-site partition function:
\[
z = 6 + 8 e^{-1/T} + 2 e^{-2/T},
\]
as derived from the Boltzmann factors for 16 possible
configurations of four hydrogen atoms; see Fig. 1) and
the term \(2^{2N}\) in the denominator appears to avoid count-
ing links with zero or two H atoms. In fact, the high-
temperature limit of \(Z\) in Eq. (6) is \(Z_\infty = 16^N/4^N =
2^{2N}\), which is the number of configurations compatible
with the condition of having an H atom per link. The
energy per site is
\[
\langle u \rangle = \frac{4}{z} \left(2 e^{-1/T} + e^{-2/T}\right)
\].
For the actual ice structures, the corresponding oxygen networks contain loops, which means that the factorization in the partition function in Eq. (6) is not possible. However, at high temperatures thermodynamic variables for the real structures converge to those of the independent-site model. At high temperature, \( \langle u \rangle \) in Eq. (5) can be expanded in powers of \( 1/T \) so that

\[
\langle u \rangle = \frac{3}{4} - \frac{7}{16T} + \frac{3}{64T^2} + \frac{19}{768T^3} + \ldots
\]

and using Eqs. (2) and (4) we find for the entropy

\[
s(T) = s(\infty) - \frac{7}{32T^2} + \frac{1}{32T^3} + \frac{19}{1024T^4} + \ldots
\]

Keeping terms for \( s(T) \) up to \( 1/T^4 \), we find \( s(T = 10) = 1.38414 \). We have checked that at temperatures \( T \sim 10 \), both the energy and heat capacity derived from this model coincide (within error bars) with those derived from our Monte Carlo simulations for the actual networks studied here. Thus, to obtain the configurational entropy for the ice structures, our thermodynamic integration in fact begins at \( T = 10 \), a temperature at which the entropy of the actual network is taken as that of the analytical (no loops) model. We note that at lower temperatures (\( T \sim 1 \)), the simulations for the considered networks yield energy values different from those derived from the “independent-node” model in Eqs. (6) and (7), which is in fact the reason why we find for these networks entropy values different from the Pauling result.

With this simple scheme for the energy, we have carried out Monte Carlo simulations on ice networks of different sizes. The largest networks employed here included 3600, 2880, and 3430 sites for the square lattice, ice Ih, and ice VI, respectively. Periodic boundary conditions were assumed. Sampling of the configuration space was carried out by the Metropolis update algorithm. For each network we considered 360 temperatures in the interval between \( T = 10 \) and \( T = 1 \), and 200 temperatures in the range from \( T = 1 \) to \( T = 0.01 \). For each considered temperature, the simulation started from the last hydrogen configuration in the previous temperature, and then we carried out \( 10^4 \) Monte Carlo steps for system equilibration, followed by \( 8 \times 10^6 \) steps for averaging of thermodynamic variables. Each Monte Carlo step consisted of an update of \( 2N \) (the number of H-bonds) hydrogen positions successively and randomly selected. Finite-size scaling was then employed to obtain the configurational entropy per site \( s_{th} \) corresponding to the thermodynamic limit (extrapolation to infinite size).

Using a simple energy model as that employed here, an alternative procedure to calculate the configurational entropy can consist in obtaining directly the density of states as a function of the energy, as described elsewhere for order/disorder problems in condensed matter. Then, in our case the entropy could be obtained from the number of states with zero energy, i.e., compatible with the ice rules.

![Graph showing entropy per site as a function of the inverse lattice size (1/N) for the two-dimensional square lattice.](image)

**FIG. 2:** Entropy per site as a function of the inverse lattice size \((1/N)\) for the two-dimensional square lattice. Open circles indicate results of our thermodynamic integration in the limit \( T \to 0 \). Error bars are in the order of the symbol size. A solid circle shows the exact analytical result obtained by Lieb.\(^{15}\)

### III. RESULTS AND DISCUSSION

We have applied the method described above to calculate the configurational entropy of the ice model in three different networks. First, we check the precision of the method for the two-dimensional square lattice, for which an exact analytical solution is known. Then, we calculate \( s_{th} \) for the familiar ice Ih, and compare our results with those obtained in earlier work. Finally, we present results for the configurational entropy of ice VI, for which one expects \( s_{th} \) to be appreciably different from ice Ih, due to the presence of four-membered rings of water molecules in its structure.

