

A First-Order Phase Transition in a Three-Dimensional Vertex Model

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For a specific three-dimensional vertex model, it is proven that it will show a first-order phase transition. The critical temperature is given in terms of the energy of some local vertex configurations. The approach used is similar to the Nagle approach. Some classes of compounds are considered which may be related to this model.

KEY WORDS: Vertex models; phase transitions.

1. INTRODUCTION

In the past half century many exact results have been obtained concerning the thermodynamic properties of so-called vertex models. Originally vertex models were devised to describe compounds containing hydrogen bonds.⁽¹⁾ Examples of such compounds are ice and KH_2PO_4 (KDP), which both contain units (oxygen or phosphate) coordinated tetrahedrally by four hydrogen atoms.⁽²⁾ The coordination of these hydrogens satisfies the ice rule: two hydrogens are proximal to the central ion and the other two are distal to this ion. This rule can be obeyed by several configurations and for four-coordinated ions this number equals six, hence the name six-vertex model. Although the ice-type compounds in fact consist of diamond-like networks, a simple square lattice network has in most cases been employed. The reason for this is the fact that there exists a relation between this model and the one-dimensional $s = 1/2$ Heisenberg model, which allows for a solution of this Heisenberg model. Figure 1a shows an example of a state which may occur in such a six vertex model, where every vertex represents

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a coordinated ion and the position of the hydrogen ion is depicted by an arrow on its edge.

There are six possible configurations around a vertex, which are given in Fig. 1b. A numbering is also given to the different arrangements by specifying their energies. The general six-vertex model is defined by $\epsilon_1 = \epsilon_2$, $\epsilon_3 = \epsilon_4$, and $\epsilon_5 = \epsilon_6$. Special cases are $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6$ (two-dimensional analog of ice), $\epsilon_1 = \epsilon_2 = 0$, $\epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 > 0$ (two-dimensional analog of KDP, a ferroelectric), and $\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 > 0$, $\epsilon_5 = \epsilon_6 = 0$ (an antiferroelectric).

For these types of models and extensions thereof (notably the eight vertex model) many thermodynamic properties have been calculated, such as the free energy, classification of possible phases, the spontaneous staggered polarization and correlation length of the antiferroelectric phase, and many other properties.⁽³⁾ For three-dimensional vertex lattices our knowledge of their properties is not as extensive as in the two-dimensional case. However, in the past 10 years, considerable success has been obtained in solving another three dimensional classical model, called the Zamolodchikov model and extensions thereof.⁽⁴⁻⁶⁾ This model is a special case of the so-called "interaction-round-a-cube" model, consisting of a cubic lattice of interacting spins. When the spins can have two values (the generalization to multivalued spins also has been considered) and the Boltzmann weights occurring in this model are chosen in a specific way, the Zamolodchikov model emerges, which turns out to satisfy the tetrahedron relations (a three-dimensional analog of the star-triangle relation in ice-type models) and to have commuting transfer matrices. Using these properties, the free energy of the model has been calculated.⁽⁵⁾

To enlarge our knowledge of properties of three-dimensional lattice models, we have previously considered a three-dimensional 20-vertex model⁽⁷⁾ especially in relation to the two-dimensional Heisenberg model. For this model we obtained exact results concerning its eigenfunctions for two reversed spins.⁽⁸⁾

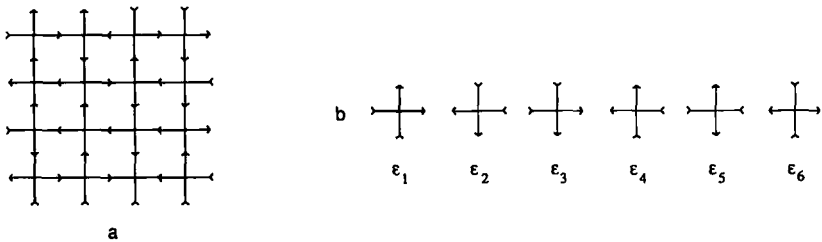


Fig. 1. (a) A possible state occurring in the six vertex model. (b) All possible edge configurations.

