

# Proof of the First Order Phase Transition in the Slater KDP Model

J. F. NAGLE

Department of Physics, Carnegie-Mellon University, Pittsburgh

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**Abstract.** The Slater KDP model defined on d-dimensional tetrahedral lattices is proved to have a phase transition for which the entropy and energy are discontinuous functions at a transition temperature  $kT_c = \varepsilon/\ln 2$ , independent of dimensionality.

## I. Introduction

It has been realized for some time that the Slater KDP model has a first order phase transition at  $kT_c = \varepsilon/\ln 2$ , where  $\varepsilon$  is the anisotropy parameter [1–3]. The exact solutions to the two-dimensional case [4] and a particular one-dimensional case [5] support this, but a rigorous proof has not been given for the general case.

The argument of TAKAHASI [2] and others can be used to establish rigorously the "frozen" nature of the model for  $T < T_c$ . In particular, the following theorem is proved in Section II:

**Theorem 1.** *The limiting energy and entropy per site are zero for  $T < T_c$ , i.e.*

$$\lim_{N \rightarrow \infty} E/N = 0 \quad \text{and} \quad \lim_{N \rightarrow \infty} S/N = 0 \quad \text{for all } T < T_c.$$

TAKAHASI'S argument also leaves little doubt that the model "thaws" at  $T_c$  but it appears very difficult to prove this rigorously. Instead, in Section III use is made of the exact high temperature series expansion to prove

**Theorem 2.**

$$\lim_{T \rightarrow T_c^+} \lim_{N \rightarrow \infty} E/N \geq \varepsilon/2 \quad \text{and} \quad \lim_{T \rightarrow T_c^+} \lim_{N \rightarrow \infty} S/N \geq (k/2) \ln 2.$$

From Theorems 1 and 2 it follows that the energy per site  $E/N$  and the entropy per site  $S/N$  are discontinuous at  $T_c = \varepsilon/k \ln 2$ , which is the definition of a first order phase transition.

## II. Low Temperature Thermodynamic Behaviour

Let us first specify certain necessary properties of the crystal lattice and introduce some terminology. Of course, the crystal lattice must be four-coordinated so that the ice rule may be used<sup>1</sup>. Further, there must be an anisotropic  $c$ -axis so that two of the six possible  $\text{H}_2\text{PO}_4$  configurations (vertex configurations) at a given lattice site have zero energy, namely those vertex configurations with dipoles directed parallel or antiparallel to the  $c$ -axis, whereas the other four vertex configurations at a lattice site have energy  $\varepsilon$ . We also require that the lattice be such that the ground state has total energy  $E = 0$ . We choose "cylindrical" boundary conditions with the  $c$ -axis parallel to the cylinder axis; that is, periodic boundary conditions are imposed in  $(d - 1)$  coordinate directions; it is not important whether periodic boundary conditions are also imposed in the  $c$ -axis direction as well. A typical example which satisfies these conditions is shown in Fig. for the two-dimensional case. The usual three-dimensional case involves the diamond, i.e. tetrahedral lattice. Also, let  $N$  be the total number of sites on the lattice and  $n$  be the number of sites in a  $(d - 1)$  dimensional layer perpendicular to the  $c$ -axis and  $m$  be the number of sites in a column along the  $c$ -axis, so  $N = nm$ .

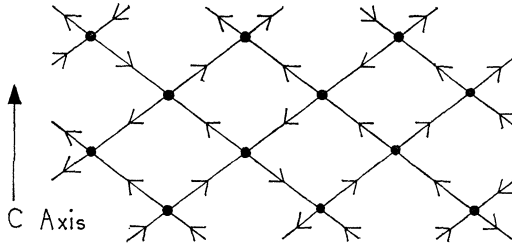


Fig. 1. A two-dimensional example of the kind of lattice considered in this paper. Because of the periodic boundary conditions the half-bonds on the right of the figure are joined to the half-bonds on the left. The particular arrow, i.e. H-bonded, configuration shown corresponds to four (+) chains and two (-) chains

The low temperature partition function is given by

$$Z(T) = \sum_{\text{states}} e^{-N_0 K} \quad (1)$$

where  $K = \varepsilon/kT$  and the sum is over all states of the system consistent with the ice rules. The state function  $N_0$  is the number of vertex configurations which have energy  $\varepsilon$ . Also, the state functions  $N_+$  and  $N_-$

<sup>1</sup> References 1—5 give a basic description of the Slater KDP model which will not be repeated here.

are the number of vertex configurations which point parallel and antiparallel, respectively, to the  $c$ -axis; thus,  $N = N_0 + N_+ + N_-$ .

