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Residual entropy of two-dimensional ice on a Kagomé lattice

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Abstract. We have calculated the residual entropy of two-dimensional ice on a Kagomé lattice by the method of series expansion. Based on the first six terms of the series, we have found that the residual entropy is $S = Nk \ln W$ where N is the number of molecules and $W = 1{\cdot}60615 \pm 0{\cdot}00001$.

1. Introduction

At temperatures well below the freezing point, ice has a residual entropy caused by an indeterminacy in the positions of the hydrogen atoms (Pauling 1935). The residual entropy of ice can be calculated using the ice rules (Bernal and Fowler 1933, Pauling 1935, Slater 1941): (*a*) there is one and only one hydrogen atom on each bond; (*b*) there are exactly two hydrogen atoms near to (and away from) each oxygen atom (vertex).

The ice rules imply that the residual entropy is given by

$$S = Nk \ln W \tag{1}$$

where N is the number of vertices, k is Boltzmann's constant, and W^N (for large N) is the number of ways to arrange the arrows such that there are precisely two arrows pointing towards and two arrows pointing away from each vertex.

Nagle (1966) developed a series expansion method which can be used to estimate numerically the residual entropy of ice on any lattice of coordination number four. His results which are based on the first five terms of the series are:

$$W(\text{real ice}) = 1{\cdot}50685 \pm 0{\cdot}00015 \tag{2}$$

$$W(\text{square lattice}) = 1{\cdot}540 \pm 0{\cdot}001. \tag{3}$$

Lieb (1967) calculated W on a square lattice exactly by the method of transfer matrix (Lieb and Wu 1972). His result is

$$W(\text{square lattice}) = (\tfrac{4}{3})^{3/2} = 1{\cdot}5396007\ldots, \tag{4}$$

in excellent agreement with Nagle's result.

The purpose of this paper is to calculate the residual entropy of ice on a Kagomé lattice. The corresponding transfer matrix is much more complicated than that of ice on the square lattice and we are unable to find the exact solution. We have evaluated the entropy numerically by the method of series expansion. Two different series are used and the results are consistent with each other. Based on the first ten terms of the Nagle's series without extrapolation, we have found

$$W(\text{Kagomé lattice}) \approx 1{\cdot}6052. \tag{5}$$

A more precise result is obtained by using the series of F Y Wu (1975, private communication). Based on the first six terms of Wu's series with extrapolation, we have found

$$W(\text{Kagomé lattice}) = 1{\cdot}60615 \pm 0{\cdot}00001. \tag{6}$$

We shall describe Nagle's series in § 2 and Wu's series in § 3. A conclusion is given in § 4.

2. Nagle's series

The ice model is equivalent to a counting problem involving closed polygon configurations. In a configuration of closed polygons, the number of bonds incident at each vertex is zero, two or four. The number of ice configurations is given by (Nagle 1966, Lieb and Wu 1972)

$$W_N = (\tfrac{3}{2})^N \sum (\tfrac{1}{3})^n \tag{7}$$

where N is the total number of vertices, n is the number of vertices with two bonds incident in a given polygon configuration, and the summation is taken over all closed polygon configurations that can be drawn on the ice lattice. In the limit of infinite N, we have

$$W = \lim_{N\to\infty} (W_N)^{1/N}. \tag{8}$$

It follows from equation (7) that $1{\cdot}5$ is a lower bound to W.

Equation (7) can be written in the form

$$W_N = (\tfrac{3}{2})^N \Big(1 + \sum_n \phi_n(N) 3^{-n}\Big), \tag{9}$$

where $\phi_n(N)$ is the total number of polygon configurations of order n. To get W from W_N formally for a lattice with periodic boundary conditions, one simply replaces N wherever it appears in W_N by one (Domb 1960). Therefore we have (Nagle 1966)

$$W = \tfrac{3}{2}\Big(1 + \sum_n \phi_n(1) 3^{-n}\Big) \tag{10}$$

which applies to any lattice of coordination number four.

We now apply the above result to a Kagomé lattice (figure 1) with $3N$ vertices. The lattice with periodic boundary conditions consists of N hexagons and $2N$ triangles. Following Nagle, we write

$$W_{3N} = (\tfrac{3}{2})^{3N}\Big(1 + \sum_n \phi_n(N) 3^{-n}\Big). \tag{11}$$

The reason why we use W_{3N} instead of W_N is to make sure that $\phi_n(1)$ are integers. In the limit of infinite N we have

$$W = \lim_{N\to\infty} (W_{3N})^{1/3N} = 1{\cdot}5\Big(1 + \sum_n \phi_n(1) 3^{-n}\Big)^{1/3}. \tag{12}$$

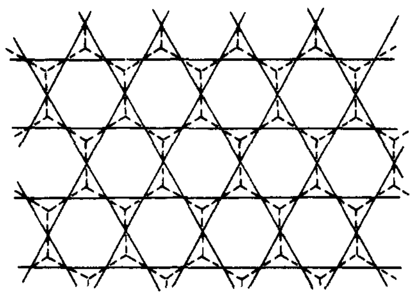

Figure 1. A Kagomé lattice (full line) and the associated honeycomb lattice (broken line).

