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Lattice Models of Hydrogen-Bonded Solvents. II

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We consider a lattice model of a binary mixture in which each molecule of one component can form zero, one, or two bonds to molecules of the same species on neighboring vertices of the square lattice. We allow the energy of molecules with two bonds to depend on the valence angle, thus generalizing the first paper in this series. If "straight" polymeric configurations are favored over all others, then a phase transition occurs for low enough temperature. On the other hand, if bent configurations are favored, there is no phase transition. Analogous results are obtained for the hexagonal lattice, where we distinguish energetically between *cis* and *trans* isomerism of four bonded molecules.

KEY WORDS: Polymer; hydrogen bond; phase transition; liquid crystals; zeros of partition function; lattice model; ferroelectric model; 16-vertex problem.

1. INTRODUCTION

In a recent paper,$^{(1)}$ referred to hereafter as I, we described a class of lattice models for binary mixtures with structural constraints. For the chain polymer model on a lattice or graph any vertex may be left unoccupied or covered with one or at most two dimers, and in the latter case, the vertex energy is *independent* of the angle between two dimers. Each edge may be empty or covered with a single dimer. The model is thus a natural extension, in which

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the hard dimers are softened, of the monomer–dimer problem analyzed by Heilmann and Lieb.(2) The main result established in I is that such systems cannot undergo phase transitions. This raises the intriguing possibility that a phase transition might be induced by allowing the vertex Boltzmann weights to depend on the angle between two contiguous dimers. On the square lattice, for instance, if the "straight" vertices are favored over the "bent" ones, then one might have a phase transition with two coexisting states at low temperature consisting of mainly straight polymers, the states being related by a rotation through $\pi/2$ radians. Possible physical applications might be found in liquid crystals(3) and in silicate structures. In the second section of this paper we shall establish rigorously the existence of such phase transitions by means of the Peierls argument with the reflection principle recently introduced by Heilmann.(4) We have also shown that if the bent vertex configurations are favored, then there is no phase transition. This is reported in Section 3; it is an extension of the monomer–dimer argument used in I.

In Section 4 we consider the analogous features on the hexagonal lattice. Here we must consider the energies of groups of three consecutive chains: If the *trans* conformation is favored over *cis*, then there is a phase transition.

2. THE 11-VERTEX PROBLEM ON A SQUARE LATTICE: PEIERLS' ARGUMENT

In the 11-vertex problem only the subset shown in Fig. 1 of the complete set of 16 vertices(5) is allowed. Below each vertex the equivalent polymer configuration is given. The weight for a canonical ensemble with temperature T is given in terms of vertex energies ϵ by

$$\omega_j = e^{-\epsilon_j/kT} \tag{1}$$

k being the Boltzmann constant. The model which we consider satisfies the obvious symmetry restrictions:

$$\begin{aligned} \omega_3 &= \omega_4 &&= w_s \\ \omega_5 &= \omega_6 = \omega_7 = \omega_8 &&= w_b \\ \omega_9 &= \omega_{10} = \omega_{11} = \omega_{12} &&= w_1 \end{aligned} \tag{2}$$

Further, we take

$$\omega_1 = 1 + z_0 = w_0 \tag{3}$$

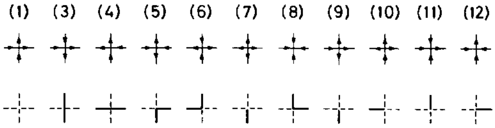

Fig. 1. Allowed vertices and equivalent polymer configurations for the 11-vertex problem.

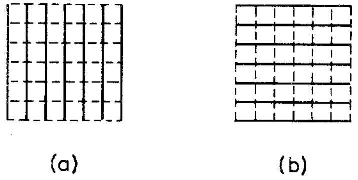

Fig. 2. Ordered structures for the polymer model: (a) has all type 3 vertices, (b) has all type 4 vertices, except at the boundary.

where z_0 is the monomer fugacity, and we have introduced the variable w_0 for convenience. If we take $\omega_2 = 0$, then a generalization of the eight-vertex problem discussed by Baxter$^{(6)}$ is obtained. Baxter's method apparently requires that $\omega_1 = \omega_2$; our model has yet to be solved exactly. Several other modifications have been discussed in I.

