Boundary conditions and the residual entropy of ice systems

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In this work we address the classical statistical mechanical problem of calculating the residual entropy of ice models. The numerical work found in the literature is usually based on extrapolating to infinite-size results obtained for finite-size systems with periodic boundary conditions. In this work we investigate how boundary conditions affect the calculation of the residual entropy for square, cubic, and hexagonal lattices using periodic, antiperiodic, and open boundary conditions. We show that periodic boundary conditions lead to noticeable oscillations in the entropy as a function of lattice size, and we calculate in open finite systems the contribution to the entropy from the open boundary. For our calculations we introduce a variation on multicanonical simulation methods that directly calculate the number of states in the ground state without the need of a Hamiltonian.

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I. INTRODUCTION

Ice-type models, together with the Ising and dimer models, are classical problems in statistical mechanics of which exact solutions are known. However, for the ice model, like in the case of the Ising model, while an exact solution has been found for two-dimensional systems, the three-dimensional case remains unsolved [1]. There are several realizations of ice-type models in nature, such as water ice [2], potassium dihydrogen phosphate (often referred to as KDP) which has ferroelectric order at low temperatures [3], and spin-ice materials [4].

A. Water ice and the ice model

The history of ice models begins with water ice. The structure of ice was subject to early x-ray studies: in 1922 Bragg had already correctly identified the structure of the oxygen sites [5], but proposed a ionic model where the hydrogen ions occupied positions midway between the oxygen sites. A qualitative change in the understanding of the structure and challenges of water ice came from the introduction of the *Bernal and Fowler rules*, or *ice rules*, in 1933 [6] that put constraints on the positions of hydrogen atoms but do not fully determine them. Pauling, in 1935, postulated that the hydrogen atoms in the structure are disordered even at temperatures well below the melting point [7].

The Pauling model was put to the test in the experiments of Giauque and Stout [8] and, given the simplicity of the assumptions, gave a remarkably good agreement. Four assumptions are given explicitly. The first three are a statement of the ice rules: (i) the water molecule retains its structure, (ii) the orientation of the molecules is such that two hydrogen atoms form hydrogen bonds with two of the four neighboring oxygen atoms, and (iii) only one hydrogen lies along each oxygen-oxygen axis. The fourth assumption states that all the configurations satisfying the preceding rules are equally probable under ordinary conditions. The fifth (unstated) assumption Pauling made is that correlations are negligible in the ground state. In correcting this last assumption lays the basis of all further work on the subject.

Pauling estimates the residual number of microestates, W_{Pauling}, by a simple reasoning: assumptions 1 to 4 mean that for a given water molecule there are six possible equivalent configurations. Assuming no correlations, these have a 1/4 probability of being matched with its neighbors. This gives

$$W_{\text{Pauling}} = \left(\tfrac{6}{4}\right)^N = \left(\tfrac{3}{2}\right)^N. \tag{1}$$

The entropy per site is then

$$\frac{s_{\text{Pauling}}}{k} = \frac{S_{\text{Pauling}}}{kN} = \frac{\log W_{\text{Pauling}}}{N} \approx 0.4054, \tag{2}$$

where N is the number of sites and k is Boltzmann's constant, which will be taken to be 1 in the rest of the article. This compares very well with the currently accepted experimental value of 0.410(20) [2].

In addressing the experimental question of the origin of the excess entropy in water ice, Pauling introduced the first example of a class of vertex models, the *ice-type models* or *six-vertex models*. In general, an ice-type model is a lattice model, defined on lattices of coordination number 4. The state of the system is defined in terms of the bonds between the vertices, which can take two values, indicated, for example, by inward or outward pointing arrows. The constraint for the ground state is local in nature and prescribes that the only valid configurations are those where there are two inward and two outward pointing arrows in each vertex. This gives six possible configurations for each vertex (see Fig. 1). In Pauling's model, the vertices are the centers of the water molecules, which are connected to four neighbors, and the two states of the bonds correspond to the state of the hydrogen: either covalently bonded or making a *hydrogen bond*.