A specific case of this 20-vertex model is comparable to the specific case of the 6-vertex model considered by Nagle.⁽⁹⁾ He obtained proof of the occurrence of a first-order phase transition in this model. In this paper we will apply his method to a specific case of the 20-vertex model, and prove that also in this case a first-order phase transition will occur.

In the next section the model will be defined, in Sections 3 and 4 the free energy below and above T_c , respectively, will be calculated, and in the final section the results will be discussed.

2. DEFINITION OF THE MODEL

As a basic lattice for the three-dimensional lattice model the ReO_3 lattice is used with a simple cubic lattice for the Re atoms and an O atom linearly between two neighboring Re atoms, such that Re is octahedrally coordinated and the octahedrons are corner connected.

From this structure we make an abstract lattice of vertices (which are placed at the Re atom positions) and edges (connecting the nearest-neighbor Re atoms), which can have two directions as in the four-coordinated vertex model. Around one vertex one can construct 20 edge configurations as shown in Fig. 2.

We will derive that a first-order phase transition occurs in a special case of the 20-vertex model. In this model we assume that the first two leftmost vertex configurations above each other in Fig. 2 have an energy equal to zero, whereas all others have an equal energy ϵ larger than zero. For this special case it is possible to obtain the critical temperature in terms of ϵ and show that the phase transition at that temperature is indeed of first order. The derivation runs similarly to the one given by Nagle⁽⁹⁾ for four-coordinated compounds and will be repeated here with some modifications.

We will consider a normal three-dimensional lattice, of the ReO_3 type, and assume normal cyclic boundary conditions in a layer perpendicular to the (1,1,1) axis. If we view the lattice along the (1,1,1) axis, it is clear that every octahedron is connected to three other octahedra in the layer below and above its own layer (i.e., connected to six octahedra in total). Note

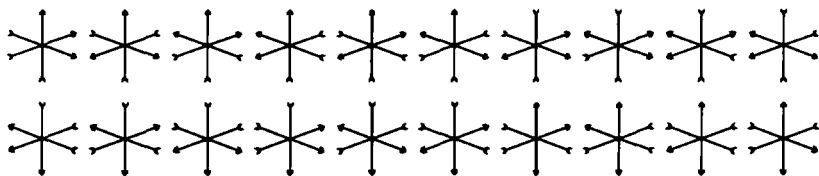


Fig. 2. The 20 different edge configurations around a six coordinated vertex.

that in these layers perpendicular to the (1,1,1) axis none of the octahedra is directly connected to any other octahedron in that same layer. Actually, all results we will derive only require that every vertex is connected to three vertices in the layer below and to three vertices in the layer above its own layer. Hence, the results will also apply to cubic and hexagonal close packings of the vertices (although the space group of the total structure will in general be lower even in the high-temperature phase).

Instead of considering the direction of the edges, we will specify a state of a vertex by drawing (+) and (-) lines along its connected edges. A (+) line is drawn along an edge when the projection of its orientation on the (1,1,1) axis is up and otherwise a (-) line is drawn. In fact we will connect every (+) line below the central atom with an arbitrary (+) line above the central atom, and likewise for the (-) lines, such that we have three lines [(+) or (-) or any combination] running from the lower triangle through the octahedron to the upper triangle [all of course still viewed along the (1,1,1) axis]. It is then clear that every possible configuration of lines specifies a state of the vertex, although some line configurations may specify the same state. If we connect all lines coinciding on the same edge, we get in total $3n$ lines describing the state of the system, where we have n octahedra per layer. The two vertex configurations with energy zero have either three (+) lines or three (-) lines running through them, whereas all other configurations have either two (+) and one (-) lines or one (+) and two (-) lines running through them. First it will be shown that below T_c the internal energy per site and the entropy per site equal zero.

