

Lattice Models for Hydrogen-Bonded Solvents

Douglas B. Abraham^{1,2} and Ole J. Heilmann^{1,3}

Received April 30, 1971

A class of lattice models for a binary mixture is defined by assuming that one of the components may form bonds to neighboring molecules of the same species. It is assumed that the fugacity of a molecule depends on the number of bonds which connect the molecule to other molecules. If no molecule is allowed to be connected by more than two bonds to other molecules, then no phase transition occurs, while phase transition can occur if more than two bonds are allowed. If only two or no bonds are allowed, then the model can be solved rigorously for certain planar lattices by transforming it to a dimer covering problem; this model shows behavior similar to the Ising model in zero magnetic field.

KEY WORDS: Polymer; hydrogen bond; phase transition; zeros of partition function; lattice model; binary mixture; ice-rule ferroelectric.

1. INTRODUCTION

Since the monumental achievement of Onsager⁽¹⁾, the Ising model in two dimensions has provided for some time the only reasonably physical statistical mechanical description of the location and nature of a phase transition. This model gave important insight into the problem of critical behavior caused by

Work supported by National Science Foundation grant GP-26526.

¹ Department of Mathematics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

² On leave of absence from Corpus Christi College, Cambridge, England.

³ On leave from the University of Copenhagen. Permanent address: Department of Chemistry, H. C. Ørsted Institute, Copenhagen, Denmark.

attractive forces in liquid-gas systems and binary mixtures of structureless particles. Unfortunately, it gives little insight into the importance of constraints imposed by particle structure. Nevertheless, some rigorous results have been obtained on this problem. They include (1) the solution of the dimer covering problem on a planar lattice⁽²⁾; (2) the proof by Dobrushin⁽³⁾ of the existence of a phase transition in a hard-square model; (3) the proof by Lebowitz and Gallavotti⁽⁴⁾ of the existence of a phase transition in a system of hard rods on a square lattice; (4) the comprehensive treatment of the monomer-dimer problem by Heilmann and Lieb⁽⁵⁾; (5) the ice-rule ferroelectrics⁴ represent a rather different class of system with structural constraints; their statistical mechanical behavior is quite well understood, but little has been published concerning their impact on the theory of binary mixtures.

It is the aim of this paper to present rigorous results on a certain class of lattice models for binary mixtures with structural constraints. The second section describes a "soft" dimer model; this means that any vertex of the lattice may be either unoccupied, or occupied by one or, at most, two dimers. Each edge may be empty or covered by a single dimer. Clearly, this is a natural extension of the monomer-dimer model (which has "hard dimers"). One may, however, establish a more interesting interpretation of the soft dimer system as a model for a binary mixture one of the components of which may form up to two bonds with neighboring molecules of the same species. One might, for example, think of alcohol molecules, which can form hydrogen bonds according to the above prescription. It seems appropriate to call the above a chain-polymer model. The main result of Section 2 is that such a system cannot undergo a phase transition.

In Section 3, this model is generalized by allowing the formation of more than two bonds from a given molecule. The result will be termed the branching-polymer model. In contrast to the chain-polymer model, it can exhibit a phase transition.

Finally, in Section 4, the chain-polymer model will be restricted by only allowing zero or two bonds at each vertex. This will be termed the polygon model. It can be solved rigorously in certain cases on planar lattices. This property also holds for some branching-polymer models if the number of bonds meeting at any vertex is restricted to be either even or odd. This class of system may exhibit critical behavior.

We should like to stress that we do not consider that the class of models described in this paper is new. In fact, one can find ideas along these lines

⁴ For an excellent review, see Ref. 6.

in the book by Hurst and Green⁽⁷⁾; also, Levine and Perram⁽⁸⁾ investigated the statistics of hydrogen bond formation in water using a model of this type.

2. THE CHAIN-POLYMER MODEL

2.1. The Model

In a given graph G , the vertices can either be occupied by a monomer unit or be empty. If two neighboring points are both occupied by a monomer unit, then these two units can be joined by a bond. No monomer unit is allowed to be joined by more than two bonds to other monomers (the condition for chain polymers). Monomer units with zero, one, and two bonds are given fugacities z_0 , z_1 , and z_2 , respectively.