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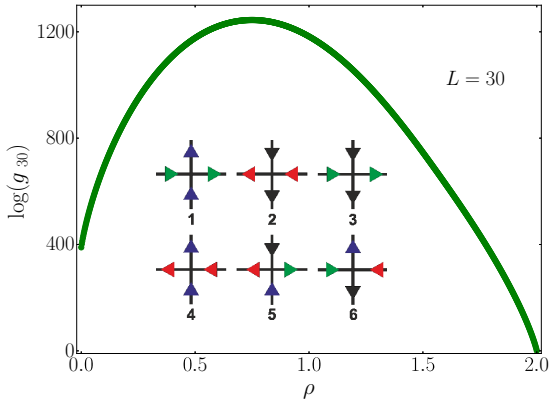

FIG. 1. Logarithm of the density of states, $\log(g)$, as a function of ρ as obtained from WL simulations on a 30×30 square lattice. Inset: A schematic view of the six possible *ice* configurations of a vertex.

Water ice is then the eponymous example where an ice model is realized in a range of temperatures. A more recent example, from the realm of magnetism, is the aptly called "spin-ice" materials (for a review see, e.g., Refs. [9,10]). These oxide materials, such as $Dy_2Ti_2O_7$ or $Ho_2Ti_2O_7$, can be grown in a single-crystalline form. The magnetic ions Ho^{3+} or Dy^{3+} (Ti^{4+} is nonmagnetic) form a pyrochlore lattice of corner-linked tetrahedra. The median lattice—connecting the center-points of the tetrahedra—is a diamond lattice equivalent to the I_c phase of water ice.

B. Improvements

Onsager and Dupuis give a proof that Pauling's calculation for the entropy of an ice model gives a lower bound [11]. The proof is valid for any ice structure with coordination number 4. Further refinements on Pauling's estimate depend on the exact topology and dimensionality of the lattice [12–14]; in all cases, the correction to Pauling estimate is below 1%. Currently, the best estimate for the entropy of the three-dimensional ice comes from the work of Nagle in 1966 [15].

Nagle developed a controlled series expansion for the square, cubic, and hexagonal cases in terms of cycle corrections:

$$W = \left(\frac{3}{2}\right)^N \left[1 + \sum_n \frac{\phi_n}{3^n}\right]^N. \tag{3}$$

In the case of three-dimensional lattices, cubic and hexagonal, it gives explicit values for the coefficients in the expansion, ϕ_n, up to the cycle of order 14, and estimates a lower and upper bound for the rest of the terms. The terms in the expansion for hexagonal and cubic ice coincide up to $n = 10$, after which the prefactors for the hexagonal ice become consistently larger. This in agreement with a proof given by Onsager that $W_{\text{hex}} \geqslant W_{\text{cubic}}$ (see footnote 11 of Ref. [15]). In the following we find it easier to speak in terms of $w = W^{1/N}$. The final estimate, using the upper and lower remainders, coincides within the error for cubic and hexagonal lattices and is bounded by

$$1.5067 < w < 1.5070,$$

that is, $w_{\text{Nagle}} = 1.506\,85(15)$.

Nagle also provides a very good estimate of the entropy for square ice; however, in this case, an exact solution was obtained by Lieb in 1967 using the transfer-matrix method [16,17]. The exact result for square ice gives

$$w_{\text{Lieb}} = \left(\tfrac{4}{3}\right)^{\frac{3}{2}} \approx 1.5396, \tag{4}$$

considerably higher than the three-dimensional counterparts.

C. Finite-size systems

All previous calculations assume an infinite size system—a sample in the thermodynamic limit. In two papers published in 1966 and 1967, Suzuki investigates the entropy of a finite system where entropy contribution from the surfaces is non-negligible [18,19]. He gives three reasons for his analysis: (i) one needs to have a concrete measure of the surface contribution in order to be able to decide what constitutes the thermodynamic limit; (ii) the surface effect may be non-negligible for very small crystals, such as crystals at the early stage of growth; and (iii) surface effects are important when discussing surface properties.