The calculation of $\phi_n(1)$ is straightforward. For example, we have $\phi_3(N)=2N$ since we can draw exactly $2N$ triangles (each one has three vertices) on the Kagomé lattice with periodic boundary conditions. The first four terms of the series (11) can be written down easily:

$$\phi_3(N)=2N \qquad \phi_4(N)=3N \qquad \phi_5(N)=6N \qquad \phi_6(N)=16N+N(2N-4). \tag{13}$$

The $N(2N-4)$ part of $\phi_6(N)$ corresponds to two unconnected triangles. The polygons which can be drawn on the Kagomé lattice with $n=3, 4, 5$ are shown in figure 2. For $n>6$, the calculation of $\phi_n(1)$ becomes quite tedious. We have evaluated $\phi_n(1)$ up to $n=12$. The results are summarized in table 1.

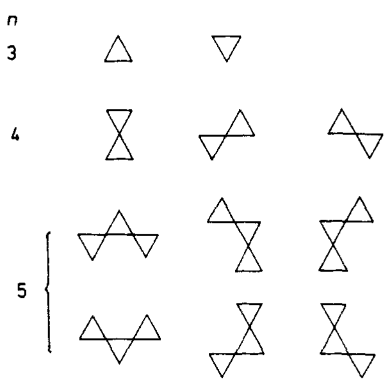

Figure 2. The polygons which can be drawn on the Kagomé lattice with $n=3$, 4 and 5.

Adding up the terms which we have computed yields

$$W=\tfrac{3}{2}(1+0{\cdot}22587)^{1/3}=1{\cdot}6052. \tag{14}$$

In the case of the square lattice, n is an even integer and Nagle (1966) plotted $\phi_{n+2}(1)/\phi_n(1)$ against $1/n$. He obtained a fairly smooth curve. By straightforwardly extrapolating that curve he was able to compute estimates for ϕ_n with $n>12$. The same technique fails in the case of the Kagomé lattice because it is clear from table 1 that the relation between $\phi_{n+1}(1)/\phi_n(1)$ and $1/n$ cannot be represented by a smooth curve. Therefore we are unable to compute estimates for ϕ_n with $n>12$.

Table 1. Summary table of Nagle's series expansion for the Kagomé lattice. The column headings mh give the number m of hexagons surrounded by the connected polygons of nth order. The column headings md give the number m of disconnected parts in a given closed polygon configuration of order n.

n	0h	1h	2h	3h	4h	5h	6h	7h	2d	3d	4d	$\phi_n(1)$	$\frac{\phi_{n+1}(1)}{\phi_n(1)}$
3	2											2	1·5
4	3											3	2
5	6											6	2·333
6	14	2							−2			14	2·571
7	36	12							−12			36	2·583
8	93	48	3						−51			93	2·559
9	244	172	24	2					−210	6		238	2·609
10	648	579	147	27	3				−843	60		621	2·696
11	1716	1902	744	198	42	6			−3318	384		1674	2·594
12	4603	5849	3168	1137	336	66	14	1	−12923	2114	−23	4342	

3. Wu's series

It has been pointed out by F Y Wu (1975, private communication) that the ice model on a Kagomé lattice is equivalent to a counting problem involving closed polygon configurations on the associated honeycomb lattice (figure 1). Consider a Kagomé lattice with $3N$ vertices, the number of ice configurations is

$$W_{3N}=2^{2N}\left(1+\sum 2^{l-b}\right) \tag{15}$$

where b and l are respectively the number of bonds and loops in a given polygon configuration, and the summation is taken over all closed polygon configurations that can be drawn on the associated honeycomb lattice. To see this, notice that there exists a 2^{2N+l-b} to 1 mapping between ice configurations on the Kagomé lattice (with periodic boundary conditions) and the closed polygon configurations on the associated honeycomb lattice according to the following rule.

Mapping rule: consider a triangle on the Kagomé lattice (figure 3). A vertex is connected to the centre of the triangle by a broken line if the arrows around this triangle are arranged in such a way that one arrow points away from and one arrow points towards this vertex. Otherwise a vertex is connected to the centre of the triangle by a full line. The full lines drawn on bonds of the associated honeycomb lattice form closed polygons.