If $z_2 = 0$, then one recovers the monomer-dimer problem.⁽⁵⁾ If $z_1 = 0$, then the case obtains in which only closed polygons are allowed; this will be considered in some detail in a subsequent section. It is possible to assign different fugacities to different vertices and different bond energies to different edges. Just as in the monomer-dimer case,⁽⁵⁾ this will not change essentially the analytical behavior or the principles of the proofs; it will, however, vastly complicate the notation; we shall avoid it in this article. One should note that the analysis in Sections 2 and 3 in general does not work if one allows the energy of a double-bonded monomer to depend on the angle between the bonds.

The *grand canonical partition function* for the model is given by

$$\bar{E}(G; z_0, z_1, z_2) = z_2^N P(G; (1 + z_0)/z_2, z_1/z_2) \quad (1)$$

where N is the number of vertices in G and

$$P(G; x_0, x_1) = \sum_{n=0}^N x_0^n \sum_{j=0}^{(N-n)/2} x_1^{2j} \#(\text{walks}; G, j, N - n) \quad (2)$$

$\#(\text{walks}; G, j, N - n)$ is the number of possible ways to arrange j polymers with free ends and any number of polygons on G such that $N - n$ vertices are covered and no vertex is covered more than once.

The model can be rewritten as a Monomer-Dimer problem on a related graph G' . In order to obtain G' from G , one proceeds as follows (see Fig. 1): The original edges of G are conserved and are given unit edge weights in G' ; they will be called external edges in G' . At each of the vertices in G , a new vertex (external vertex) is added for each of the incident edges such that edges are incident on separate vertices; these vertices are given monomer fugacity zero. Further, two new vertices (internal vertices) are added for each vertex in G ; the two internal vertices are joined together by an edge with edge

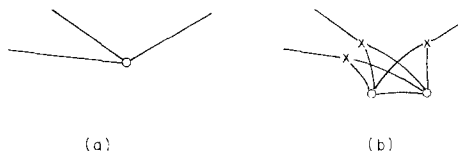


Fig. 1. The transformation from the chain-polymer model to a monomer-dimer problem; (a) a vertex of the graph for the chain-polymer model; (b) the corresponding configuration in the graph for the monomer-dimer problem.

weight w and each of them is joined to all the external vertices originating from the same vertex in G with edges having unit weight. The internal vertices are assigned monomer fugacities m_1 and m_2 respectively.

In the monomer-dimer problem, for a given graph with weights on both edges and vertices, an allowed configuration is any arrangement of dimers on the edges such that two edges incident on the same vertex are not occupied simultaneously. A dimer is supposed to cover the two vertices on which the edge is incident; vertices not occupied by dimers are filled with monomers. The fugacity of a dimer is the edge weight; the fugacity of monomer is the vertex weight. The canonical weight of a configuration is the product of the fugacities.

The correspondence between configurations in the two models will be as follows: a bond along an edge in G corresponds to the absence of a dimer on the same (external) edge in G' . After the dimer configuration on the external edges in G' has been specified thus, one sums over the remaining degrees of freedom in G' , that is, the configurations on the internal vertices. Since the configurations on the pairs of internal vertices are independent of each other, this sum factorizes into separate factors for each of the vertices in G . If $P_{MD}(G')$ is the monomer-dimer partition function for G' , we shall then derive the relation

$$P(G'; x_0, x_1) = f^N P_{MD}(G') \quad (3)$$

by proving that it is possible to choose m_1 , m_2 , w , and f such that for each configuration on G , any vertex in G gives the same contribution as the corresponding subgraph in G' does, aside from a factor f which is independent of the configuration. The appropriate conditions are

$$x_0 = (w + m_1 m_2) f \quad (4)$$

$$x_1 = (m_1 + m_2) f \quad (5)$$

$$1 = 2f \quad (6)$$

or, in a more suggestive form,

$$f = \frac{1}{2} \quad (7)$$

$$m_1 + m_2 = 2x_1 \quad (8)$$

$$m_1 m_2 = 2x_0 - w \quad (9)$$

This shows that we can choose w at will and then determine m_1 and m_2 for any values of x and y .

2.2. A Bound on the Location of Zeros of the Grand Partition Function

According to Heilmann and Lieb,⁽⁵⁾ a sufficient condition for $P_{MD}(G')$ to be nonzero is that the real parts of m_1 and m_2 shall have the same sign. If $P(x)$ is a polynomial in x with complex coefficients, one can readily infer from a theorem by Hermite and Biehler⁵ a necessary and sufficient condition that all the roots of $P(x) = 0$ shall have real parts with the same sign. If one writes

$$P(ix) = Q(x) + iR(x) \quad (10)$$

where $Q(x)$ and $R(x)$ are polynomials with real coefficients, then the condition is that $Q(x)$ and $R(x)$ should have all zeros real and further that the zeros of $Q(x)$ should interlace the zeros of $R(x)$ [this implies that the degrees of $Q(x)$ and $R(x)$ can at most differ by one].