In this section we shall define a phase transition as an instability: The state of the system can be altered *in the thermodynamic limit* by a suitable adjustment of the limiting sequence of boundary configurations. This approach is very well reviewed by Gallavotti$^{(7)}$; the connection with analyticity properties, although established for the Ising ferromagnet with pair interactions,$^{(8)}$ is not obvious here.

The Peierls argument$^{(9)}$ is particularly suitable to exploit the definition of phase transition given above. We now list the requirements for using its extension by Heilmann.$^{(4)}$

1. There exist two possible ordered structures, denoted A and B, on the lattice Λ. The A structure has every vertical, but no horizontal, edge of Λ covered. The B structure is obtained mutatis mutandis as shown in Fig. 2.
2. A method of drawing contours can be specified uniquely for a given polymer configuration on Λ. Each contour has a unique energy and the total energy of the system is a sum of contour energies; the contours do not interact. Such a method is summarized in Fig. 3, and an example is given in Fig. 4.

The rules for drawing contours in the present case are actually analogous to the rules for drawing contours for the antiferromagnetic Ising model.$^{(10)}$

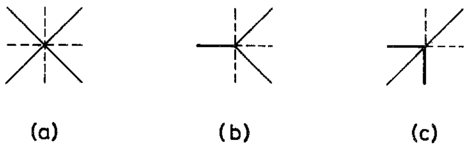

Fig. 3. Construction of contours for the Peierls' argument: The heavy lines indicate polymer segments and the light lines the associated contours on the edges of a square lattice based on the diagonal of Λ.

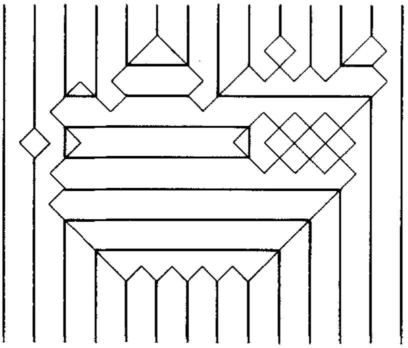

Fig. 4. A typical polymer structure. The light line shows the associated contours.

To see this (following Suzuki and Fisher(11)), one associates with each edge in our model an Ising spin which is up if the edge is covered with a bond and down if it is empty. These spins form a new square lattice with twice as many vertices as the original square lattice and it is easily seen that allowed configurations for the present case are a subset of those allowed for the Ising model.

Unlike the Ising case, the energy $E(C)$ of a contour C depends on its shape, but we can obtain a lower bound to this which is proportional to the contour length $l(C)$; this suffices for the argument. The unit of length for specification of $l(C)$ is half the diagonal of the unit square on Λ. We have

$$E(c) > \epsilon l(C)$$

provided

$$\epsilon = \min\{\tfrac{1}{4}(e_0 - e_3), \tfrac{1}{4}(e_5 - e_3), \tfrac{1}{2}(e_9 - e_3)\} \tag{4}$$

The crux of the argument is to obtain a suitable upper bound on the probability $p(C)$ that an allowed contour C can be found. This can be done using the reflection principle of Heilmann: The reflection plane to be used is a diagonal through the vertices of the square lattice Λ. For further details the reader is referred to the literature.(4)

We deduce the following *theorem*: The model exhibits a phase transition in the sense of instability for β sufficiently large provided

$$w_s > w_b, \qquad w_s > w_0, \qquad w_s > w_1 \tag{5}$$

Evidently, the present method may be applied more generally to the 16-vertex problem(5,11) to show the existence of a phase transition if vertices 3 and 4 are favored over all other vertices. This result supplements the earlier result by Brascamp *et al.*(12) who proved existence of a phase transition if vertices 5 and 6 are favored over all other vertices.

3. ABSENCE OF PHASE TRANSITION: A MONOMER–DIMER ARGUMENT

Another definition of a phase transition is that there is a lack of analyticity in some of the variables of the limiting free energy. We reiterate that this is not necessarily the same as the instability definition exploited in Section 2. But it is well-adapted to the Yang–Lee arguments$^{(13)}$ embodied in the monomer–dimer treatment$^{(2)}$ used in I. These arguments were restricted to the case $w_s = w_b$, for which a phase transition is impossible. Here we show that no phase transition can occur if $w_s \leqslant w_b$, which is to be contrasted with Eq. (5).

