Thermodynamics of two lattice ice models in three dimensions

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In a recent paper we introduced two Potts-like models in three dimensions, which share the following properties: (A) One of the ice rules is always fulfilled (in particular also at infinite temperature, $\beta = 0$). (B) Both ice rules hold for groundstate configurations. This allowed for an efficient calculation of the residual entropy of ice I (ordinary ice) by means of multicanonical simulations. Here we present the thermodynamics of these models. Despite their similarities with Potts models, no sign of a disorder-order phase transition is found.

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I. INTRODUCTION

By experimental discovery<sup>1</sup> it was found that ice I (ordinary ice) has in the zero temperature limit a residual entropy $S/N = k \ln(W_1) > 0$ where $N$ is the number of molecules and $W_1$ the number of configurations per molecule. Subsequently Linus Pauling<sup>2</sup> based the estimate $W_{\text{Pauling}}^1 = 3/2$ on the ice rules:

1. There is one hydrogen atom on each bond (then called hydrogen bond).

2. There are two hydrogen atoms near each oxygen atom (these three atoms constitute a water molecule).

Pauling’s combinatorial estimate turned out to be in excellent agreement with subsequent refined experimental measurements<sup>3</sup>. This may be a reason why it took 25 years until Onsager and Dupuis<sup>4</sup> pointed out that $W_1 = 1.5$ is only a lower bound. Subsequently Nagle<sup>5</sup> used a series expansion method to derive the estimate $W_{\text{Nagle}}^1 = 1.50685 (15)$.

In<sup>6</sup> we introduced two simple models with nearest neighbor interactions on 3D hexagonal lattices, which allow one to calculate the residual entropy of ice I by means of multicanonical (MUCA)<sup>7, 8, 9</sup> simulations. The hexagonal lattice structure is depicted in Fig. 1. In the first model, called 6-state (6-s) H$_2$O molecule model, ice rule (2) is always enforced and we allow for six distinct orientations of each H$_2$O molecule. Its energy is defined by

$$E = - \sum_b h(b, s_b^1, s_b^2).$$

(1)

Here, the sum is over all bonds $b$ of the lattice ($s_b^1$ and $s_b^2$ indicate the dependence on the states of the two H$_2$O molecules, which are connected by the bond) and

$$h(b, s_b^1, s_b^2) = \begin{cases} 1 \text{ for a hydrogen bond,} \\ 0 \text{ otherwise.} \end{cases}$$

(2)

In the second model, called 2-state (2-s) H-bond model, ice rule (1) is always enforced and we allow for two positions of each hydrogen nucleus on a bond. The energy is defined by

$$E = - \sum_s f(s, b_s^1, b_s^2, b_s^3, b_s^4),$$

(3)

where the sum is over all sites (oxygen atoms) of the lattice and $f$ is given by

$$f(s, b_s^1, b_s^2, b_s^3, b_s^4) =$$

(4)
The groundstates of either model fulfill both ice rules.

In this paper we use units with \( k = 1 \) for the Boltzmann constant, i.e., \( \beta = 1/T \). At \( \beta = 0 \) the number of configurations is \( 6^N \) for the 6-s model and \( 2^{2N} \) for the 2-s model. This sets the normalization, which can then be connected by a MUCA simulation of the type \( S \) to \( \beta \) values large enough so that groundstates get sampled. In reasonably good agreement with Nagle the estimate \( W_{\text{MUCA}} = 1.50738 \) (16) was obtained in [6]. In Ref. [11] these calculation were extended to partially ordered ice for which corrections to groundstate entropy estimates by Pauling’s method were previously not available.

A considerable literature \([12, 13, 14, 15, 16, 17, 18, 19]\) exists on lattice ice models. Most of these papers deal with 2D square ice. An extension to 3D is considered in \([13, 14, 19]\). All these models have in common that they enforce both ice rules generically and not just for the groundstates. So, they are non-trivial at all coupling constant values, while it is precisely the triviality of our ice models at \( \beta = 0 \), which allows one to set the normalization for the entropy and free energy, and they share with certain spin models \([20]\) that the residual entropy of their groundstates violates the third law of thermodynamics.

Superficially our models are similar to \( q \)-state Potts models \([21]\) with \( q = 6 \) and the Ising case \( q = 2 \), which have first \( (q = 6) \) and second \( (q = 2) \) order phase transitions in 2D as well as in 3D. In contrast to that, we provide numerical evidence in this paper that our ice models do not undergo a disorder-order phase transition at any finite value of \( \beta \). Our results are presented in section [11].