These conditions are applied to the polynomial

$$P(z) = z^2 - 2x_1 z + 2x_0 - w \quad (11)$$

which, according to Eqs. (8) and (9), has zeros at m_1 and m_2 . One obtains

$$P(iz) = -z^2 + 2(\text{Im } x_1)z + 2(\text{Re } x_0) - w + i[-2(\text{Re } x_1)z + 2(\text{Im } x_0)] \quad (12)$$

The zeros of

$$Q(z) = -z^2 + 2(\text{Im } x_1)z + 2(\text{Re } x_0) - w \quad (13)$$

are

$$z = (\text{Im } x_1) \pm [(\text{Im } x_1)^2 + 2(\text{Re } x_0) - w]^{1/2} \quad (14)$$

while

$$R(z) = -2(\text{Re } x_1)z + 2 \text{Im } x_0 \quad (15)$$

⁵ See, e.g., Ref. 9.

has the zero

$$z = (\text{Im } x_0)/\text{Re } x_1 \quad (16)$$

It obviously preferable to choose

$$w = 0 \quad (17)$$

which leads to the following condition (see Fig. 2):

$$2(\text{Re } x_0)(\text{Re } x_1)^2 + 2(\text{Im } x_0)(\text{Im } x_1)(\text{Re } x_1) - (\text{Im } x_0)^2 > 0 \quad (18a)$$

The above discussion implies that the grand canonical partition function cannot be zero if (18a) is satisfied, with

$$x_0 = (1 + z_0)/z_2, \quad x_1 = z_1/z_2 \quad (18b)$$

Since the equivalent monomer-dimer description has zero monomer weights, it is not very useful for the analysis of the behavior for small bond energies, nor is it useful to prove the existence of the thermodynamic limit. For this purpose, it is more expedient to make the transformation to a lattice gas with pair interactions.

Definition. For a given set of points S , one has a mapping from the set K of unordered k -tuples of distinct points in S into the set of nonnegative

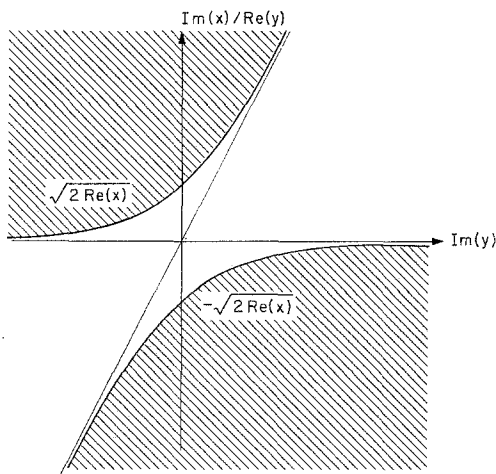


Fig. 2. The bound on the zeros imposed by Eq. (18a). One should take $x = (1 + z_0)/z_2$ and $y = z_1/z_2$. The zeros are confined to the shaded, hyperbolic area; the slope of the oblique asymptote is 2. It is assumed that the real part of x is positive.

real numbers, $z: K \rightarrow R_+$. One defines the subset K_+ of K by $\{k: k \in K, z(k) > 0\}$ and one further has a mapping from the set K_2 of unordered pairs of elements in K_+ into the real numbers, $U: K_2 \rightarrow R$. An allowed configuration of n k -mers on S is then any set of n elements k_1, k_2, \dots, k_n of K_+ such that no point of S occurs in more than one of the n k -tuples k_1, k_2, \dots, k_n . The canonical measure $Q(k_1, k_2, \dots, k_n)$ of the configuration is then given by

$$Q(k_1, k_2, \dots, k_n) = \exp \left[- \sum_{(i,j)} U(k_i, k_j) \right] \prod_{i=1}^n z(k_i) \quad (19)$$