According to Suzuki the entropy of an ice crystal consisting of N sites and having f surface bonds can be written as

$$S/k = N\left(\log\frac{3}{2} + \log q_\infty\right) + \frac{f}{2}(\log 2 - \delta). \tag{5}$$

The first term, the bulk entropy, is expressed as Pauling entropy plus an additional term to account for corrections due to correlations, and q_∞ is a non-negative number depending on the structure of the lattice. The second term, the surface entropy, is expressed as a difference between the entropy of completely free bonds and a negative correlation term, δ, which is a number smaller than $\ln 2$ and dependent on both the shape and the size of the crystal.

Suzuki calculates q_∞ in the form of a series expansion, for both three-dimensional and square ice, with results compatible with Nagle, and for the square lattice shows that $\delta < \log(4/3)$. Additionally, he presents numerical calculations of the terms in the series. These are rather limited, due to the constraints given by the calculation power available at the time.

D. Numerical work

With the advent of easily available high-performance computing there have been several efforts to independently calculate the residual entropy of ice using a variety of methods. In 2004, Isakov and collaborators [20], in the context of spin-ice systems (i.e., on a cubic lattice), calculated from the integration of energy and magnetization data obtained by loop Monte Carlo simulations $W_I = 1.5071(3)$, very close to Nagle's result. In 2007, Berg *et al.* [21] used multicanonical simulations in two simple nearest-neighbor ice models in three-dimensional hexagonal lattices, the six-state H_2O molecule model and the two-state H-bond model, to calculate the residual entropy. Their calculation is within 0.035% of Nagle's estimate. Singh and Oitmaa in 2012, used a numerical linked cluster expansion to calculate the entropy of the cubic lattice [22]. This method is closely related to the one used by

Nagle and gives compatible results. Herrero and Ramírez in 2013 integrated the specific heat in Monte Carlo simulations of ice models in two and three dimensions and gave values for the residual entropy of two-dimensional ice and hexagonal ice (both in accordance to previous estimates) and for ice *V I* [23]. In a subsequent work [24] they studied the entropy of several ice polymorphs and correlated the corrections with the mean loop size of the different structures. In a work published in 2014 Kolafa [25] also calculated the entropy from thermodynamic integration. In this case the extrapolation is based on a very careful analysis of finite-size effects and corrections due to the presence of Bjerrum defects and therefore is more trustworthy than previous works. This being said, there are disagreements with other work, such as Ref. [21], which remains unclear. Finally, in 2016, Ferreyra *et al.* [26], used Wang-Landau (WL) simulations in nearest-neighbor spin-ice to give an estimate of the residual density of states, which is also in accordance with Nagle's estimate.

In all these cases the procedure used to determine the thermodynamic residual entropy is by extrapolating the results obtained for finite lattices of increasing size subject to periodic boundary conditions. As we show in this work, this is not necessarily a safe procedure. Even though the ice state is disordered it still has long-range correlations [27], which means that boundary conditions affect the number of possible states of a system, which in the case of small systems can be a significant part of the total number of states. We show that boundary conditions can lead to noticeable oscillations in the entropy as a function of lattice size when alternating between even- and odd-sized lattices. This oscillation has been missed in Ref. [23] since only even-sized lattices were investigated.

This article develops as follows. In Sec. II we discuss the numerical method we introduce to determine the residual entropy, a variation of the Wang-Landau Monte Carlo method [28]. In the first part of Sec. III we discuss our results for finite-size square lattices under different boundary conditions and provide different estimates of the thermodynamic residual entropy as well as the surface entropy term for semi-infinite systems with open boundaries. In the second part of Sec. III we discuss our results on cubic and hexagonal latices.

