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Corrections to Pauling residual entropy and single tetrahedron based approximations for the pyrochlore lattice Ising antiferromagnet

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We study corrections to single tetrahedron based approximations for the entropy, specific heat and uniform susceptibility of the pyrochlore lattice Ising antiferromagnet, by a Numerical Linked Cluster (NLC) expansion. In a tetrahedron based NLC, the first order gives the Pauling residual entropy of $\frac{1}{2} \log \frac{3}{2} \approx 0.20273$. A 16-th order NLC calculation changes the residual entropy to 0.205507 a correction of 1.37 percent over the Pauling value. At high temperatures, the accuracy of the calculations is verified by a high temperature series expansion. We find the corrections to the single tetrahedron approximations to be at most a few percent for all the thermodynamic properties.

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I. INTRODUCTION

The residual entropy of ice was first calculated in a classic paper by Pauling.¹ This entropy arises from the fact that an oxygen atom in ice is surrounded by four protons. Any two of them can move in close to it, making up the H_2O unit, while the other two stay away becoming part of the neighboring water molecules. Extensive ground state entropy is a hallmark of highly frustrated systems, and is well appreciated in context of Ising models, at least since the exact solution of the triangular-lattice antiferromagnet.² A direct connection between the entropy of ice and ground state entropy of Ising spin models was first shown by Anderson.³ Accurate calculations of thermodynamic properties of systems with extensive ground state degeneracy⁴⁻⁶ remains a challenging task.

Interest in such systems has grown considerably with the discovery of spin-ice materials.⁷ These are pyrochlore-lattice spin systems with strong uniaxial anisotropy. In each tetrahedron of the lattice, two spins point in and two point out, providing an exact realization of Anderson's spin-ice mapping. In the real materials, the spin-ice states arise from a combination of nearest-neighbor exchange and long-range dipolar interactions.^{7,8} Due to the unusual angles between the easy-axis directions at neighboring sites, antiferromagnetic exchange leads to a lower energy for all-in/all-out configurations in a tetrahedron, while ferromagnetic exchange leads to the two-in/two-out spin-ice configurations. The measured residual entropy, in these systems, is in good agreement with the Pauling value.⁹

In this paper, our focus is the study of an Ising antiferromagnet on the pyrochlore lattice, which from a statistical mechanics point of view is equivalent to a ferromagnetically exchange coupled spin-ice material. It is defined by the Hamiltonian

$$\mathcal{H} = \sum_{i,j} S_i S_j, \quad (1)$$

Here the spins S_i take values ± 1 and the sum runs over all nearest-neighbor bonds of the pyrochlore lattice. Single tetrahedron based approximations for the thermodynamic properties of this model are common.^{1,4,5,8,10,11} We note that single tetrahedron based approximation for residual entropy is not the same as the entropy of a single tetrahedron. Translating Pauling's argument to the spin language, each spin has two states, but in each tetrahedron only 6 out of 16 spin configurations obey the ice-rules. Treating the constraint in each tetrahedron as independent, a system with N spins has $2^N (\frac{6}{16})^{N_t}$ ground states, where N_t is number of tetrahedra. Since, N_t equals $N/2$, this leads to a ground state entropy per spin of $S = \frac{1}{2} \log \frac{3}{2}$.

Corrections to the Pauling expression for residual entropy of ice have been studied before.¹² Following earlier work by Takahashi¹³ and DiMargio and Stillinger,¹⁴ Nagle used graphical methods on Vertex models¹² to study ground state residual entropy for cubic ice corresponding to the pyrochlore lattice as well as the more common ice structure known as Layered Hexagonal ice. He found that the difference in residual entropy between the two structures was negligible. The corrections to the Pauling expression was estimated to be about 1.1 percent. Comparable corrections (approximately 1.2 percent) have been estimated in more recent computational studies.¹⁵ Here, we will calculate the thermodynamic properties of the antiferromagnetic Ising model on the pyrochlore lattice using series expansion methods.¹⁶

In a Numerical Linked Cluster expansion (NLC),¹⁷ an extensive property P for a large lattice \mathcal{L} of N -sites is expressed as

$$P(\mathcal{L})/N = \sum_c L(c) \times W_P(c). \quad (2)$$

The sum is over distinct clusters of the lattice. $L(c)$ is the lattice constant of the cluster, given by the number of embeddings of the cluster in the lattice, per site. The quantity $W_P(c)$ is the weight of the cluster associated

with the property P , which is defined by the subgraph subtraction scheme

$$W_P(c) = P(c) - \sum_s W_P(s), \quad (3)$$

where the sum runs over all subclusters of the cluster c . Thus, to carry out the calculation up to some order, one needs a count of all the clusters up to some order, and the property $P(c)$ needs to be calculated for every cluster to high precision using numerical methods.