We now follow TAKAHASI [2] who described the states of the lattice in terms of sets of  $2n$  chains of length  $m$ . Each chain consists of a connected sequence of hydrogen bonds, one from each  $(d - 1)$  dimensional layer in the lattice. Each chain is either a (+) chain or a (-) chain. All the directed hydrogen bonds in (+) chains have projections onto the  $c$ -axis which are parallel to the  $c$ -axis. All the directed hydrogen bonds in (-) chains have projections onto the  $c$ -axis which are antiparallel to the  $c$ -axis. To put the argument another way, a vertex configuration with dipole pointing parallel to the  $c$ -axis must arise from the intersection of two (+) chains whereas a vertex configuration with dipole antiparallel to the  $c$ -axis must arise from the intersection of two (-) chains. Other vertex configurations with dipole perpendicular to the  $c$ -axis must be the intersection of one (+) chain and one (-) chain.

Clearly each configuration of (+) and (-) chains specifies a state of the system and because of the ice rule each state of the system is specified by some chain configuration. However, many chain configurations may specify the same state. In particular, two (+) chains (or two (-) chains) can intersect at a site in two ways, each way specifying the same hydrogen bond directions. On the other hand given specified hydrogen bond directions a (+) chain and a (-) chain may intersect in at most one way at a site. Therefore, the partition function can be written as a sum over chain configurations, with a factor to correct for overcounting, as follows:

$$Z(T) = \sum_{\text{chains}} 2^{-(N_+ + N_-)} e^{-N_0 K} = (\mathbf{1}/2)^N \sum_{\text{chains}} \exp[N_0(\ln 2 - K)], \quad (2)$$

where the last equality follows trivially from  $N = N_+ + N_- + N_0$ .

Let us evaluate  $Z(T)$  when  $T = T_c$ , i.e. when  $K = \ln 2$ . From Eq. (2)  $Z(T_c)$  is the number of chain configurations divided by  $2^N$ . First consider the number of chain configurations if the (+) and (-) chains are indistinguishable. Since there are precisely 2 ways to thread two chains through each of the  $N$  sites of the lattice, this number is just  $2^N$ . Taking into account the distinguishability of (+) and (-) chains then gives  $Z(T_c) = 2^{N+2n}/2^N = 2^{2n}$ .

Since the lowest energy of a state is zero,  $Z(T)$  in Eq. (1) is a monotonically increasing function of  $T$ . Also, it is usual to take the limit of large lattices in such a way that  $\lim n/N = 0$  as  $N \rightarrow \infty$ . Thus  $\lim_{N \rightarrow \infty} (-F/NkT) = \lim_{N \rightarrow \infty} (1/N) \ln Z(T) = 0$  for all  $T < T_c$ . Hence,  $E/N = -\partial(F/NkT)/\partial\beta = 0$  and  $S/N = -\partial F/\partial T = 0$  and Theorem 1 is proved.

Eq. (2) also provides insight into the behavior of the model for  $T > T_c$ . It seems plausible that a finite fraction of chain configurations should have a finite fraction  $b = N_0/N$  of  $N_0$  sites and this is sufficient for the  $\lim_{N \rightarrow \infty} (1/N) \ln Z(T)$  to go like  $b(\log 2 - K)$  for  $T > T_c$ . However, attempts to prove this statement involve one in a morass of knotty geometrical problems.

### III. High Temperature Thermodynamic Behaviour

Let us recall the exact high temperature series expansion which is an identity derived in Ref. [3]. (A shorter way to obtain this identity is outlined in the appendix.)

$$Z(T) = \left(\frac{1}{2} + e^{-K}\right)^N \left[1 + \sum_{\substack{\text{graphs} \\ \neq \emptyset}} \frac{(1 - 2e^{-K})^g}{(1 + 2e^{-K})^j}\right] \quad (3)$$

where the sum is performed over all subgraphs of the lattice (not necessarily connected) with the restriction that any subgraph with any vertices of degrees one or three is neglected. (The contribution of the null subgraph is explicitly written outside the sum.) The weight of a graph in Eq. (3) requires the number of vertices,  $j$ , of degree two in the graph and the number of vertices,  $g$ , of degree two which additionally are local maxima or minima of the graph with respect to the  $c$ -axis, i.e. the two bonds incident to the vertex which are contained in the graph are in the same horizontal layer of the crystal lattice. For the remaining  $j - g$  vertices of degree two contained in the graph the two incident bonds come from adjacent layers.