II. METHODS

In this work we make a direct numerical calculation of the number of states obeying the ice rule for lattices of different shapes and sizes and with different boundary conditions. For this we use a variation of the Wang-Landau method where the density of states of a system, g, is calculated in the absence of any Hamiltonian. A lattice is defined with N_v vertices and with the coordination number 4 (in these work we use square, cubic, and hexagonal lattices), and the state of each of the $N = 2N_v$ bonds, i, is characterized by a number, $v_i = \pm 1$, corresponding to an inward or outward pointing arrow (a covalent bond or a hydrogen bond). The state of the vertex is characterized by the sum of the states of its bonds, and the global state of a given configuration is labeled by a number, ρ, defined as

$$\rho = \frac{1}{N_v} \sum_n \left| \sum_{\square} v_i \right|, \tag{6}$$

where $\square$ indicates a sum over bonds in a vertex, and the sum over n runs over all vertices. With this definition, ρ can take values from 0 to 2. The states obeying the ice rules correspond to $\rho = 0$, and there are only two possible configurations that give $\rho = 2$.

The algorithm mimics the usual Wang-Landau procedure [28,29], albeit, without a Hamiltonian.

(i) The initial density of states is fixed uniformly as $g(\rho) = 1$. An initial (random) configuration is proposed and is labeled by ρ_0.

(ii) A new configuration with $\rho = \rho_1$ is determined from the previous one by changing the state of a bond taken at random. The probability of accepting this configuration is given by

$$p(\rho_0 \to \rho_1) = \min\left(\frac{g(\rho_0)}{g(\rho_1)}, 1\right).$$

(iii) At each step, the density of states of the resulting configuration, $\rho_F = \rho_{0,1}$, is modified by a factor f: $g(\rho_F) \to f g(\rho_F)$, and a histogram is computed. Initially a large value is chosed for f, and it is reduced as the algorithm progresses.

(iv) Steps (ii) and (iii) are repeated until the histogram becomes *flat* according to some criterion. After this, f is reduced by a factor, the histogram is reset, and the process is repeated. Usually, the criterion used for flatness is that every entry should not be smaller than a percentage of the average histogram.

(v) Once f falls below a given value, f_{final}, the algorithm stops and the final result is a relative density of states, $g(\rho)$. f_{final} is a measure of the precision achieved for the final density of states. In our case we have used $f_{\text{final}} = \exp(10^{-9})$.

The manner in which the factor f is reduced during the process conditions the speed of convergence. We have chosen for our simulations a variation on the method proposed by Belardinelli and Pereyra [30], where the factor is eventually scaled as the inverse of the Monte Carlo time.

There are two alternative ways of normalizing $g(\rho)$: (i) by fixing the sum over all states, $\sum_\rho g(\rho) = 2^N$, and (ii) by imposing the condition $g(2) = 2$. We have used both and have taken any small difference between normalizations into account as part of the error in determining $w = g(0)$. Additionally, all quoted values of w correspond to averages over values determined from independent simulations started with different initial random configurations.

It is known that the Wang-Landau algorithm and its variants suffer from the so-called "edge" effects: that the values at the extreme values of the index parameter (ρ in our case) suffer from the fact that there are visited less often. This is particularly important here since $g(0)$ sits at one of the extremes. To avoid this we have implemented the usual windowing technique where for certain runs the parameter is kept within a distance from the edge by forbidding moves that take the system outside a given interval of ρ [31].

III. RESULTS

A. Square lattice

To determine the density of states of the ground state of the system we calculate the whole distribution of states as a