The graph (or lattice) Λ is associated with a new graph Λ' obtained by replacing each vertex of Λ by a city$^{(14)}$ containing seven vertices, with edges as shown in Fig. 5. If we choose monomer weights zero for the four vertices in Λ' on which the external edges (the edges on Λ' not within a city) are incident and if an edge in Λ is covered by a dimer when the corresponding external edge in Λ' is empty and vice versa, then each possible monomer–dimer covering of Λ' is associated uniquely with a polymer configuration on Λ which is allowed according to the model.

The edge weights (dimer weights) on the internal edges on Λ' are as shown in Fig. 5; the external edges have weight one. The three internal vertices in a city have the monomer weights given in the legend to Fig. 5. The polymer and monomer–dimer grand partition functions are identical, except for a

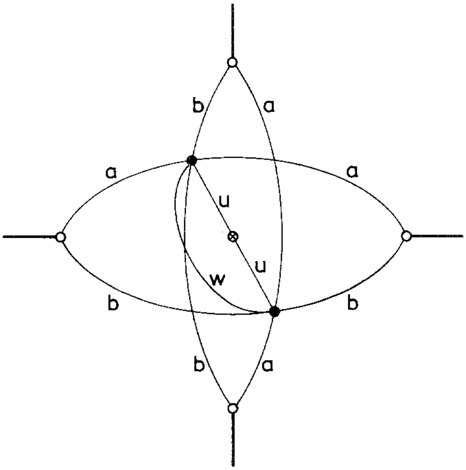

Fig. 5. The city for constructing a monomer–dimer covering equivalent to the 11-vertex problem. The external edges are heavy lines; they have unit edge weight. The remaining edges have the weights shown. The vertices on which the external edges are incident have zero monomer weight. The two dotted vertices have weight m and the vertex marked $\otimes$ has monomer weight m'.

factor f per vertex in Λ, provided that the parameters are related by

$$\begin{aligned} w_b &= (a^2 + b^2)m'f, \qquad & w_s &= 2abm'f \\ w_1 &= (a + b)(u + mm')f, \qquad & w_0 &= (m'w + 2mu + m^2m')f \end{aligned} \tag{6}$$

Heilmann and Lieb$^{(2)}$ have shown that if the edge weights (a, b, u, and w) are real and positive, then the monomer–dimer grand partition function does not vanish if the real parts of the monomer weights have the same sign ($\mathrm{Re}\{m\} > 0$, $\mathrm{Re}\{m'\} > 0$ or $\mathrm{Re}\{m\} < 0$, $\mathrm{Re}\{m'\} < 0$).

It follows from Eqs. (6) that it is possible to choose a, b, u, and w real and positive if w_b, w_s, w_1, and w_0 are real and positive and $w_s \leqslant w_b$. However, in order to discuss analyticity in the w_j, we need to consider complex values of the w_j, which can only be done if we allow complex values of a and b. Unfortunately, the general theorem 4.9 of Ref. 2, which covers the case of complex edge weights, does not allow for some of the monomer weights being zero. In the following we shall prove that the theorem can be extended to cover the present case.

The problem when one wants to extend Theorem 4.9 of Ref. 2 to the case where some monomer weights are zero is to obtain a version of Theorem 4.5 of Ref. 2, which holds with these monomer weights equal to zero. For this purpose we want to prove the following lemma.

Lemma. There exists a constant A which only depends on the numerical value of the dimer weights, a, b, u, and w [Eq. (6)], such that the monomer–dimer partition function $\Xi(m, m'; a, b, w, u|\Lambda')$ cannot be zero if

$$|m| > A, \qquad |m'| > A \tag{7}$$

The constant A is a nonincreasing function of the numerical value of the dimer weights.

Proof of Lemma. In the appendix of I, it was shown how a result due to Gruber and Kunz$^{(15)}$ could be applied to the present type of polymer. As a first step one finds bounds on the sum of the Boltzmann weights of all polymers with given length and covering a fixed vertex. The contribution from linear polymers of length $n + 2$ is bounded by

$$4|w_1|^2(|w_s| + 2|w_b|)^n \times (n + 2)/2, \qquad n \geqslant 0$$

while the contribution from closed polygons of length $n + 2$ is bounded by

$$(|w_s| + 2|w_b|)^n, \qquad n \geqslant 2$$

The next step is to multiply the above contributions with ξ^{n+2} ($\xi > 0$) and sum over n from 0 to ∞; if ξ is chosen as

$$\xi = \eta/(|w_s| + 2|w_b|)$$

with

$$0 < \eta < 1$$

then we obtain the following result for the sum:

$$\hat{S}(\xi) = \frac{|w_1|^2}{(|w_s| + 2|w_b|)^2} \frac{4\eta^2 - 2\eta^3}{(1 - \eta)^2} + \frac{\eta^4}{1 - \eta} \tag{8}$$

