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A vertex model for hydrogen-bonded solvents or molecules with hydrophobic and hydrophilic ends

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Abstract. A model for hydrogen-bonded solvents or molecules with hydrophobic and hydrophilic ends is considered in which the bonds of a square or cubic lattice are completely occupied by molecules with two chemically different types of ends. These molecules are represented by arrows. Molecules on neighbouring bonds exhibit angle dependent head-to-tail interactions. The resulting vertex model can be transformed into an Ising model on a line graph. A method due to Heilmann is used to prove that certain regions of parameter space are free of phase transitions. Reflection positivity and the Peierls argument are used to prove the existence of phase transitions in other regions of parameter space.

1. Introduction

We consider a square lattice $\Lambda = \{(a, b)\colon a, b = 0, \ldots, M-1\}$ with periodic boundary conditions and assume that each of its bonds is covered by a 'linear' asymmetric molecule with two different chemically active ends. If the molecules are represented as arrows, and if only neighbouring molecules interact, then the model is equivalent to the 16-vertex model (Lieb and Wu 1972). (We also consider a three-dimensional version of the model on the simple cubic lattice).

If we allow only 'head-to-tail' interactions between neighbouring molecules, the model can perhaps be used to study a hydrogen-bonded solvent or a system of molecules each of which contains both a hydrophobic and a hydrophilic end. Since interaction energies between such molecules are angle-dependent, we will assume the interaction energy between two neighboring molecules in our model is $-I'$ if the molecules are parallel and $-I$ if they are perpendicular.

Table 1 lists the four different vertex energies which can occur in this two-dimensional 16-vertex model, and table 2 lists the six different vertex energies which

Table 1. The four different vertex energies possible in the two-dimensional model with angle-dependent, head-to-tail interactions.

$e_a = -2I - 2I'$
$e_b = 0$
$e_c = -4I$
$e_d = -2I - I'$

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Table 2. The six different vertex energies possible in the three-dimensional model with angle-dependent, head-to-tail interactions.

$e_f = -6I - 3I'$
$e_g = 0$
$e_h = -8I$
$e_i = -8I - I'$
$e_j = -4I - I'$
$e_k = -6I - 2I'$

can occur in the corresponding three-dimensional 64-vertex model. Using the numbering convention of Lieb and Wu (1972) for the configurations of the two-dimensional 16-vertex model, we find that configurations 1–4 have energy e_a, configurations 5 and 6 have energy e_c, configurations 7 and 8 have energy e_b, and configurations 9–16 have energy e_d.

In two dimensions it is straightforward to show that the ground states are composed of configurations having vertex energies equal to

$$e_a \quad \text{if} \quad I' > |I|,$$

$$e_b \quad \text{if} \quad I' < |I|, I < 0,$$

$$e_c \quad \text{if} \quad I' < |I|, I > 0.$$

In three dimensions the ground states are composed of configurations having vertex energies equal to

$$e_f \quad \text{if} \quad I' > \max\{I, -2I\}$$

$$e_g \quad \text{if} \quad I < \min\{0, -I'/2\},$$

$$e_h \quad \text{if} \quad I > 0, I' < 0,$$

$$e_i \quad \text{if} \quad 0 < I' < I.$$

The regions of the $(I, I', T = 0)$ plane corresponding to different ground states are illustrated for the two-dimensional model in figure 1 and for the three-dimensional model in figure 2.

In § 2 we shall use an argument due to Heilmann (1971) to show that the grand partition function is free of zeros in two dimensions if $I' > |I|$ and in three dimensions if $I' > I > 0$. In particular, if the model is used to model hydrogen-bonded solvents, for which I and I' are both positive, then there is no phase transition so long as a bond between parallel molecules is stronger than a bond between perpendicular molecules.

The ground state of our model is two-fold dengerate in regions in which the ground state is composed of vertices with energy e_b or e_c in two-dimensions or is composed of vertices with energy e_g in three dimensions. Other regions have highly degenerate ground states.

In § 3 we use reflection positivity combined with the Peierls argument (Fröhlich *et al* 1980) to prove the existence of multiple equilibrium states in the model at sufficiently low temperature for regions of (I, I', T) space with a corresponding ground state which is two-fold degenerate. This indicates the existence of an order–disorder phase transition in the model for such a range of the parameters I and I'. In particular, if

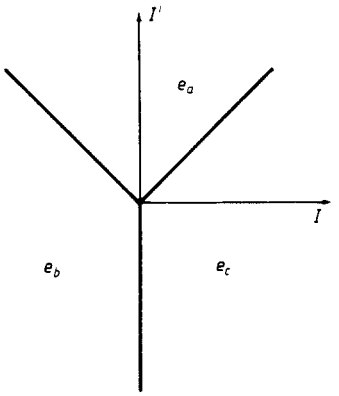

Figure 1. Regions of the $(I, I', T=0)$ plane which correspond to different ground states in the two-dimensional model.