The number of clusters, needed in the study, is significantly reduced if it can be shown that only star-graphs contribute.¹⁸ Consider a graph as a collection of sites that are connected pair-wise by the bonds of the graph. A site is a point of articulation in a graph, if cutting all the bonds incident on the site, makes the rest of the graph disconnected. A star-graph is one that has no such articulation site. Star graph expansions have been used to develop high temperature expansions for various classical spin models.¹⁸ But, they can also be used in a Numerical Linked Cluster (NLC) scheme, where no small expansion parameter is needed.¹⁷ Rather, thermodynamic properties of finite clusters can be calculated at a given temperature and then the principle of inclusion and exclusion can be used to calculate the thermodynamic property of the infinite system by summing up contributions from all allowed clusters.

A star graph expansion requires that all articulated graphs have zero weight. This is very simple to see for properties that can be obtained from the logarithm of the zero-field partition function. For any articulated graph, one can show that a partition function, that is normalized to unity in the absence of interactions, becomes a product of partition functions over the two subgraphs articulated at a point. Hence $\log Z$ becomes a sum. Thus for an articulated graph c made up of parts a and b , which only share a point of articulation, the property satisfies

$$P(c) = P(a) + P(b). \quad (4)$$

This is enough to ensure that after subgraph subtraction the articulated graph has zero weight. It is a little harder to see how to develop star-graph expansion for the uniform susceptibility. One needs to consider the matrix M with elements^{19,20}

$$M_{ij} = \langle S_i S_j \rangle, \quad (5)$$

where i and j are sites of the cluster and angular brackets denote thermal expectation values. One can show that for a graph articulated at site k into parts a and b (with spin normalization $\langle S_k^2 \rangle = 1$)

$$\langle S_i S_j \rangle = \langle S_i S_k \rangle_a \langle S_k S_j \rangle_b, \quad (6)$$

when i and j belong to a and b respectively. And within a and b , the correlations remain the same as in the subcluster. This can be used to further show that^{19,20}

$$\psi = \sum_{i,j} M_{ij}^{-1}, \quad (7)$$

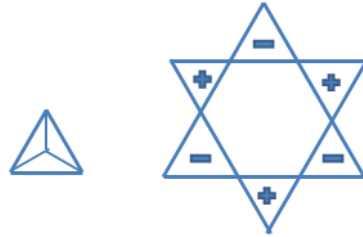


FIG. 1: (color online) First two star-graphs of the pyrochlore lattice made up of complete tetrahedra. The first one is a single tetrahedron. The second is a ring of six tetrahedra that alternately point in and out of the board (denoted by + and - signs).

where M^{-1} is the inverse of the matrix M , has a star graph expansion. Furthermore, for the infinite lattice, this is related to the inverse of the uniform structure factor, or temperature times the uniform susceptibility by the relation,

$$T\chi = \frac{1}{N} \sum_{i,j} \langle S_i S_j \rangle = \frac{N}{\psi}. \quad (8)$$

In a lattice of corner-sharing tetrahedra, it is natural to consider an NLC expansion scheme, in which all interactions are grouped into tetrahedra. Thus, apart from a single site, all graphs are made up of complete tetrahedra. This scheme is particularly useful because the tetrahedra are joined at corners in the lattice. In a graph with two tetrahedra, the site where they are joined becomes a point of articulation. Cutting all the bonds at that site makes the graph disconnected. Thus, in a star-graph expansion, the two-tetrahedron graph makes no contribution. It also means that the single tetrahedron approximation becomes exact on a Husimi tree of tetrahedra,^{21,22} where there are no other closed loops of tetrahedra.

The tetrahedra of a pyrochlore lattice are known to form a diamond lattice. Thus any graph counting problem involving tetrahedra is equivalent to counting graphs on the diamond lattice, where sites of the diamond lattice represent tetrahedra while bonds of the diamond lattice represent shared sites between neighboring tetrahedra. All star graphs on the diamond lattice up to 16 bonds have been listed by Sykes *et al.*²³ We will make use of these to calculate the expansions to 16-th order. One should note that all lattice constants of the diamond lattice need to be divided by 2, because the number of tetrahedra is $\frac{1}{2}$ the number of sites in the pyrochlore lattice.