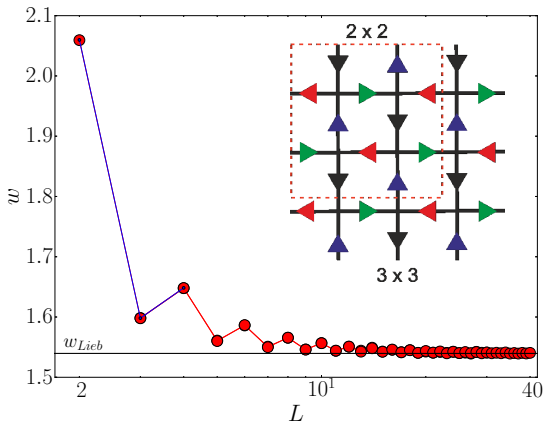

FIG. 2. w as a function of the lattice size L for different square lattices with periodic boundary conditions (PBCs). The blue circles and lines correspond to the exact calculation for small lattices. The exact value for infinite lattices, w_{Lieb}, is indicated by a black line. The inset shows an ice configuration on a square lattice: while PBCs cannot be imposed on the 3×3 lattice, if the system is reduced to 2×2 the configuration satisfies the constraints of PBCs.

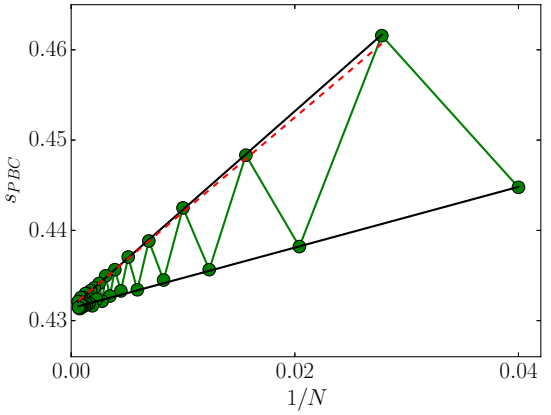

FIG. 3. The residual entropy density under periodic boundary conditions, s_{PBC}, as a function of the inverse number of sites, $1/N$, for lattices with $L > 5$. The black lines correspond to fits to even and odd lattice sizes. The red dashed line is the one determined in Herrero and Ramírez [23] by integrating simulated specific heat.

function of a parameter, ρ, that singles out the ground state. Our choice of such a parameter, defined in Eq. (6), is the average of the absolute value of the local sum of the states of the bonds of a given vertex. In this case, ρ ranges from 0 to 2, and its value quantifies the degree of departure from a perfect ice state. Figure 1 shows a typical example of the logarithm of the density of states for a finite system, g_L, as a function of ρ for a square lattice with $L = 30$ with periodic boundary conditions. The two possible normalizations for these data are indistinguishable on the scale of this plot. By repeating this analysis over different lattice sizes we can determine $w(L) \equiv g_L(0)$. This is shown in Fig. 2 (red circles) using a logarithmic scale. For small lattices, $L \leqslant 4$, it is still possible to calculate this number exactly within reasonable computational times. These exact calculations are shown as blue circles in the same figure and coincide perfectly with those determined by the WL method. $w(L)$ tends rapidly towards an asymptotical value, which coincides with the exact value for an infinite lattice determined by Lieb [16,17]. The approach towards the asymptotic limit is characterized by a decay with noticeable oscillation between lattices of odd and even sizes.

The origin of the decay are the long-range correlations present in the ice ground state. Despite the fact that the ice rule is local in nature, and one would naively expect exponentially decaying correlations, they are instead power-law decaying, with the spatial dependence of dipole-dipole interactions [27,32,33]. This fact is seldom taken into account, and the dependence has been, for example, wrongly attributed to border effects (see Refs. [23,24]). In simple terms, if the lattice size is smaller than the mean correlation length, the entropy density $s = S/N$ is being overestimated, since the size of the system can be extended, extending N without any increase in the extensive entropy S.

The oscillations between even and odd lattice sizes are a further indication of the presence of correlations. These are a consequence of the restrictions set on long-range ordered states by boundary conditions. Imposing periodic boundary conditions along the x and y axes of a two-dimensional square lattice is equivalent to folding and connecting its borders in order to construct a three-dimensional torus. This introduces a topological constraint: paths along the x and y axes become irreducible closed loops. In lattices of $L \times L$ the minimal number of elements in these loops is L. This constraint frustrates some bond arrangements in lattices with odd values of L. While this effect is negligible in the thermodynamic limit, it has a strong effect in the residual entropy of small lattices. For example, a $q = \pi$ *antiferromagnetic* arrangement in the s_i (see inset of Fig. 2) satisfies the ice rule, but is only possible if L is even. For small L, these types of restrictions suppress a sizable number of configurations.