For each considered network, we have obtained the configurational entropy \( s_N \) in the limit \( T \to 0 \) for several system sizes \( N \), as described in Sect. II. In Fig. 2 we present \( s_N \) for the ice model on the two-dimensional square lattice. Open symbols represent the configurational entropy derived from our thermodynamic integration, as a function of the inverse system size. We find that \( s_N \) decreases for increasing system size \( N \), and in fact there is a linear dependence of \( s_N \) on \( 1/N \) for \( N \gtrsim 150 \), in the form

\[
s_N = s_{th} + \frac{a}{N},
\]

where \( a \) is a network-dependent parameter. For smaller system sizes (not shown in the figure), \( s_N \) deviates slightly from the linear behavior, becoming smaller than the value predicted from a linear fit for \( N > 150 \) sites. Extrapolation of the linear fit for \( 1/N \to 0 \) gives a value...
s_{th} = 0.43153(3), in good agreement with the exact solution for the square lattice found by Lieb\textsuperscript{18} by the transfer-matrix method: \( s_{th} = \frac{3}{4} \ln(4/3) = 0.43152 \). Information on the least-square fit carried out here is given in Table I.

An argument why the entropy per site should decrease for increasing size is the following. Let us call \( \Omega_N \) the number of configurations compatible with the ice rules for size \( N \). For two independent cells of size \( N \) the number of possible configurations would be \( \Omega_N^2 \). Then, putting both cells together to form a larger cell of size \( 2N \), we have \( \Omega_{2N} < \Omega_N^2 \), because one has to discard configurations that do not “match” correctly in the border between both \( N \)-size cells. The decrease of \( s_N \) for increasing \( N \) can thus be viewed as an effect of the boundary conditions. Assuming that \( s_N \) behaves regularly as a function of \( 1/N \) in the thermodynamic limit (\( 1/N \to 0 \)), one expects for large \( N \) a dependence of the form \( s_N = s_{th} + a/N + b/N^2 + \ldots \). This is in fact what we find from our simulations, with the parameter \( b \) so small that the linear dependence of \( s_N \) on \( 1/N \) is clearly consistent with the results at least for \( N > 150 \).

For the three-dimensional structure of ice Ih we also find a linear dependence of the configurational entropy on the inverse network size. This is shown in Fig. 3, where one observes that the slope (parameter \( a \) in Eq. \((11)\)) is larger than in the case of the two-dimensional lattice. The entropy in the thermodynamic limit is lower for ice Ih, as expected from earlier results for this ice structure\textsuperscript{10,11}. We find \( s_{th} = 0.41069(8) \). As already observed in the analytical result by Nagle\textsuperscript{10} and in the multicanonical simulations by Berg \textit{et al.}\textsuperscript{11} the configurational entropy is higher than the earlier estimate by Pauling. Moreover, our result is slightly higher than that of Nagle\textsuperscript{10}, who found \( s_{th} = 0.41002 \). Our result is a little higher than that found by Berg \textit{et al.}\textsuperscript{11}, although we consider that both data are compatible one with the other, given the error bars (see Table I).

Apart from ice Ih and cubic ice Ib, we are not aware of any direct calculation of the configurational entropy of H-disordered ice for other ice structures. To assess the influence of the ice network on the entropy, we have also considered the case of ice VI, where H-atoms are known to be disordered\textsuperscript{2,4,23}. In Fig. 4 we display our results for the configurational entropy of ice VI, as a function of the inverse network size. We find in this case a slope \( a = 3.44 \), much larger than for the square lattice and ice Ih. The extrapolation of \( s_N \) to infinite network size gives \( s_{th} = 0.42138(11) \), clearly higher than the value corresponding to ice Ih (a 2.6% larger). This result is remarkable, since up to now the only comparison in this respect concerned ice Ih with the Pauling estimate, being the entropy an 1.3% larger in the former case than in the latter. Now we see that for ice VI the configurational entropy for this H-disordered structure is 3.9% larger than the Pauling result.

We note the tendency of the entropy \( s_{th} \) to increase due to the presence of loops in the ice structure. In fact, the Pauling approximation neglects the presence of loops, as happens in the so-called Bethe lattice (also known as Cayley tree)\textsuperscript{16,17}. This gives a value \( s_{th} = 0.40547 \). For ice Ih, which contains six-membered rings of water molecules, the entropy is higher by an 1.3%, and it is still higher for the square lattice with four-membered rings (a
TABLE I: Entropy for the ice model on the square lattice, ice Ih, and ice VI, as derived from our Monte Carlo simulations. \( n_p \): number of data points employed in the linear fits; \( a \): slope of the linear fit as in Eq. (11); \( \rho \): correlation coefficient. For comparison, we give the entropy values obtained in earlier works.