The canonical partition function for n k -mers then becomes the sum over all allowed configuration of n k -tuples:

$$Q_n(S, z, U) = \sum_{(k_1, \dots, k_n)} Q(k_1, \dots, k_n) \quad (20)$$

and the grand canonical partition function can then be written as

$$\Xi(S, z, U) = 1 + \sum_{n=1} Q_n(S, z, U) \quad (21)$$

2.3. Equivalence to a Trimer Problem

The set S shall contain one point for each edge in G , and two points for each vertex in G . The set K_+ shall contain four elements for each edge in G , namely, the four three-tuples which can be formed by taking the point corresponding to the edge and for each of the two vertices on which the edge is incident, taking one of the two corresponding points in S . The fugacity z will be

$$z = \frac{1}{4} z_1^2 / (1 + z_0)^2 \quad (22)$$

i.e., $\frac{1}{4}$ times the relative fugacity of a dimer on G . U should be zero for any pair in K_+ such that the corresponding edges in F are not incident on the same vertex. If they are incident on the same vertex, then U should be given by

$$e^{-U} = 2z_2(1 + z_0)/z_1^2 \quad (23)$$

It is not difficult to perceive that

$$\Xi(G; z_0, z_1, z_2) = \Xi(S, z, U)(1 + z_0)^N \quad (24)$$

2.4. Another Bound on the Location of Zeros

One can now apply Ruelle's theory^(10,11) for the solubility of the Kirkwood-Salsburg equations to the trimer model given above.⁶ If one defines

$$e^B = \max\{|e^{-U}|, 1\} \quad (25)$$

⁶ The theory of Gallavotti and Miracle⁽¹²⁾ cannot be applied since their theory of a lattice gas is limited to a monomer gas.

and

$$C = 4q - 1 + 4(q - 1)|e^{-U} - 1| \quad (26)$$

where q is the maximum coordination number of the vertices in G , then one finds that $\Xi(G; z_0, z_1, z_2)$ is not zero if

$$\frac{1}{4} |z_1^2 / (1 + z_0)^2| < e^{-2B-1} C^{-1} \quad (27)$$

2.5. Thermodynamics

Since the model in its original formulation cannot be described by a simple classical potential, the question of whether the model possesses a thermodynamic limit cannot be settled by a direct reference to the well-known work by Fisher⁽¹³⁾ and Ruelle⁽¹⁴⁾.⁷ Fortunately, the trimer version is a genuine classical hard-core model; as a consequence, one has the following theorem.

Theorem 1. Let L be a lattice which has the usual property of translational invariance⁸ and which has vertices with finite coordination number. If one considers a sequence of section graphs G of the lattice L such that the sequence tends to infinity in the sense of Fisher,⁹ then the following limit exists and is unique:

$$p(z_0, z_1, z_2) = \lim_{N \rightarrow \infty} (1/N) \log[\Xi(G; z_0, z_1, z_2)] \quad (28)$$

provided $z_1 > 0$. The pressure p is an increasing function of the fugacities.

Ruelle's theory applied to the trimer version implies that in the thermodynamic limit defined in Theorem 1, correlation functions exist in the region given by Eq. (27) and are analytic there. When one applies the theory of the monomer-dimer problem to the region given by (18), one can deduce that the correlation functions are uniformly bounded in any closed subdomain of that region. Since the intersection of the region given by Eq. (18) with the region given by Eq. (27) is nonempty, the following is seen to result by application of Vitali's theorem.

Theorem 2. If one takes the thermodynamic limit as in Theorem 1, then the correlation functions exist in the union of the regions given by Eqs. (18) and (27) and both correlation functions and the pressure p are analytic in this region.

Finally, we shall consider the problem of whether the compressibility is finite. For a general fugacity z_i , one defines the corresponding density by

$$\rho_i = z_i dp/dz_i \quad (29)$$

⁷ See also Ruelle,⁽¹¹⁾ Chapter 3.

⁸ Essam and Fisher,⁽¹⁵⁾ Definition 2.32.

⁹ Fisher⁽¹³⁾ and Ruelle,⁽¹¹⁾ Definition 2.1.2.

and the compressibility χ by

$$\chi_i = (\rho_i^{-1} d\rho_i/dz_i)^{-1} \quad (30)$$

If the compressibility is finite and $\rho(z)$ is analytic in z , then the inverse function $z(\rho)$ will also be analytic (the inverse function will always exist since the compressibility can never be negative).