Using the result by Gruber and Kunz,(14) we find that the partition function is not zero if

$$|w_0| \geqslant [1 + \hat{S}(\xi)]/\xi$$

When Eqs. (8) and (6) are substituted into this condition the following inequality obtains:

$$\begin{aligned} &|m'w + 2mu + m^2m'|\,|f| \\ &\quad \geqslant 2|m'|\,|f| \frac{\alpha}{\eta}\left(1 + \frac{|a + b|^2|u + mm'|^2}{4\alpha^2|m'|^2} \frac{4\eta^2 - 2\eta^3}{(1 - \eta)^2} + \frac{\eta^4}{1 - \eta}\right) \end{aligned} \tag{9}$$

where

$$\alpha = |a^2 + b^2| + |ab|$$

Rearranging the terms, one finds that the inequality (9) is implied by the following inequality:

$$\begin{aligned} &|m|^2|m'|\left(1 - \frac{2\eta - \eta^2}{(1 - \eta)^2} \frac{|a + b|^2}{\alpha}\right) \\ &\quad > 2|m|\,|u| + |m'|\left[|w| + \frac{2}{\eta}\alpha\left(1 + \frac{\eta^4}{1 - \eta}\right)\right] \\ &\quad + \left(\frac{|u|^2}{|m'|} + 2|u|\,|m|\right) \frac{2\eta - \eta^2}{(1 - \eta)^2} \frac{|a + b|^2}{\alpha} \end{aligned} \tag{10}$$

A simple computation verifies that

$$|a + b|^2/(|a^2 + b^2| + |ab|) < 2$$

for all a and b. By choosing η sufficiently small $[\eta < \frac{1}{4}(3 - \sqrt{5})]$ one has

$$1 - \frac{2\eta - \eta^2}{(1 - \eta)^2} \frac{|a + b|^2}{\alpha} > 0$$

and one can easily verify the lemma from the inequality (10).

Now, using the above lemma in place of Theorem 4.5, it is easy to go through the "Alternative Proof of Theorem 4.9" in Ref. 2 and convince oneself that Theorem 4.9 remains valid in the present case with the constant A from Eq. (17) entering as the constant A in Theorem 4.9 of Ref. 2. The

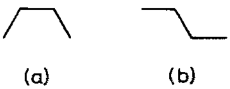

Fig. 6. Three consecutive bonds forming (a) a *cis* configuration and (b) a *trans* configuration.

important conclusion which can be drawn from this theorem is that the free energy for the monomer–dimer problem

$$f(m, m'; a, b, u, w) = \lim_{\Lambda' \to \infty} \frac{1}{|\Lambda'|} \log \Xi(m, m'; a, b, u, w|\Lambda') \tag{11}$$

is jointly real-analytic in m, m', a, b, u, and w for positive values of all six variables.

It follows from Eqs. (6) that if $w_b > w_s$ and all four w_j are real and positive, then the free energy for the polymer problem

$$f(w_s, w_b, w_1, w_0) = \lim_{\Lambda \to \infty} \frac{1}{|\Lambda|} \log \Xi(w_s, w_b, w_1, w_0|\Lambda) \tag{12}$$

is jointly real-analytic in w_s, w_b, w_1, and w_0 for positive values of all four weights.

4. CIS–TRANS ISOMERISM ON THE HEXAGONAL LATTICE

On the hexagonal lattice all the valence angles are 120°; therefore, one does not have the possibility of assigning different weights to different valence angles. In I we tried to let the weights depend on the directions of the bonds. Here we shall choose the physically more interesting possibility of distinguishing between *cis* configurations and *trans* configurations (see Fig. 6).

On each vertex we allow the seven different configurations shown in Fig. 7. To vertex configuration 1, which has no bonds coming in, we attach

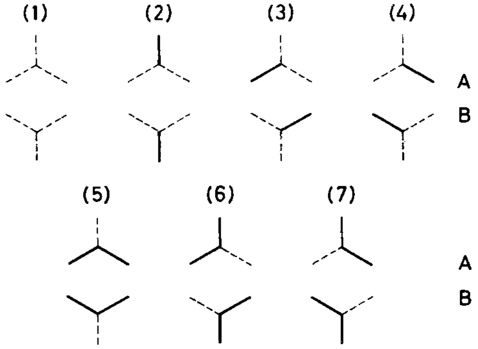

Fig. 7. The seven allowed vertex configurations on the two sublattices of the hexagonal lattice (denoted *A* and *B*, respectively), together with the numbering of the vertex configurations.