A procedure usually found in the literature to determine $s_0(\infty)$ is to extrapolate the behavior of the entropy density, $s = S/N = \log w$, as a function of the inverse number of sites $1/N$ (see, for example, Fig. 2 in Ref. [21] for a hexagonal lattice or Fig. 2 in Ref. [23] for a linear extrapolation of the square lattice). Figure 3 shows s vs $1/N$ for our data on the square lattice with PBCs (green circles). Clearly a linear fit to the whole data is meaningless. However, if one performs a linear fit, $s = s_0 + m/N$, to separate odd and even lattice sizes, shown as black lines in the figures, it gives $m^o = 0.336(8)$ and $m^e = 1.09(8)$, and $s_0^o = 0.43150(9)$ and $s_0^e = 0.43149(9)$, for odd and even lattices, respectively. That is, the extrapolated residual entropies are unaffected, within the error, by the conditions imposed by the lattice and compare well with the exact result $s_{\text{Lieb}} = \log w_{\text{Lieb}} = 0.431\,52\ldots$ obtained by Lieb [16]. This independence explains why the fit from Ref. [23], performed to the entropy determined by integration of a simulated specific heat from lattices with PBCs, has given the correct result for s_0 even though it was restricted to even lattices only. This fit, from Herrero and Ramírez [23], is shown in the figure as a red dashed line. The odd and even data do not each follow an exact linear dependence on $1/N$, so there is some arbitrariness in the choice of the smallest lattice used in the fit. Hence, the error in the magnitudes has a contribution from the variation that

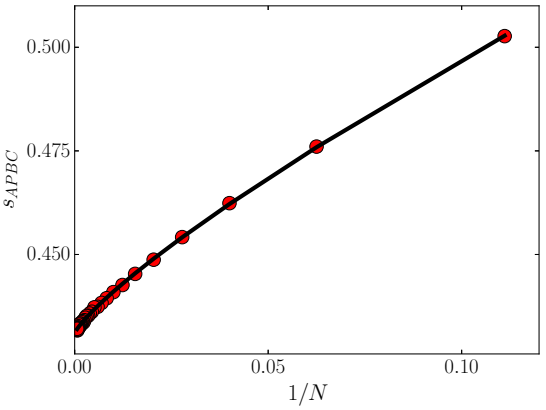

FIG. 4. The entropy density under antiperiodic bounday conditions, s_{APBC}, as a function of the inverse number of sites, $1/N$. The black line corresponds to power law fit $s = s_0(\infty) + A(1/N)^{\alpha}$, with $s_0 = 0.4313(3)$, $A = 0.431\,26(4)$, and $\alpha = 0.8157(3)$

occurs when the linear fit is done within different ranges of lattice sizes.

To explore with more detail the contribution of boundary conditions to the determination of the residual entropy, we performed the simulation under different constraints. As discussed in the previous paragraph, some *ice* states form *antiferromagnetic* structures of sorts and thus seem better suited to antiperiodic boundary conditions (APBCs), that is, boundary conditions where the state of the vertex is reversed when connected to the other side: $v_{L+1} = -v_1$, in geometrical terms this is equivalent to a Möbius strip or a Klein bottle rather than a ring or a torus. Figure 4 shows the residual entropy density s determined under APBCs (red dots). As expected, the oscillations have vanished, but, as the comparison in Fig. 5 shows, some states are still being suppressed by the boundary conditions (only noticeable for small lattice sizes). The black line in Fig. 4 corresponds to a power-law fit,