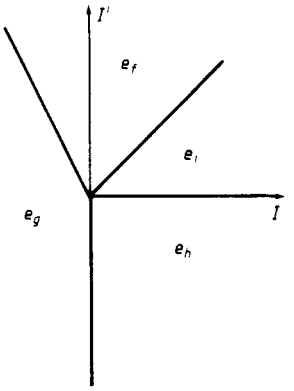

Figure 2. Regions of the $(I, I', T=0)$ plane which correspond to different ground states in the three-dimensional model.

the model is used to model the cooperative effects of repulsive hydrophobic–hydrophilic interactions, then there is an order–disorder transition in the model. In the ordered phase, each site of one sublattice of Λ is surrounded by only hyrophobic ends of molecules, the sites of the other sublattice being surrounded by only hydrophilic ends of molecules.

2. Transition-free regions of (I, I', T) space

Consider the lattice Λ' with sites at the midpoints of the bonds of Λ and with bonds between sites if molecules on the sites could interact. Λ' then forms a line graph (Heilmann 1971). A portion of Λ' for the two-dimensional case is illustrated in figure 3.

The square and simple cubic lattices Λ can each be considered to be composed of two sublattices, α and β, such that every bond of Λ connects a site of the α sublattice with a site of the β sublattice. If an arrow on a bond of Λ points away from (toward)

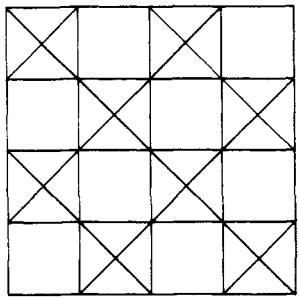

Figure 3. A portion of the lattice Λ' for the two-dimensional model.

a site of the α sublattice of Λ, we shall associate a spin variable $\sigma_i = +1$ ($\sigma_i = -1$) with the site $i \in \Lambda'$ which is at the midpoint of the bond of Λ. The Hamiltonian for our model can then be written as

$$H = -I \sum_{\mathrm{NN}}{}' 1/2(1-\sigma_i\sigma_j) - I' \sum_{\mathrm{NNN}}{}' 1/2(1-\sigma_i\sigma_j). \tag{1}$$

Here the first sum is over the first-neighbour bonds of Λ', and the second sum is over the second-neighbour bonds of Λ'. Thus, except for a constant term, our model is equivalent to a spin-$\frac{1}{2}$ Ising model on Λ' with coupling constants $\frac{1}{2}I$ on first-neighbour bonds and $\frac{1}{2}I'$ on second-neighbour bonds.

Heilmann (1971) examined the distribution of zeros of the partition functions of antiferromagnetic Ising models on line graphs. As an example of an extension of his theorem 3, he considers the two-dimensional Ising model on Λ' with Hamiltonian given by equation (1) above. He proves the model has no transition if $I' > I > 0$.

His induction argument for this case follows his method of proving theorem 3, but first raises ($0 \rightarrow I^*$) the edge weights of each two-site complete graph connecting second neighbours of Λ', then raises the edge weights ($0 \rightarrow I$) of the four-site complete graphs. The result is to prove that an Ising model on Λ', with first-neighbour couplings equal to $I > 0$ and second-neighbour couplings equal to $I' = I + I^* > I$, has no phase transition.

Precisely the same method can be used to prove our three-dimensional model has no transition if $I' > I > 0$. Hence there is no transition in our model for hydrogen bonded solvents so long as the bond between parallel molecules is stronger than the bond between perpendicular molecules.

For the two-dimensional case, flipping all vertical spins changes the sign of the NN term in equation (1) but leaves the NNN term unaffected. Hence the partition function is an even function of I. There is therefore no transition in the two-dimensional model for $I' > |I|$.

3. Reflection positivity and the Peierls argument

Brascamp *et al* (1973) have proved the existence of a phase transition in the general 16-vertex model for the case when configurations 5 and 6 are dominant. These configurations in our model have energy e_c. Their result, combined with the fact that the partition function for the two-dimensional version of our model is an even function of I, is sufficient to prove the existence of a transition in the model so long as the

ground state is composed of configurations in which every vertex has energy e_b or every vertex has energy e_c. Using reflection positivity, we shall give an alternative proof of their result which does not use the fact that the partition function is an even function of I and which is easily extended to the three-dimensional version of our model.

Reflection positivity combined with the Peierls argument (Fröhlich *et al* 1980) can be used to prove the existence of multiple equilibrium states at sufficiently low temperature for cases in which the ground state is two-fold degenerate. Stilck (1983) has recently applied this method to a class of 16-vertex models. Here we shall use an argument which is essentially the same as presented by Huckaby and Kowalski (1984). We outline the argument here for the two-dimensional case. The three-dimensional case proceeds in a similar fashion.