3. THE FREE ENERGY BELOW T_c

If we have N vertices in the system and call the number of vertices with three (+) lines running through them N_{3+} , the number of vertices with two (+) lines N_{2+} , the number of vertices with one (+) line N_{2-} , and those with no (+) lines N_{3-} , we find that $N = N_{3+} + N_{3-} + N_{2+} + N_{2-}$. The partition function has the following form:

$$Z(T) = \sum_{\text{states}} e^{-(N_{2+} + N_{2-})K}, \quad K = \frac{\varepsilon}{kT} \quad (1)$$

We define T_c as

$$kT_c = \frac{\varepsilon}{\ln 3} \quad (2)$$

which, as will become apparent later, is indeed the critical temperature. Instead of summing over the possible states in (1), we will sum over the

possible line configurations. Since many line configurations specify the same state, we must correct for this. Three (+) lines can run through a vertex in six different ways [the same goes for three (-) lines] still specifying the same edge directions around the vertex. Two (+) lines [and also two (-) lines] can run through a vertex in two different ways for a given edge configuration. Hence we find

$$\begin{aligned} Z(T) &= \sum_{\text{lines}} 6^{-(N_{3+} + N_{3-})} 2^{-(N_{2+} + N_{2-})} e^{-(N_{2+} + N_{2-})K} \\ &= \sum_{\text{lines}} 6^{-N} 2^{-N} e^{-(N_{2+} + N_{2-})(K - \ln 6)} e^{(N_{3+} + N_{3-}) \ln 2} \end{aligned} \tag{3}$$

At T_c this leads to

$$Z(T_c) = \sum_{\text{lines}} 6^{-N} 2^{-N} e^{N \ln 2} = \sum_{\text{lines}} 6^{-N} \tag{4}$$

We now just have to count the number of possible different line configurations. If the lines were indistinguishable, three lines could run at six different ways through every vertex, leading to 6^N different line configurations. Since every one of the $3n$ lines may be either (+) or (-), we find in total $2^{3n} 6^N$ possible line configurations. Therefore

$$Z(T_c) = 2^{3n} \tag{5}$$

If we take the thermodynamic limit $N \rightarrow \infty$ such that $n/N \rightarrow 0$, then

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z(T_c) = 0 \tag{6}$$

$Z(T)$ is a monotonic increasing function, because all its terms in the summation (1) are positive and increase with temperature. When $T \rightarrow 0$ all contributions to $Z(T)$ of the states with N_{2+} or N_{2-} larger than zero vanish, such that only two states remain with $N_{3+} = N$ and $N_{3-} = N$. Hence

$$\lim_{T \rightarrow 0} \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z(T) = 0 \tag{7}$$

Because of the following relations, with F the free energy, E the internal energy, and S the entropy:

$$\lim_{N \rightarrow \infty} \frac{-F}{NkT} = \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z(T), \quad \frac{E}{N} = \frac{\partial F / NkT}{\partial 1/kT}, \quad \frac{S}{N} = -\frac{1}{N} \frac{\partial F}{\partial T} \tag{8}$$

we find for all $T < T_c$

$$-\frac{F}{NkT} = 0, \quad \frac{E}{N} = 0, \quad \frac{S}{N} = 0, \quad \text{for } T < T_c \quad (9)$$

This can be interpreted as having, below T_c , a frozen state with N_{3+} or N_{3-} configurations, the ferroelectric state. In the next section, an exact high-temperature series expansion of $Z(T)$ will be derived which will then be used to obtain a lower bound for E and S for T approaching T_c from above.