$$s = s_0(\infty) + A(1/N)^{\alpha}, \tag{7}$$

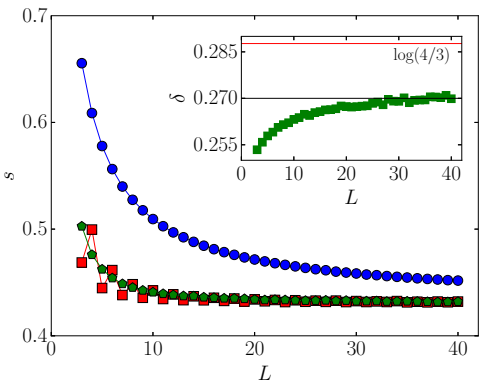

FIG. 5. A comparison between the residual entropy density under periodic (red squares), antiperiodic (green pentagons), and open (blue circles) boundary conditions as a function of lattice size for square ice. The inset shows the open boundary contribution to the entropy δ as a function of lattice size [see Eq. (8) and text for details].

with $s_0 = 0.4313(3)$, $A = 0.431\,26(4)$, and $\alpha = 0.8157(3)$. In this case, the extracted $s_0(\infty)$ also matches the exact result, and the error in the determination has been greatly reduced.

In Fig. 5 we have plotted for comparison the residual entropy for the square lattice under three different boundary conditions: periodic, antiperiodic, and open. As mentioned before, both the periodic and antiperiodic cases extrapolate to the same value for $L \to \infty$, and while the antiperiodic conditions are better suited for hosting the ground state, which translates into a suppression of the oscillations, there are still some missing states noticeable for low L values. The residual entropy for open boundary conditions (OBCs) is, as expected, considerably larger for small system sizes, where the boundary contribution is important. A power-law fit for the OBC data gives $s_0 = 0.430(3)$, $A = 0.694(4)$, and $\alpha = 0.470(3)$. Here the power-law dependence is dominated by the open boundary term, which goes like $L = N^{1/2}$, and the big error bars come from the variation in the parameters depending on the range of L used to do the fit. The data are better analyzed in the framework of the work by Suzuki discussed in Sec. I. We can rewrite Suzuki's expression to read

$$s_{\mathrm{OBC}}(L) = s(L) + n_s(L)[\log 2 - \delta(L)], \tag{8}$$

where $s(L)$ is the bulk entropy, $n_s(L) = f(L)/2N$ with f being the number of surface vertices, and δ is Suzuki's parameter that takes into account the reduction in entropy to the surface vertices due to correlations. f can be determined exactly for each lattice size. A fit to this expression gives a limiting value for s identical to previous determinations and a limiting value for $\delta = 0.270(3)$ (see inset of Fig. 5), which is close to the upper limit calculated by Suzuki of $\log(4/3) \approx 0.287$.

B. Three-dimensional lattices

We applied this same simulation procedure and analysis to cubic (ice Ic) and hexagonal (ice Ih) ice. In both these cases, periodic and antiperiodic boundary conditions show no appreciable difference. Figure 6 shows w as a function of the number of vertices, N, for both cubic (blue circles) and hexagonal (red squares) lattices. This is the three-dimensional equivalent of Fig. 2; the reason for using N instead of L is that, due to the shape of the two unit cells, hexagonal and cubic lattices of size L^3 have different numbers of vertices. As it can be seen in the figure even for PBCs no oscillations are noticeable in the data. Like in the two-dimensional case, the data rapidly tend to an asymptotic value which matches well Nagle's calculation [15] (shown in the figure as a black horizontal line). A fit of the cubic data to an expression of the type of Eq. (7) gives $w_0^c(\infty) = 1.506\,94(12)$, $A^c = 1.565(9)$, and $\alpha^c = 0.885(3)$. This is shown in the inset as a solid black line. An equivalent fit to the hexagonal data, shown in the figure as a dotted line, gives $w_0^h(\infty) = 1.5070(9)$, $A^h = 2.010(9)$, and $\alpha^h = 0.920(3)$. Both $w_0^c(\infty)$ and $w_0^h(\infty)$ compare well with Nagle's value $w_{\mathrm{Nagle}} = 1.506\,85(15)$, but offer no significant improvement in accuracy. We have mentioned before that a proof exists by Onsager that shows that the residual entropy of the hexagonal lattice is higher than the corresponding entropy for the cubic lattice. However, this difference is extremely small: in Nagle's calculation the first difference shows in the 12th term of the series expansion of Eq. (3), where $\phi_n = 111$