We illustrate how the method works by showing the first two orders of the calculation for the ground state entropy (with the Boltzmann constant $k_B = 1$). The first two star-graphs with complete tetrahedra are shown in Fig. 1. They have a lattice constant per site of the

pyrochlore lattice of $\frac{1}{2}$ and 1 respectively. One also needs to consider a single-site, which provides all contributions before any interactions are included. It has a count of unity.

For our illustration, the ground state entropy is the property P . In zeroth order, the single site has two ground states, giving an entropy of $\log 2$. It has no subgraphs. Hence, its weight is also $\log 2$. The first star graph, a single tetrahedron, has 6 ground states. Hence the property P for the graph equals $\log 6$. To obtain its weight, one must subtract the weights of the 4 sites. Thus the weight of the single tetrahedron is

$$W = \log 6 - 4 \log 2 = \log 3/8$$

Thus, to first order the ground state entropy, per site, for the infinite system is

$$S = \log 2 + \frac{1}{2} \log 3/8 = \frac{1}{2} \log 3/2 \approx 0.20273.$$

Note that the factor of $\frac{1}{2}$ in front of $\log 3/2$ is the count of number of tetrahedra per lattice site, which is one-half. This is the Pauling answer. The next star graph is a graph of 6 tetrahedra (See Fig. 1). It has 730 ground states. It has 6 single tetrahedron subgraphs and 18 sites. Thus, its weight is

$$W = \log 730 - 6 \log 3/8 - 18 \log 2 = \log 730/729$$

Thus, to this order, the entropy per site, becomes

$$S = \log 2 + \frac{1}{2} \log 3/8 + \log 730/729 \approx 0.20410.$$

These first corrections are analogous to triangle-based NLC calculations done by Rigol et al for the kagome lattice.¹⁷ In that case, the Pauling expression for ground state entropy is 0.50136. Adding the next correction brought the entropy to 0.50182, much closer to known exact answer of approximately 0.50183.²⁴ Because the count of longer loops increases much more rapidly in a 3-dimensional lattice, a high order calculation is needed to assess the corrections more accurately. Here we have done only the first corrections for the uniform susceptibility, but a 16-th order correction for the entropy and specific heat.

High temperature series expansions for this system were derived some years ago: to order 19 for $\log Z$ (See Ref.²⁵) and to order 16 for χ .²⁶ We have reanalyzed these series using Padé and d-log Padé approximants to yield the series results for comparison at high temperatures.

Fig. 2 shows a plot of the entropy. The single tetrahedra approximation is denoted NLC-1. NLC-6 includes the next order correction. NLC-16 gives the result up to 16th order. Fig. 3 shows the corresponding plots of the heat capacity. Fig. 4 shows plots of the uniform susceptibility. The high temperature expansions converge really well only above a temperature of 2. Note that the spins are normalized to be ± 1 . The temperature scale would be four times lower if they were normalized to $\pm 1/2$.

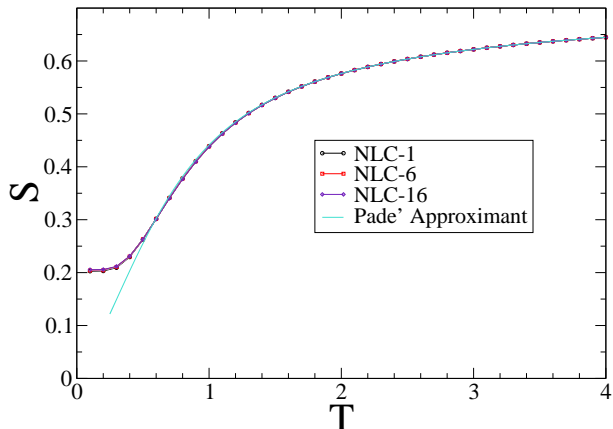


FIG. 2: (color online) Entropy of the pyrochlore lattice Ising antiferromagnet as a function of temperature.

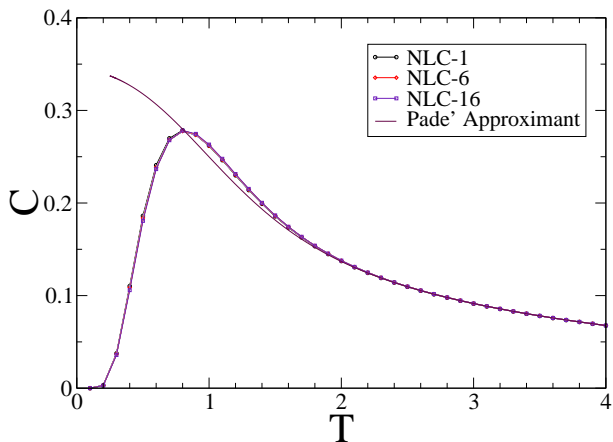


FIG. 3: (color online) Heat capacity of the pyrochlore lattice Ising antiferromagnet as a function of temperature.

