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Residual entropy of two-dimensional ice on a ruby lattice

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Abstract. We have calculated the residual entropy of two-dimensional ice on a ruby lattice by the method of series expansion. Based on the first five terms of the series, we have found that the residual entropy is $S = Nk \ln W$ where N is the number of molecules and $W = 1.560 \pm 0.001$.

1. Introduction

At temperatures near absolute zero, ice has a residual entropy due to an indeterminacy in the positions of the hydrogen atoms (Pauling 1935). The residual entropy of ice can be calculated by using the so-called ice rules (Bernal and Fowler 1933, Slater 1941): (1) there is exactly one hydrogen atom on each bond; (2) there are exactly two hydrogen atoms near to (and away from) each oxygen atom (located at the vertex of the lattice).

The ice rules imply that the residual entropy is given by (Lieb and Wu 1972)

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

where N is the number of vertices, k is the Boltzmann 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 to calculate 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

$$W(\text{real ice}) = 1.506\,85 \pm 0.000\,15 \tag{2}$$

$$W(\text{square lattice}) = 1.540 \pm 0.001. \tag{3}$$

His result for real ice agrees with experiment. Lieb (1967) calculated W on a square lattice exactly by the method of transfer matrix. The exact result is

$$W(\text{square lattice}) = (4/3)^{3/2} = 1.5396\ldots \tag{4}$$

in excellent agreement with Nagle's calculation.

Lin and Tang (1976) have calculated the residual entropy of ice on a Kagomé lattice by the method of series expansion, using a series suggested by Wu. Based on the first six terms of Wu's series, they found

$$W(\text{Kagomé lattice}) = 1.606\,15 \pm 0.000\,01. \tag{5}$$

The exact result for this lattice is still an unsolved problem. It can be shown (Lin and Wang 1977) that

$$1.708\ldots > W(\text{Kagomé lattice}) > \tfrac{1}{2}(33)^{1/3} = 1.604\ldots. \tag{6}$$

The purpose of this paper is to calculate the residual entropy of ice (ice model) on a ruby lattice by the method of series expansion.

2. Ice model on a ruby lattice

It has been pointed out by Wu (Lin and Tang 1976) that the ice model on a Kagomé lattice is equivalent to a counting problem involving closed polygon configurations on the associated honeycomb lattice. Similarly, it can be shown that the ice model on a ruby lattice (figure 1) is equivalent to a counting problem on the associated snowflake

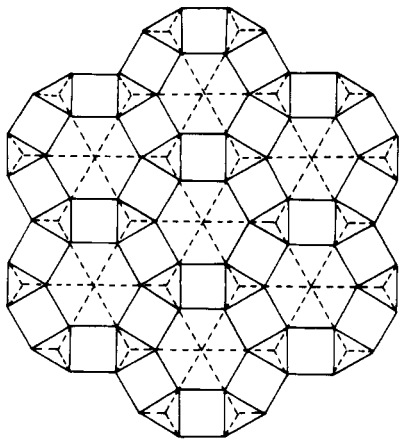

Figure 1. A ruby lattice (full line) and the associated snowflake lattice (broken line).

lattice (also called dice lattice). Consider a ruby lattice with $6N$ vertices; the number of ice configurations is

$$W_{6N} = 2^{3N}\left(1 + \sum 2^{l-v}\right) \tag{7}$$

where l and v are respectively the number of disconnected polygons and vertices in a given polygon configuration, and the summation is taken over all closed polygon configurations that can be drawn on the associated snowflake lattice. To see this, notice that there exists a 2^{3N+l-v} to 1 mapping between ice configurations on the ruby lattice (with periodic boundary conditions) and the closed polygon configurations on the associated snowflake lattice according to the following rule. Consider a polygon, which is either a triangle or a hexagon (figure 2), on the ruby lattice; a vertex is connected to the centre of the polygon by a broken line if the arrows around this polygon 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 polygon by a full line. The full lines drawn on bonds of the associated snowflake lattice form closed polygons.

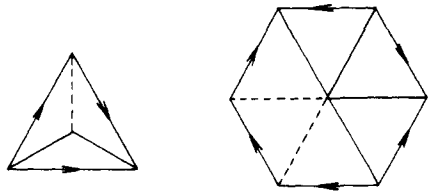

Figure 2. The mapping between ice configurations on a ruby lattice and closed polygon configurations on the associated snowflake lattice.