Summary and conclusions follow in section [III]

II. SIMULATION RESULTS

TABLE I: Overview of our multicanonical simulations. Here, \( n_x, n_y, n_z \) are the number of lattice sites along the \( x, y, z \) axes, and \( N = n_x n_y n_z \).

| \( n_x \) | \( n_y \) | \( n_z \) | \( N \) | cycles (6-s) | cycles (2-s) |
|-------|-------|-------|-----|-------------|-------------|
| 4     | 8     | 4     | 128 | 37828       | 141825      |
| 4     | 12    | 6     | 288 | 9455        | 33205       |
| 5     | 12    | 6     | 360 | 4891        | 21621       |
| 6     | 12    | 8     | 576 | 653         | 11479       |
| 7     | 16    | 8     | 896 | 412         | 6452        |
| 8     | 20    | 10    | 1600| 215         | 1587        |
| 10    | 24    | 12    | 2880| 1133        | 506         |

Using periodic boundary conditions (BCs), our simulations are based on a lattice construction \([22]\) similar to that set up for Potts models in \([9]\). The lattice sizes used are compiled in table [11]. The lattice contains then \( N = n_x n_y n_z \) sites, where \( n_x, n_y, n_z \) are the number of sites along the \( x, y, z \) axes, respectively. Periodic BCs restrict the allowed values of \( n_x, n_y, n_z \) to \( n_x = 1, 2, 3, \ldots \), \( n_y = 4, 8, 12, \ldots \), and \( n_z = 2, 4, 6, \ldots \). Otherwise the geometry does not close properly.

As proposed in \([23]\) we used a Wang-Landau \([24]\) recursion for determining the MUCA weights and performed subsequent MUCA data production with fixed weights. With one exception we used \( 32 \times (20 \times 10^6) \) sweeps per lattice for data production. For the largest lattice of the 6-s model we produced a ten times larger statistics. Table [11] listed for each lattice size and model the number of cycling events from the average disordered energy \( E_0 \) at \( \beta = 0 \) to the groundstate energy \( E_g \) and back,

\[
E_0 \leftrightarrow E_g, \tag{5}
\]

as recorded during the production part of the run. From the energy functions \([11] \) and \([3]\) one finds \( E_0 = -N \) for the 6-s model (there are two hydrogen atoms per oxygen and the probability to form a hydrogen bond is \( 1/2 \)), \( E_0 = -1.25 N \) for the 2-s model (at one site there are 16 arrangements of hydrogen atoms with average energy contribution \( -[2 \times 0 + 8 \times 1 + 6 \times 2]/16 = -1.25 \)), and \( E_g = -2N \) for both models. In the following we restrict the \( \beta \) range of our figures to \( 0 \leq \beta \leq 5 \), which is large enough to sample groundstates in sufficient numbers so that extrapolations down to temperature \( T = 0 \) become controlled.

In Fig. 2 we show the average energy per site, \( E/N \), from the MUCA simulations of our two models as obtained by the reweighting procedure \([9]\) (note that we use \( E \) for the energy of configuration as well as for average values over configuration energies and assume the reader knows to distinguish them). Obviously there are almost no finite size effects, because the curves from all lattice sizes fall within small statistical errors, which are
FIG. 3: Specific heat per site for the 6-s and 2-s models.

not visible on the scale of this figure, on top of one another.

TABLE II: Some specific heat data $C/N$ with error bars (in parenthesis) for the $N = 2880$ lattice.

| $\beta$ | 6-s model | 2-s model |
|---------|-----------|-----------|
| 0.5     | 0.1175119 (77) | 0.093780 (17) |
| 1.5     | 0.673681 (71)  | 0.48331 (11)  |
| 2.5     | 0.87873 (19)   | 0.59913 (22)  |
| 3.5     | 0.69110 (35)   | 0.46235 (42)  |
| 4.5     | 0.43066 (45)   | 0.28637 (61)  |

The specific heat per site, $C/N$, is calculated via the fluctuation-dissipation theorem,

$$C = \frac{dE}{dT} = -\beta^2 \frac{dE}{d\beta} = \beta^2 \left( \langle E^2 \rangle - \langle E \rangle^2 \right),$$  \hspace{1cm} (6)

and plotted in Fig. 3. Finite size corrections are now visible for the smallest, $N = 128$, lattice. For the other lattices the curves fall within error bars on top of one another. Error bars were calculated with respect to 32 jackknife bins and are at some $\beta$ values included for our largest, $N = 2880$, lattice. Some data for these points are given in Table II. Note that the $N = 2880$ data for the 6-s model rely on a ten times large statistics than those for the 2-s model, while the error bars are only slightly smaller. As noticed before [6], the simulations of the 2-s model are more efficient for determining the groundstate entropy than simulations of the 6-s model. Fluctuations increase with lattice size, so that it is more difficult to obtain accurate results on large than on small lattices.