It is clear from equation (15) that

$$W=\lim_{N\to\infty}(W_{3N})^{1/3N}>2^{2/3}=1\cdot587401\ldots. \tag{16}$$

Wu's series is simpler to calculate than Nagle's series because the closed polygons on the honeycomb lattice never intersect with each other. We rewrite equation (15) in the form

$$W_{3N}=2^{2N}\left(1+\sum_n \phi_n(N)2^{-5n}\right) \tag{17}$$

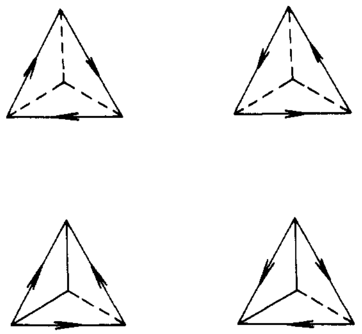

Figure 3. The mapping between ice configurations on a Kagomé lattice and closed polygon configurations on the associated honeycomb lattice.

where n is the number of honeycombs surrounded by the closed polygons on each configuration, and each term is a partial sum of the series in equation (15) over all configurations with the same order n. In the limit of infinite N we have

$$W = 2^{2/3}\left(1 + \sum_n \phi_n(1) 2^{-5n}\right)^{1/3}. \tag{18}$$

We have evaluated $\phi_n(1)$ up to $n = 6$. The results are summarized in table 2. Adding up the terms which we have computed yields

$$W = 4^{1/3}(1{\cdot}035713)^{1/3}. \tag{19}$$

Table 2. Summary table of Wu's series expansion for the honeycomb lattice. The column headings *m*d give the number *m* of disconnected parts in a given closed polygon configuration of order *n*.

n	1d	2d	3d	4d	5d	6d	$\phi_n(1)$	$\frac{\phi_{n+1}(1)}{\phi_n(1)}$
1	1						1	3
2	6	-3					3	10
3	68	-54	16				30	$12\frac{2}{3}$
4	1000	-1012	498	-106			380	14·929
5	$2^4(1059)$	$-2^5(633)$	$2^3(1617)$	-4740	789		5673	16·449
6	$2^5(9807)$	$-2^8(1667)$	$2^4(20221)$	$-2^2(39289)$	46170	-6308	93314	

In figure 4, we have plotted $\phi_{n+1}(1)/\phi_n(1)$ against $1/n$ and obtained a fairly smooth curve. By extrapolating this curve, we can calculate estimates for ϕ_n with $n > 6$. We have found

$$\begin{aligned} 1{\cdot}60616 = 4^{1/3}(1{\cdot}035713 + 0{\cdot}000117 + 0{\cdot}000055)^{1/3} &> W > 1{\cdot}60614 \\ &= 4^{1/3}(1{\cdot}035713 + 0{\cdot}000117 + 0{\cdot}000012)^{1/3}, \end{aligned} \tag{20}$$

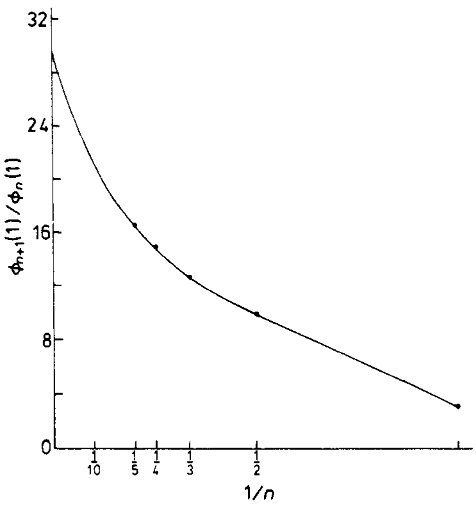

Figure 4. The term ratio $\phi_{n+1}(1)/\phi_n(1)$ against $1/n$ for Wu's series.

where the 0·000117 comes from the extrapolated values for the terms $n = 7$–12, 0·000055 and 0·000012 come from lumping all the higher n terms together with a ratio of 29·5/32 and 22/32 respectively†. Therefore we conclude

$$W(\text{Kagomé lattice}) = 1{\cdot}60615 \pm 0{\cdot}00001. \tag{21}$$

4. Conclusion

We have computed numerically the residual entropy of two-dimensional ice on a Kagomé lattice by the method of series expansion. Theoretically the series of Nagle is equivalent to the series of Wu. However, for practical purposes Wu's series converges much faster than Nagle's series. This is due to the fact that the zeroth order term of Wu's series gives $W = 4^{1/3} = 1{\cdot}587401$, which is considerably larger than the corresponding value of 1·5 given by Nagle's series. Wu's series has another advantage. One can calculate estimates for higher-order terms in Wu's series by extrapolating the term ratios while the same thing cannot be done for Nagle's series. This is probably due to the fact that the Kagomé lattice consists of two different kinds of polygons (triangle and hexagon) while the honeycomb lattice consists of only one kind of polygon (hexagon).

Acknowledgments

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† From figure 4 we get $\phi_{n+1}/\phi_n = 29{\cdot}5$ and 22 respectively for $n = \infty$ and 12.

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