We define the monomer unit fugacity z_m , the bond fugacity z_b , and the free-end fugacity z_e by

$$z_0 = z_m; \quad z_1 = z_e z_b^{1/2} z_m; \quad z_2 = z_b z_m \quad (31)$$

and get corresponding densities ρ_m , ρ_b , and ρ_e by Eq. (29) and the compressibilities χ_m , χ_b , and χ_e by Eq. (30). By substituting z_m , z_e , and z_b for z_0 , z_1 , and z_2 in the earlier equations, one obtains for the monomer-dimer version [Eqs. (8) and (9)]

$$m_1 + m_2 = 2z_e z_b^{-1/2} \quad (32)$$

$$m_1 m_2 = 2(1 + z_m) z_b^{-1} z_m^{-1} - w \quad (33)$$

By choosing w such that $m_1 m_2$ becomes zero, one finds that monomer-dimer theory requires that

$$\chi_e > 0 \quad (34)$$

Similarly, one gets for the trimer version [Eqs. (22) and (23)]

$$z = \frac{1}{4} z_b z_e^2 z_m^2 / (1 + z_m)^2 \quad (35)$$

$$e^{-U} = 2(1 + z_m) z_e^{-2} z_m^{-1} \quad (36)$$

which shows that when Ginibre's result⁽¹⁶⁾ is applied to the trimer version, it implies

$$\chi_b > 0 \quad (37)$$

We have not been able to prove $\chi_m > 0$, although we expect it to hold.

3. THE BRANCHING POLYMER MODEL

The model is similar to the chain-polymer model; but instead of having a maximum of two bonds joining a monomer unit, one is now allowed to have up to n bonds joining the same monomer unit to others. We shall use z_i , ($i = 0, 1, \dots, n$), for the fugacity of a monomer unit with i bonds.

The remarks about generalization to the case with fugacities dependent on the vertices carry over immediately to this model. Moreover, the definition

of the grand partition function should not either produce any special complications.

3.1. Rewriting the Model as a Monomer-Dimer Model

The recipe for the chain-polymer model applies essentially unchanged; one should just add n internal vertices in G' instead of two for each vertex in G . The monomer fugacities for the n internal vertices become m_1, m_2, \dots, m_n and the weights on the edges joining these vertices become $w_{12}, w_{13}, \dots, w_{n-1,n}$.

Using the same rules for the correspondence between configurations, one can deduce the following system of equations:

$$1 + z_0 = fP_L$$

$$z_i = f \cdot i! \cdot \sum_{\substack{\#M=n-i \\ M \subset \mathcal{N}}} P_M, \quad i = 1, 2, \dots, n \quad (38)$$

where the sum runs over all subsets M with $n - i$ members taken from the set of n integers $\mathcal{N} = \{1, 2, \dots, n\}$ and where P_M for $M = \{1, 2, \dots, i\}$ is given by

$$P_0 = 1 \quad (39)$$

$$P_{\{1\}} = M_1 \quad (40)$$

$$P_{\{1,2,\dots,i\}} = m_i P_{\{1,2,\dots,i-1\}} + \sum_{j=1}^{i-1} w_{j,i} P_{\{1,2,\dots,j-1,j+1,\dots,i-1\}} \quad (41)$$

(The analogous formulas for M not being the first i integers should be trivial to produce.) If one looks at Eqs. (38) for $i = n, n - 1$, and $n - 2$, they strongly suggest that it is advantageous to set $w_{12} = w_{13} = \dots = w_{n-1,n} = 0$ if one wants to find as large parts of the real axis of z_0, z_1, \dots, z_n as possible included in the zero-free domain. Since this agrees with the findings for the chain-polymer model and since it vastly facilitates the computations, we shall assume that. Then, P_M degenerates to

$$P_M = \prod_{i \in M} m_i \quad (42)$$

and

$$S_j = \sum_{\substack{M \subset \mathcal{N} \\ \#M=j}} P_M \quad (43)$$

become the elementary symmetric functions of the numbers $m_j, j = 1, 2, \dots, n$. Setting

$$f = z_n/n! \quad (44)$$

$$x_i = z_i/z_n, \quad i = 0, 1, \dots, n - 1 \quad (45)$$

Eqs. (38) become

$$S_{n-i} = x_i \cdot n!/i!, \quad i = 0, 1, \dots, n-1 \quad (46)$$

In order to facilitate the computations further, we shall restrict ourselves to find the intervals on the real x_i axis ($i = 0, 1, \dots, n-1$) such that the grand partition function is nonzero in a neighborhood in the combined complex planes. To do this, we apply the Hurwitz theorem¹⁰ (which is consequence of the Hermite-Biehler theorem). From this, we get that a necessary and sufficient condition for m_i to have positive real part is that the determinants

$$D_k = \begin{vmatrix} S_1 & S_0 & 0 & 0 & 0 & \cdots \\ S_3 & S_2 & S_1 & S_0 & 0 & \cdots \\ \vdots & & & & & \\ S_{2k-1} & S_{2k-2} & \cdots & \cdots & \cdots & \cdots & S_k \end{vmatrix}, \quad k = 1, 2, \dots, n \quad (47)$$

are all positive. One should define

$$S_0 = 1 \quad \text{and} \quad S_k = 0 \quad \text{for} \quad k > n \quad (48)$$