4. EXACT HIGH-TEMPERATURE SERIES EXPANSION OF $Z(T)$

The partition function may be rewritten as follows:

$$Z(T) = \sum_{\text{states}} \prod_{\text{edges } ij} \frac{1}{2} [1 + c_{ij}(\xi_i) c_{ji}(\xi_j)] \prod_{\text{vertices } i} B(\xi_i) \quad (10)$$

where ξ_i specifies the edge configuration around vertex i . The function $B(\xi_i)$ equals 1 when ξ_i consists of three (+) or three (-) lines and e^{-K} otherwise; $c_{ij}(\xi_i)$ equals +1(-1) if the projection of the direction of the edge between vertices i and j as specified by ξ_i is parallel (antiparallel) to the (1,1,1) axis. This means that the quantity $\frac{1}{2} [1 + c_{ij}(\xi_i) c_{ji}(\xi_j)]$ equals 1 when the two edge directions specified by ξ_i and ξ_j are compatible and otherwise equals zero. Hence, we may replace the summation over the states by a summation over all individual possible vertex states. That is,

$$Z(T) = \sum_{\{\xi\}} \prod_{\text{edges } ij} \frac{1}{2} [1 + c_{ij}(\xi_i) c_{ji}(\xi_j)] \prod_{\text{vertices } i} B(\xi_i) \quad (11)$$

If we expand the product over the edges and make use of the fact that the summation of $B(\xi_i)$ over all possible ξ_i equals $(2 + 18e^{-K})$, we obtain

$$Z(T) = \left(\frac{1}{2}\right)^{3N} (2 + 18e^{-K})^N \times \sum_{\text{graphs}} \prod_{\text{vertices } i \in \text{graph}} \left[\sum_{\xi_i} \frac{B(\xi_i)}{2 + 18e^{-K}} \prod_{\text{edges } ij \in \text{graph}} c_{ij}(\xi_i) \right] \quad (12)$$

where the summation is over all subgraphs, not necessarily connected. Now consider the single-vertex summation in brackets. If the order s_i of the vertex i in the graph is odd, there is always, for every state ξ_i , occurring in the summation, another state ξ'_i , for which the product over the edges has

a reversed sign but equal energy. Hence, for s_i odd, the single-vertex summation equals zero. When $s_i=2$ we have to distinguish two cases: both edges may point to either the lower or upper triangle of the octahedron, or they may point to both triangles. In the first case the summation equals $(2 - 6e^{-K})/(2 + 18e^{-K})$ and in the second case $(2 + 2e^{-K})/(2 + 18e^{-K})$. The same applies when $s_i=4$. When $s_i=6$, we find $(2 + 18e^{-K})/(2 + 18e^{-K})$. Therefore, the high-temperature series expansion is

$$Z(T) = \left(\frac{1}{4} + \frac{9}{4}e^{-K}\right)^N \left[1 + \sum_{\text{graphs} \neq \emptyset} \frac{(1 - 3e^{-K})^{g_2 + g_4} (1 + e^{-K})^{j_2 + j_4 - g_2 - g_4}}{(1 + 9e^{-K})^{j_2 + j_4}} \right] \tag{13}$$

where the null graph contribution has been written outside the summation. The variable j_2 denotes the number of vertices of degree two and g_2 the number of vertices whose degree is two and with such a placement of the edges that they all either lie above or below the vertex. The same definition applies to j_4 and g_4 . Note that the summation is only over graphs containing solely vertices of even degree. This means that there exists a Eulerian path through every connected part of the graph. A Eulerian path is a connected path traversing all edges exactly once. This will be used to show that $g_2 + g_4$ is even. If one traverses such a Eulerian path starting at the middle of one edge, the projection of this path on the (1,1,1) axis must contain an even number of reversals of directions to be able to reach this same edge from the other side. A vertex of degree two, not contributing to g_2 , does not give rise to a reversal of direction, whereas it does when it belongs to g_2 . A similar argument applies to vertices of order four. When the order of a vertex is six, it can give rise to either no or two reversals of direction, which is still an even number. Therefore, since the total number of direction reversals must be even, $g_2 + g_4$ must be even. This means that the summation contains only positive terms, leading to

$$Z(T) \geq \left(\frac{1}{4} + \frac{9}{4}e^{-K}\right)^N$$

$$\lim_{N \rightarrow \infty} \left(-\frac{F}{NkT}\right) \geq \ln\left(\frac{1}{4} + \frac{9}{4}e^{-K}\right) \tag{14}$$

$$\lim_{T \downarrow T_c} \lim_{N \rightarrow \infty} \left(-\frac{F}{NkT}\right) = 0$$