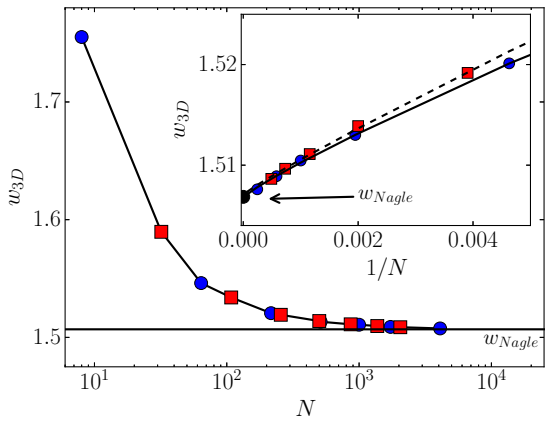

FIG. 6. w as a function of the number of vertices, N, for three-dimensional lattices: red squares correspond to hexagonal lattices and blue circles to cubic ones. The value calculated by Nagle [15] is shown as a black horizontal line. The inset shows the same data as a function of the inverse number of vertices, $1/N$. The solid (dotted) line is a fit to the cubic (hexagonal) data using Eq. (7) (see text). The value calculated by Nagle for an infinite lattice is shown as a black dot.

for the cubic lattice and $\phi_n = 114$ for the hexagonal case. In our results, $w(L)$ is consistently higher for the hexagonal lattice, and although the extrapolated value $w_0^h(\infty)$ coincides with the cubic value $w_0^c(\infty)$ within the error, which is higher than the first difference calculated by Nagle, it should be noted that the absolute error includes systematic contributions that make the relative error smaller. Finally, our value for $w_0^h(\infty)$ coincides well with the estimate by Berg *et al.* [21] for two ice models in a hexagonal lattice.

IV. CONCLUSIONS

In this work we study the ground state of icelike systems and the influence of boundary conditions on the determination of their residual entropy. To do this we introduce a variation on the Wang-Landau algorithm that does not require a Hamiltonian. Due to its simplicity, this technique allows for accurate calculations of the density of states of the ground state at a fraction of the computational cost of usual methods (such as the calculation of the specific heat and ulterior numerical integration) and is easily parallizable. We have used it to calculate the residual entropy for the ice model in the square, cubic, and hexagonal lattices and to investigate in detail the effect of periodic, antiperiodic, and open boundary conditions. We show that, when periodic boundary conditions are imposed on square ice, correlations of the ice-state lead to noticeable oscillations in the entropy as a function of lattice size. These can be substantially reduced by the use of antiperiodic boundary conditions. The existence of these oscillations are a consequence of the nature of the ground state, which despite being constructed from local rules shows dipolarlike correlations [27]. We also calculated the residual entropy of open square systems and determined the contribution to the entropy from the open boundary. We have shown that for large systems this contribution tends to a limiting value $(\log 2 - \delta)$ with $\delta = 0.270(3)$, which is below the upper limit estimated by Suzuki. For cubic and hexagonal lattices we show that the oscillations are much less pronounced. The extrapolation of our results to the thermodynamic limit for the different boundary conditions tends to the same limit, w, in coincidence with previous investigations by Tavares and co-workers [34,35]. Our calculation of w for these lattices coincides well with Nagle's result within the error. Although the absolute errors are comparable with other calculations, this is not true for the relative error, and we determine the residual entropy in the hexagonal lattice to be higher than the corresponding one in the cubic lattice, as predicted by Onsager.

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