We want to contrast Fig. 3 with specific heat results for the 6-state and 2-state Potts models on $L^D$ lattices. Immediately, one notices that it is not entirely clear whether this comparison should be done in 2D or 3D. While the space dimension in which our ice models are embedded is clearly 3D, each site is connected through links with four neighboring sites, which is the Potts model situation in 2D. The 2D and 3D Ising models are well known for their second order phase transitions. The specific heat is logarithmically divergent in 2D [25] and has a critical exponent $\alpha \approx 0.1$ in 3D (see [26] for a review). The 2D and 3D 6-state Potts models have first order transitions with a larger latent heat per spin in 3D than in 2D (in the normalization of $\Delta E/N = 0.40292828$ in 2D [28] and $\Delta E/N = 2.36442 \pm 0.00017$ in 3D [29]).

For second order transitions the maximum of the specific heat diverges $\sim \ln(L)$ for a logarithmic divergence ($\alpha = 0$) and $\sim L^{\alpha/\nu}$ for $\alpha > 0$, where $\nu$ is the critical exponent of the correlation length. In case of first order phase transitions the peak in the specific heat diverges $\sim L^D$, where the proportionality factor is $27 (\beta_t)^2 (\Delta E/N)^2$ with $\beta_t$ the inverse transition temperature and $\Delta E/N$ the latent heat per spin.
In Figs. 4 and 5 we plot the specific heat on various lattices for the two extremes, the weak logarithmic divergence for the 2D Ising model and the strong divergence for the 3D 6-state Potts model. For the 2D Ising model the analytical solutions of Ferdinand and Fisher [30] are plotted, while the plots for the 3D 6-state Potts model rely on recent numerical results [29]. It is clear that even the case of a weak logarithmic divergence is markedly distinct from the behaviors in Fig. 3, where no finite size effects are observed within the rather accurate statistical errors. This distinction becomes all too obvious when the comparison is made with the strong first order phase transition of the 3D 6-state Potts model.

To complete the picture of our two ice models we plot in Figs. 6 and 7 their free energy and entropy densities as obtained from our simulations, using as input the known normalizations at $\beta = 0$. In the cases at hand these are $S_0/N = \ln(6)$ for the 6-s and $S_0/N = \ln(4)$ for the 2-s model. Relative statistical errors are smaller than those in Fig. 3 for the specific heat. In the $\beta \to \infty$ limit our data improve slightly on the results reported in Ref. [6], because we have with $N = 2880$ one larger lattice added. Consistent fits to the previously discussed form $W_1(x) = W_1^{\text{MUCA}} + a_1 x^\theta$, $x = 1/N$ combine to

$$W_1^{\text{MUCA}} = 1.50721 (13) \quad \text{and} \quad \theta = 0.901 (16). \quad (7)$$

The error bars in parenthesis are purely statistical and do not reflect eventual, additional systematic errors due to higher order finite size corrections.

### III. SUMMARY AND CONCLUSIONS

The unusual properties of water and ice owe their existence to a combination of strong directional polar interactions and a network of specifically arranged hydrogen bonds [31, 32, 33]. The groundstate structure of such a network can be described by simple lattice models, which are defined by the energy functions (1) and (3).

In the present paper we have presented finite size scaling evidence that there is no phase transition between $\beta = 0$ and the groundstate region of these models. This lack of a transition makes reliable estimates of the combinatorial groundstate entropy of ice I particularly easy.

Tentatively, we like to see a reason for the marked difference to $q = 6$ and $q = 2$ Potts models in the large groundstate entropy, $S/N = \ln(W_1)$, of our ice models, which violates the third law of thermodynamics, while the groundstate entropy of Potts models, $S/N = \ln(q)/N$, approaches zero in the $N \to \infty$ limit. This is not an entirely convincing argument as the effective number of states $W_1$ per spin is still about 2 (i.e., larger than 1.5) for the 3D 6-state Potts model at the ordered endpoint of the transition [29].

Note that we did not investigate bond statistics in the groundstate ensemble, which one may expect to exhibit critical correlations.

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