| Ice   | Author      | \( n_p \) | \( a \)   | \( s_{th} \)  | \( W \)        | \( \rho \) |
|-------|-------------|----------|----------|----------------|----------------|--------|
| Square| This work   | 12       | 1.05(1)  | 0.43153(3)     | 1.53961(5)     | 0.9994 |
| Square| Lieb\cite{4} |          |          | 0.431523       | 1.539601       |        |
| Ih    | This work   | 9        | 1.84(2)  | 0.41069(8)     | 1.50786(12)    | 0.9994 |
| Ih    | Nagle\cite{10} |        |          | 0.41002(10)    | 1.50685(15)    |        |
| Ih    | Berg et al.\cite{11} |      |          | 0.4104(2)      | 1.5074(3)      |        |
| VI    | This work   | 9        | 3.44(6)  | 0.42138(11)    | 1.52406(16)    | 0.9990 |
| Generic| Pauling\cite{7} |      |          | 0.405465       | 1.5            |        |

6.4\% respect the Pauling approach). With this trend in mind, we could expect for ice VI a value of the entropy intermediate between those of ice Ih and the square lattice, as it contains four- and six-membered rings (apart from other larger loops).\cite{4,24,25} Similarly, for ice networks with larger ring sizes, one can expect a smaller configurational entropy for disordered hydrogen distributions, and thus closer to the Pauling result.

Some further comments on Table I are in order. In most papers dealing with the configurational entropy of ice, it is the parameter \( W \) which is given, instead of the entropy \( s_{th} \) itself. As we find directly \( s_{th} \) from our thermodynamic integration, we have calculated \( W \) in the different cases as \( W = \exp(s_{th}) \). Also the error bars \( \Delta W \) and \( \Delta s_{th} \) in the values of \( s_{th} \) and \( W \), respectively, are related by the expression \( \Delta W = W \Delta s_{th} \), as can be derived by differentiating the exponential function. Our error bars for \( s_{th} \) represent one standard deviation, as given by the least-square procedure employed to fit the data. In the result by Nagle\cite{10} the error bar was estimated by this author from an extrapolation of the series terms calculated in his analytical procedure. Note also that, although the result obtained by Pauling was intended to reproduce the residual entropy of ice Ih, it does not take into account the actual ice network, but only the four-fold coordination of the structure. For this reason we qualify it as “generic”. Concerning the results by Berg et al.\cite{11}, we note that these authors have recently\cite{26} given an entropy value for ice Ih slightly smaller than their earlier result, but both of them are compatible one with the other, taking into account the statistical error bars.

To avoid any possible confusion, we emphasize that the simple model employed in our calculations is not intended to reproduce any physical characteristic of ice (such as order/disorder transitions) further than calculating the entropy of an H distribution compatible with the ice rules. It implicitly assumes that the distribution of H atoms on the ice network has no long-range order, and only imposes strict fulfillment of the ice rules (short-range order) in the limit \( T \to 0 \). The configurational entropy obtained in this way is what has been traditionally called residual entropy of ice.\cite{2} With this in mind, we are not allowing for any violation of the third law of Thermodynamics.

In this context, it is generally accepted that the equilibrium ice phases in the low-temperature limit (at low and high pressures) display ordered proton structures, as expected from a vanishing of the entropy. Order-disorder transitions have been observed between several pairs of ice phases.\cite{4,24,25} These transitions are accompanied by orientational ordering of the water molecules, which implies a kinetically unfavorable reorganization of the H-bond network. In several cases, the transition from a disordered to an ordered phase only occurs after doping the sample, which seems to provide a mechanism favoring the rearrangement of the H-bond network.\cite{25,27,28} Thus, at low temperature ice Ih transforms into ice XI, an H-ordered phase, but this transition has never been observed in pure ice, only in doped materials at 72 K.\cite{27,29} Something similar happens for high-pressure phases, and ice VI in particular transforms into proton-ordered ice XV.\cite{2,24}

Given the entropy difference found here for real structures such as ice Ih and ice VI, a detailed knowledge of the configurational entropy for the different ice phases can be important for precise calculations of the phase diagram of water.\cite{30,31} As noted earlier for ice phases with
partial proton ordering.

IV. CONCLUSIONS

We have presented results for the configurational entropy of H-disordered ice structures, calculated by means of a thermodynamic integration. A simple model allowed us to derive the entropy corresponding to each structure. This procedure has turned out to be very precise, indicating that the associated error bars can be made very small without employing sophisticated methods, but only using standard statistical mechanics and numerical procedures.

For real ice structures, such as ice Ih and ice VI, we find a difference in configurational entropy of 2.6%. For ice VI we obtain an entropy value 3.9% higher than the Pauling estimate, as a consequence of its particular network connectivity. This method can be applied to other ice structures with hydrogen disorder, which will presumably give different values for the configurational entropy, due to differences in their network topology.

Acknowledgments

This work was supported by Dirección General de Investigación Científica y Técnica (Spain) through Grant FIS2012-31713 and by Comunidad Autónoma de Madrid through Program MODELICO-CM/S2009ESP-1691.

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