We consider the model defined on the lattice Λ, but with Ising spins on the bond midpoints. The Hamiltonian is then given by equation (1).

We define reflection lines $R_a^{\pm}$ for $0 \leqslant a \leqslant M-1$ as $R_a^- = \{(a+1/2, y): y \in \mathbb{R}\}$ and $R_a^+ = R_{a+M}^-$. There is a natural involution $\theta_a: (x, y) \to (2a+1-x, y)$ which reflects the coordinates through the reflection lines $R_a^{\pm}$. The Hamiltonian can be written as $H = H_a^+ + \theta_a H_a^+$, where H_a^+ is the Hamiltonian restricted to the region $\Lambda_a^+ = \{(x, y): M+a+\frac{1}{2} \leqslant x \leqslant 2M+a+\frac{1}{2}, y \in \mathbb{R}\}$ and $\theta_a H_a^+$ is the Hamiltonian on Λ_a^+ after the spins at the bond midpoints have been reflected by θ_a. As a consequence, the model satisfies reflection positivity (Fröhlich *et al* 1980).

A square-shaped region of Λ with centre at a lattice site $r = (a, b) \in \Lambda$ and with vertices at $(a \pm \frac{1}{2}, b \pm \frac{1}{2})$ shall be called a *square* S_r. If, in a configuration ξ, a square has spins on its edges which are compatible with a ground state configuration, the square is said to be a *ground state square*. Otherwise, it is said to be a *disordered square*. Reflection positivity can then be used to show that the probability a set of L squares in a configuration are all disordered squares is less than g^L, where $g < 4\,e^{-\alpha/kT}$. Here $\alpha = H_* - H_0 > 0$, where H_0 is the Hamiltonian restricted to a ground state square, and H_* is the smallest value of the Hamiltonian restricted to a disordered square.

If a disordered square and a ground state square share an edge, the edge is said to be a contour segment. Two contour segments are connected if they share a common end, and if they divide into two sets the four squares with which they share a vertex, such that one of the two sets contains only ground state squares. The latter stipulation prevents the branching of contours.

Suppose $S_r(\xi)$ is a ground state square and $S_{r'}(\xi)$ is in a configuration which does not belong to the same ground state as $S_r(\xi)$. Then either $S_r(\xi)$ or $S_{r'}(\xi)$ is surrounded by a closed contour γ composed of $L \geqslant 4$ segments. Since each contour segment is bordered by a disordered square, and since no disordered square is bordered by more than four contour segments, then γ borders at least $\frac{1}{4}L$ disordered squares. Therefore, a contour of length L occurs with probability less than $g^{L/4}$.

The probability that a configuration about $S_{r'}(\xi)$ is not in a ground state configuration compatable with the ground state square $S_r(\xi)$ is less than

$$h(\alpha/kT) = \sum_{L=4} g^{L/4} n(L) L, \tag{2}$$

where $n(L) < (\frac{4}{3})3^L$ is the maximum number of contours composed of L segments which can be generated beginning at a certain square. The factor L results since all such contours can be generated beginning at one of $\frac{1}{2}L$ squares connected in a straight line to r or to r'.

The probability $P(\alpha/kT)$ that $S_r(\xi)$ and $S_{r'}(\xi)$ are both ground state squares belonging to the same ground state is then bounded as

$$P(\alpha/kT) > f(\alpha/kT) = [1 - g(\alpha/kT)][1 - h(\alpha/kT)]. \tag{3}$$

If T_0 is the positive real solution of the equation $f(\alpha/kT_0) = \frac{1}{2}$, then $P(\alpha/kT) > \frac{1}{2}$ if $T < T_0$, and an ordered phase with a two-fold degenerate equilibrium state exists in which most of the squares of Λ belong to the same ground state configuration.

4. Discussion

We have proved that the two-dimensional model has no transition when the ground state is composed of configurations in which each vertex has energy e_a, and has an order–disorder transition when the ground state is composed of configurations in which each vertex has energy e_b or each vertex has energy e_c. This accounts for the entire $(I, I', T = 0)$ plane as illustrated in figure 1.

We have shown that the three-dimensional model has a transition when the ground state is composed of configurations in which each vertex has energy e_g and has no transition when the ground state is composed of configurations with each vertex having enegy e_f with $I > 0$. The remaining regions of the $(I, I', T = 0)$ plane have highly degenerate ground states, but we have not proved whether or not a phase transition occurs as the temperature is raised in these regions.

Further research is planned for these models for the case of two components. Two subsequent phase transitions can then occur for some ranges of the interaction parameters and chemical potentials.

Acknowledgments

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