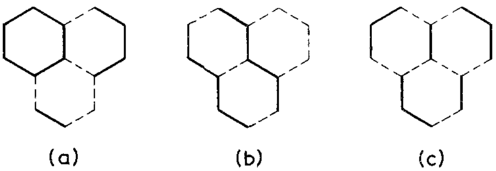

Fig. 8. Three possible configurations on a small part of the hexagonal lattice. The Boltzmann weight of (a) is $w_0 w_1{}^4 w_2{}^8 x_c{}^7$; the Boltzmann weight of (b) is $w_0{}^3 w_1{}^4 w_2{}^6 w_t{}^4$; the Boltzmann weight of (c) is $w_1^{10} w_2{}^3$.

the weight w_0; to the three configurations 2–4, with one bond, we attach the weight w_1; and to the three configurations 5–7, with two bonds, we attach the weight w_2. Finally, for any pair of consecutive vertices in a polymer we include in the Boltzmann weight of the configuration an extra factor w_c if the pair forms a *cis* configuration and an extra factor w_t if the pair forms a *trans* configuration (see Fig. 8 for some examples).

If the *trans* configuration is sufficiently favored over the other possibilities, one will expect to get long, stretched polymers all lined up in one of the three possible directions (Fig. 9). It is therefore natural in this case to look for a phase transition of the same type as the one encountered in Section 2.

In order to apply Peierls' argument we start by defining the appropriate local structure. Here we have three possible ordered states, which we shall denote α, β, and γ. We shall define the local structure by the vertex configuration; configuration 5 corresponds to the α structure, configuration 6 corresponds to the β structure, and configuration 7 corresponds to the γ structure. The remaining four configurations all correspond to disordered structures.

We shall draw the segments of the contours perpendicularly to the edges of the hexagonal lattice from the midpoint of a hexagon to the midpoint of a neighboring hexagon. We shall draw a segment of a contour through an edge if either the edge goes between two vertices with different ordered structure or the edge is incident on at least one vertex with a disordered structure (see Fig. 10). In order to make a one-to-one correspondence between the system of contours and the configuration, it is necessary to include with each contour

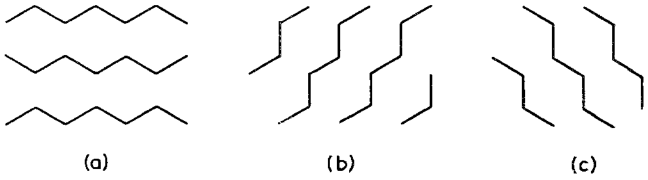

Fig. 9. The three different ordered structures resulting from favoring the *trans* configuration.

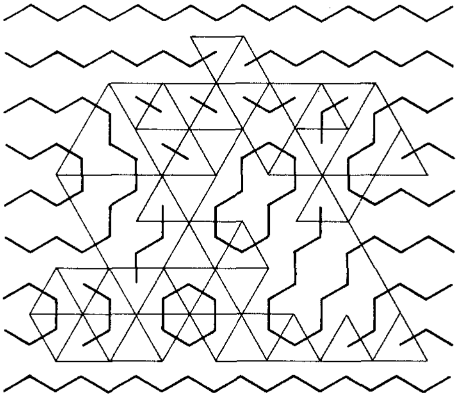

Fig. 10. A configuration of polymers on the hexagonal lattice and the associated contour.

segment information on whether the edge which the piece of contour crosses is empty or covered by a bond.

The next step is to estimate the number of ways of drawing a contour of given length. When a piece of contour is continued one can attach one, two, three, four, or five segments; this can be done in $\binom{5}{1}$, $\binom{5}{2}$, $\binom{5}{3}$, $\binom{5}{4}$, and $\binom{5}{5}$ ways, respectively. We want to get a bound q on the number of ways per segment; this means that we want q to satisfy

$$\binom{5}{1} + \binom{5}{2}\Big/q + \binom{5}{3}\Big/q^2 + \binom{5}{4}\Big/q^3 + \binom{5}{5}\Big/q^4 \leqslant q \tag{13}$$

or

$$[(1 + 1/q)^5 - 1]q \leqslant q \tag{14}$$

This will be so if

$$q = 20/3 \tag{15}$$

The factor η, which takes care of end effects, can in this case be chosen as

$$\eta = 6/q \tag{16}$$

since the first piece of contour can be chosen in six different directions.