In all cases, the single tetrahedron based approximation is quite accurate. Let us define percent correction for the three quantities a = entropy (s), heat capacity (c) and susceptibility (χ) as

$$P_a = 100 * (a(N) - a(1))/a(1). \quad (9)$$

Here $a(N)$ is the quantity after N th order NLC. and $a(1)$ is the property with only the one tetrahedron cluster. A plot of P_a with temperature is shown in Fig. 5. The largest corrections are near $T = 0$. They are a little over one percent for the entropy and about 5 percent for the specific heat.

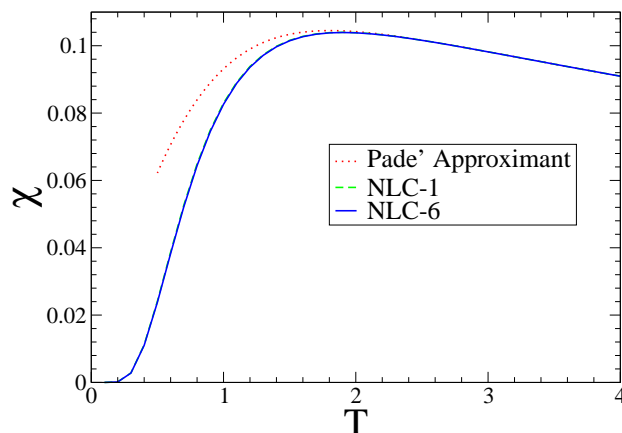


FIG. 4: (color online) Uniform susceptibility of the pyrochlore lattice Ising antiferromagnet as a function of temperature. Note that NLC-1 and NLC-6 can barely be differentiated in the plot.

At $T = 0$, our graphical scheme, reduces to one of counting ground states on increasingly larger clusters. While this scheme is not identical to the one used by Nagle,¹² it is closely related. As found by Nagle, the first few orders give the same answer for the cubic and layered hexagonal structures of ice. We also find that the first corrections to the Pauling entropy are identical for the two lattices. Since, our interest is in the pyrochlore lattice spin model, we have not studied the layered hexagonal structure in higher orders.

In conclusion, we have used a star-graph expansion scheme to show that the Pauling approximation for the entropy of ice and calculation of other properties of the pyrochlore lattice Ising model based on a single tetrahedron is really a first term in a Numerical Linked Cluster (NLC) scheme. In the corner sharing lattice, this scheme is highly accurate. We have calculated corrections to the single tetrahedron approximations and found them to be at most a few percent for different thermodynamic quan-

tities.

These ideas of star-graph expansions are also valid for continuous spin models, where also single tetrahedra based schemes have been used successfully.¹⁰ However, it should be noted that finite-size calculations of properties of the continuous spin systems can be a non-trivial task. Star graph expansions are also valid in presence of dilution and quenched disorder.^{20,27} Star graph expansions are not valid for quantum spin models and hence all connected clusters of tetrahedra need to be included in these cases.

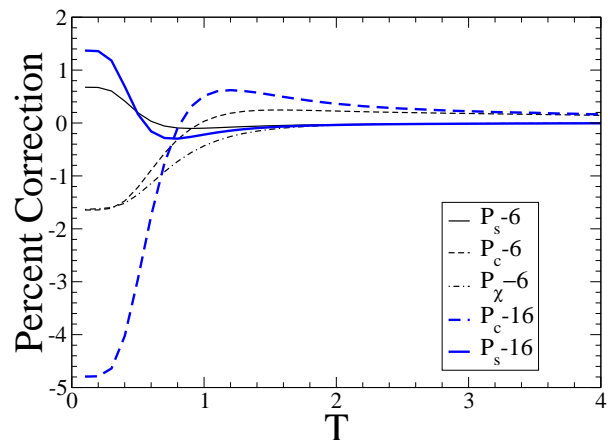


FIG. 5: (color online) Percentage correction to the quantities, entropy (P_s), heat capacity (P_c) and susceptibility (P_χ) after 6th and 16th order NLC calculations (denoted by the numbers 6 and 16 in the legends).

Acknowledgments

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