We can rewrite equation (7) in the form

$$W_{6N} = 2^{3N}\left(1+\sum_n f_n(N)2^{-3n}\right) \tag{8}$$

where n is the number of quadrilaterals (rhombs) surrounded by the closed polygons on each configuration, and each term is a partial sum of the series in equation (7) over all configurations with the same order n. In the limit of infinite N, we have (Domb 1960)

$$W = 2^{1/2}\left(1+\sum_n f_n(1)2^{-3n}\right)^{1/6}. \tag{9}$$

The calculation of $f_n(N)$ is straightforward. For example, we have $f_1(N) = 3N$ because we can draw exactly $3N$ quadrilaterals on the snowflake lattice with periodic boundary conditions and $l - v = 1 - 4 = -3$ for each quadrilateral. We have evaluated f_n up to $n = 5$:

$$\begin{aligned} &f_1 = 3N \qquad f_2 = 12N + 3N(3N-5)/2 \qquad f_3 = N(9N^2+27N+50)/2 \\ &f_4 = N(27N^3+162N^2+681N+546)/8 \\ &f_5 = N(81N^4+810N^3+5715N^2+12210N+17544)/40. \end{aligned} \tag{10}$$

To calculate $f_2(N)$, we consider a pair of rhombs. There are $6N$ ways to draw a pair of rhombs which share a common edge and $l - v = 1 - 6 = -5$. The contribution of these twin rhombs to $f_2(N)$ is thus twice $6N$. We are left with

$$\binom{3N}{2} - 6N = 3N(3N-5)/2$$

pairs of rhombs where $l - v = -6$ for each pair. Therefore, the total contribution is

$$12N + 3N(3N-5)/2.$$

For $i > 2$, the calculation of $f_i(N)$ is more complicated but the procedure is basically the same.

We define

$$W(n) = 2^{1/2}\left(1+\sum_{m=1}^{n} f_m(1)2^{-3m}\right)^{1/6} \tag{11}$$

where

$$\begin{aligned} &W(1) = 1.4913 \qquad W(2) = 1.5158 \qquad W(3) = 1.5293 \\ &W(4) = 1.5363 \qquad W(5) = 1.5405. \end{aligned} \tag{12}$$

In figure 3, we have plotted $W(n)$ against $1/n$ and obtained a fairly smooth curve. By extrapolating this curve, we get

$$W = W(\infty) = 1.560 \pm 0.001. \tag{13}$$

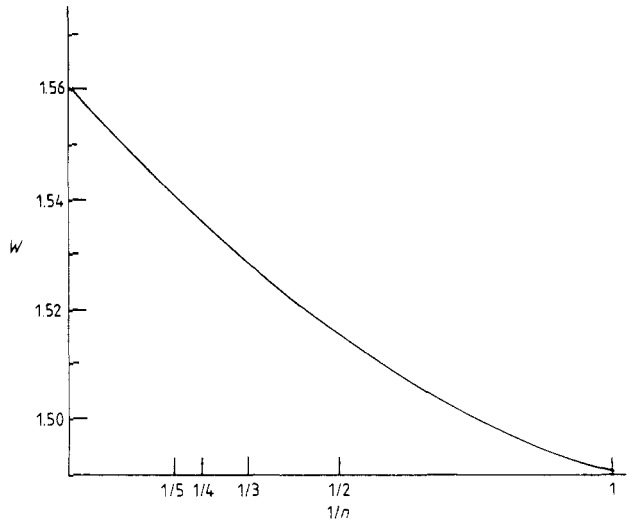

Figure 3. The value of $W(n)$ against $1/n$.

3. Discussion

The most natural grouping of terms is the one introduced by Stillinger and Cotter (1973). This grouping inherently adds another physical parameter to the model, namely the Bjerrum defect energy, which is assumed to be infinite in this paper. However, their analysis depends on the assumption that every closed polygon in the ice crystals has an even number of sides. As a result the sites may be partitioned into two sublattices, with members of one sublattice serving as nearest neighbours to members of the other sublattice. These crystals are called loose-packed. Real ice crystal and some lattices (e.g. square and simple cubic lattices) are loose-packed. It has been shown by Nagle (1968) that the property of factorisation used by Stillinger and Cotter is valid only for loose-packed lattices. Since the ruby lattice is not loose-packed, their method cannot be applied to our model.

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References

Bernal J D and Fowler R H 1933 *J. Chem. Phys.* **1** 515–48
Domb C 1960 *Adv. Phys.* **9** 149–361

Lieb E H 1967 *Phys. Rev.* **162** 162–72
Lieb E H and Wu F Y 1972 *Phase Transitions and Critical Phenomena* vol 1, ed C Domb and M S Green (London: Academic) pp 332–490
Lin K Y and Tang D L 1976 *J. Phys. A: Math. Gen.* **9** 1101–7
Lin K Y and Wang I P 1977 *J. Phys. A: Math. Gen.* **10** 1651–2
Nagle J F 1966 *J. Math. Phys.* **7** 1484–91
—— 1968 *J. Math. Phys.* **9** 1007–19
Pauling L 1935 *J. Am. Chem. Soc.* **57** 2680–4
Slater J C 1941 *J. Chem. Phys.* **9** 16–33
Stillinger F H and Cotter M A 1973 *J. Chem. Phys.* **58** 2532–41