Finally, we have to include an extra factor of two per contour segment for the possibility of having the crossed edge either empty or covered. The bound on the number of ways to draw a contour of length N then becomes $0.9(13\frac{1}{3})^N/(2N)$.

The shortest possible contour is obtained if we just take one bond out of an otherwise ordered structure (Fig. 11); this gives $\sigma = 5$.

As the last step in the preparation for the use of Peierls' argument we

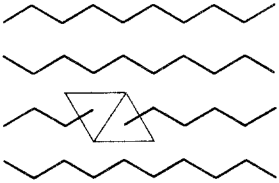

Fig. 11. The shortest contour.

need a lower bound on the energy gained by removing a contour segment. Since we get one segment per *cis* configuration and at most three segments for each vertex with disordered structure, we have

$$\beta\epsilon = \min\{\log(w_t/w_c), \tfrac{1}{3}\log(w_t w_2/w_1), \tfrac{1}{3}\log(w_t w_2/w_0)\} \tag{17}$$

In this case with three ordered structures it is easiest to use rotation of 120° around an axis through a vertex as the symmetry operation which interchanges the order structure, a possibility which is described in Section 5 of Ref. 4.

From this we conclude that there exists a positive constant such that if

$$\beta\epsilon - \log(13\tfrac{1}{3})$$

is larger than this constant, then we will have the possibility of three different ordered states.

One might alternatively have favored the *cis* configuration over the *trans* configuration. This would mean that the most stable polymer would be a hexamer forming a closed hexagon. Since the placement of hexagonal hexamers on the hexagonal lattice is equivalent to the nearest neighbor exclusion problem on the triangular lattice, a problem already treated by Heilmann(16) and Heilmann and Præstgaard,(17) we can safely conclude that the favoring of the *cis* configuration will also lead to a phase transition. We shall not explore this further.

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REFERENCES

1. D. B. Abraham and O. J. Heilmann, *J. Stat. Phys.* **4**:15 (1972).
2. O. J. Heilmann and E. H. Lieb, *Phys. Rev. Lett.* **24**:1412 (1970); *Commun. Math. Phys.* **25**:190 (1972).
3. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford (1974).
4. O. J. Heilmann, *Commun. Math. Phys.* **36**:91 (1974).
5. E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, Vol. I, ed. by C. Domb and M. S. Green, Academic Press, London.

6. R. J. Baxter, *Phys. Rev. Lett.* **26**:832 (1971); *Ann. Phys.* (*N.Y.*) **70**:193 (1972).
7. G. Gallovotti, *Riv. Nuovo Cimento* **2**:133 (1972).
8. J. L. Lebowitz and A. Martin-Löf, *Commun. Math. Phys.* **25**:276 (1972).
9. R. E. Peierls, *Proc. Camb. Phil. Soc.* **32**:477 (1936); R. B. Griffiths, *Phys. Rev.* **136A**:437 (1964); R. L. Dobrushin, *Theor. Prob. and Appl.* **10**(2):209 (1965); and *Vth Symp. Math. Stat. and Prob.*, Vol. 3 (1967), p. 73.
10. R. L. Dobrushin, *Funkcional. Anal. i Priložen* **2**(4):44 (1968) [English transl.: *Functional Anal. Appl.* **2**:302 (1968)].
11. M. Suzuki and M. E. Fisher, *J. Math. Phys.* **12**:235 (1970).
12. H. J. Brascamp, H. Kunz, and F. Y. Wu, *J. Math. Phys.* **14**:1927 (1973).
13. T. D. Lee and C. N. Yang, *Phys. Rev.* **87**:404, 410 (1952).
14. M. E. Fisher, *J. Math. Phys.* **7**:1776 (1966).
15. C. Gruber and H. Kunz, *Commun. Math. Phys.* **22**:133 (1971).
16. O. J. Heilmann, *Lett. Nuovo Cimento* **3**:95 (1972).
17. O. J. Heilmann and E. L. Praestgaard, *J. Stat. Phys.* **9**:23 (1973).