First we prove that  $g$  is even for any connected piece of a graph and therefore for any graph. A connected graph which has only vertices of even degree (two and four in our case) is an Eulerian cycle which may be traced using each edge once and only once such that one finishes at the place where one started and one does not lift one's pen from the paper, i.e. an Eulerian cycle is a closed, continuous walk on the lattice. Now, project onto the  $c$ -axis any one such walk, where for convenience we require that the starting point is at the middle of some bond. Then, clearly the projection is a one-dimensional walk and the number of immediate reversals in direction of such a walk must be even with the starting condition which we have required. Now, the number of such reversals modulo 2 must be the same as  $g$  modulo 2. The reason that the modulo 2 is required is that each vertex of degree four in the original lattice can give rise to either zero or two reversals in the projected walk. Even so, this suffices to prove that  $g$  is even.

It now follows from Eq. (3) and  $g$  even that  $Z(T) \geq \left(\frac{1}{2} + e^{-K}\right)^N$  or that

$$\lim_{N \rightarrow \infty} (-F/kTN) \geq \ln \left(\frac{1}{2} + e^{-K}\right). \quad (4)$$

In addition it is necessary that the free energy  $F/N$  be continuous at  $T_c$  in order to satisfy the convexity requirement of the partition function. Thus,

$$\lim_{T \rightarrow T_c +} \lim_{N \rightarrow \infty} (-F/NkT) = 0 \quad (5)$$

From (4) and (5) it follows that in the limit  $T \rightarrow T_c +$  the energy and entropy per site can be bounded below by taking appropriate derivatives of the right hand side of (4), thus yielding the results stated in Theorem II.

### Appendix: Derivation of Eq. (3)

This derivation of the high temperature series expansion follows the derivation of the ice series expansion in Ref. [6] rather than the more cumbersome derivation in Ref. [3]. One writes the identity

$$Z(T) = \sum_{\text{states}} \prod_{\text{edges } ij} (1/2) [1 + c_{ij}(\xi_i) c_{ji}(\xi_j)] \prod_{\text{vertices } i} B(\xi_i), \quad (6)$$

where  $\xi_i$  describes the vertex configurations at vertex  $i$ .  $B(\xi_i) = e^{-k}$  or 1 depending on whether the vertex configuration  $\xi_i$  has energy  $\varepsilon$  or 0. A convenient way to specify  $c_{ij}(\xi_i)$  is that it is +1 (-1) if the vertex configuration  $\xi_i$  directs the  $ij$  bond so that its projection onto the  $c$ -axis is parallel (antiparallel) to the  $c$ -axis. Thus, the product  $c_{ij}(\xi_i) c_{ji}(\xi_j)$  is +1 (-1) if the vertex configurations  $\xi_i$  and  $\xi_j$  of neighboring vertices  $i$  and  $j$  are compatible (incompatible) along the bond  $ij$ . (Thus, the weights of states with two or no hydrogens on any bond are zero in (4) as they should be.) Expansion of the product in Eq. (6) yields

$$Z(T) = (1/2)^{2N} (2 + 4e^{-K})^N \sum_{\text{graphs}} \prod_{\text{vertices } i} \left[ \sum_{\xi_i} \frac{B(\xi_i) [c_{ij}(\xi_i)]^{s_i}}{2 + 4e^{-K}} \right] \quad (7)$$

where  $s_i$  is the degree of the  $i$ th vertex in the graph. The single vertex configuration summation in square brackets yields 0 if  $s_i = 1$  or 3 or 1 if  $s_i = 4$ . If  $s_i = 2$  and the vertex is a local maximum or minimum the sum yields  $(1 - 2e^{-k})/(1 + 2e^{-k})$ ; otherwise it yields  $1/(1 + 2e^{-k})$ . Thus, Eq. (3) follows from Eq. (7).

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J. F. NAGLE  
Department of Physics  
Carnegie-Mellon University  
Pittsburgh, Pennsylvania 15213, USA