Because at T_c the boundary for F equals the exact value, the appropriate derivatives of the lower boundary for F give lower boundaries for E and S . We find

$$\lim_{T \downarrow T_c} \lim_{N \rightarrow \infty} \frac{E}{N} \geq \frac{3}{4} \varepsilon \quad (15)$$

$$\lim_{T \downarrow T_c} \lim_{N \rightarrow \infty} \frac{S}{N} \geq \frac{3}{4} k \ln 3$$

which shows that at T_c the internal energy per site and the entropy per site are discontinuous, proving that at T_c a first-order phase transition occurs.

5. DISCUSSION AND CONCLUSIONS

As we have now established that there is a first-order phase transition in this particular type of 20-vertex model, we must determine the kind of compounds for which the model might be used.

Obviously, one can look for analogs of KDP. In that case the vertex should be an octahedron to which three protons are bonded. The stacking of the vertices may be simple cubic, cubic close-packed, or hexagonal close-packed. The protons should be shared between two octahedra of neighboring layers.

In fact such compounds do exist in the form of salts of H_5IO_6 . The structures of $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ and $\text{Na}_2\text{H}_3\text{IO}_6$ have been determined.^(10,11) In ref. 10 it is also shown that the binding protons do indeed occupy two positions between two octahedra. However, these compounds are reported to be antiferroelectric instead of ferroelectric.⁽¹²⁾ This probably can be ascribed to the fact that the vertex energies in these compounds are different from those assumed here.

A similar ferroelectrically ordered compound is $\text{Na}(\text{H}_3\text{O})\text{H}_3\text{IO}_6$.⁽¹³⁾ Here again our model may not apply, as the oxonium ion binds preferentially to one side of an IO_6 sheet, pushing all bridging protons between sheets to the other side of the sheet. Hence, the vertex energies must be different from those assumed here. We would like to remark, however, that only a few salts have been studied, and it may be possible that different counteranions may give rise to different ordering behavior, as is the case for KDP (ferroelectric) and $\text{NH}_4\text{H}_2\text{PO}_4$ (antiferroelectric).

Another class of compounds to which the model may apply are cubic perovskites, such as CsGeCl_3 . This compound consists of Ge ions with a lone pair, surrounded by six chlorine ions. Every chlorine ion is shared between two Ge ions. The lone pair may point in different directions in the GeCl_6 octahedron, giving rise to different vertex configurations. The chosen

vertex energies may then serve as a (very) crude approximation to the energies of the octahedron, especially when a uniaxial pressure along the (1,1,1) direction is applied, such that two vertex configurations obtain a lower energy than the others (ε is nonzero). CsGeCl₃ indeed shows a paraelectric-ferroelectric phase transition at 428 K,⁽¹⁴⁾ however, at a pressure equal to zero. At zero pressure ε is zero; hence, again this shows that the 20-vertex model cannot be used to describe this specific phase transition, but it might be applicable to a possible variation of T_c with pressure. In this case, it is to be expected that two directions [parallel and antiparallel to (1,1,1)] of the lone pair will have a lower energy than the others. This may indeed change the T_c of the phase transition and probably this change can be related to a single-vertex energy difference ε as is done above. We are aware of the fact that this is all very speculative.

The important result of this work is that we have derived an exact relation between T_c and ε , and that we have shown that the phase transition is of first order, starting only from local properties (the vertex energies) of the lattice.

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