For $n \geq 3$, this condition does not allow one to include all real values in the area in which the grand canonical partition function is nonzero. For example, when $n = 3$, one finds the condition

$$3x_2x_1 - x_0 > 0 \quad (49)$$

3.2. The Problem as a Trimer Problem with n -body Interaction

Again only minor changes from the case of the chain-polymer model are necessary. One should have n points in S for each vertex in G . The set K_+ shall contain n^2 elements for each edge in G made according to the same principle of taking one point for each end point of the edge out of the corresponding set of n points. The fugacity z will be given by

$$z = (1/n^2) z_1^2 / (1 + z_0)^2 \quad (50)$$

One will now have to prescribe nonzero j -body interactions, with $2 \leq j \leq n$, between trimers corresponding to edges incident on the same vertex. With U_j for the j -body interaction, one gets the following set of defining equations:

$$e^{-U_j} = \frac{(n-j)!}{n!} \frac{z_j}{(1+z_0)} \left(\frac{1}{n} \frac{z_1}{1+z_0} \right)^{-j} \prod_{i=2}^{j-1} \exp \left[\binom{j}{i} U_i \right], \quad j = 2, 3, \dots, n \quad (51)$$

¹⁰ See, e.g., Obreschhoff,⁽⁹⁾ Section 23.2.

3.3. Thermodynamic Behavior

From the above transformation to a trimer problem one can of course still infer the existence and uniqueness of the thermodynamic limit for a sequence of section graphs G of a lattice L , provided the limit is taken in the sense of Fisher, and $z_1 > 0$.

However, since we have been forced to include n -body interactions ($n \geq 3$) in the trimer description, we can no longer apply Ruelle's theory to get a bound on the zeros similar to Eq. (27). Neither can we prove the existence of correlation functions in this case. We do, of course, believe that correlation functions exist almost everywhere, and also that a bound on the zeros similar to Eq. (27) obtains.

The most important change is, of course, that we can no longer prove the absence of phase transitions. We believe that this is significant; the branch-polymer model will indeed show phase transitions for certain ranges of the parameters if the dimension of the lattice is higher than one.

In a special case, this is immediately clear. If n is equal to the coordination number q of the lattice and if

$$z_i/z_{i-1} = z_b, \quad i = 1, 2, \dots, n \quad (52)$$

then the energy of the bonds is z_b^2 independently of the total configuration and the model is consequently equivalent with the usual (monomer) lattice gas with pair interaction U given by

$$e^{-U} = 1 + z_b^2 \quad (53)$$

The phase transition in this case follows by well-known theorems from the fact that U is clearly negative, corresponding to an attractive lattice gas (a similar observation has been made by Levine and Perram⁽⁸⁾).

4. THE POLYGON MODEL

4.1. General

In this section, we shall consider the effect of restricting the chain model to $z_1 = 0$. In Section 2, this represented a limiting case for which theorems about analyticity did not hold; this fact of course engenders a certain interest. Since it further turns out that this model can be solved exactly in certain cases, then we think it might be worthwhile to reflect on the possibility of taking the restriction $z_1 = 0$ as an approximation to actual problems.

We shall start by changing the notation from the previous sections. A vertex without bonds will be termed a hole and it will be assumed to have

fugacity z . A bond between vertex i and vertex j will be assumed to have canonical weight w_{ij} .

We shall allow the possibility of different weights for different bonds, since it turns out that the anisotropic case has some special features.

If the lattice has coordination number 3, then the problem is equivalent to an Ising model on the same lattice. This can be seen as follows: it is well known that if one uses edge weights

$$w_{ij}/z = \tilde{w}_{ij} = \tanh(-J_{ij}) \quad (54)$$

where J_{ij} is the Ising interaction between spins at vertices i and j , then the Ising partition function, aside from a trivial factor, is identical with the sum over all polygon configurations with weights equal to the product of the weights of the sides in the polygons. In the Ising version, however, one may have any even number of polygon sides going into the same vertex as long as the edges are covered at most once, but this difference disappears when the coordination number is smaller than 4, and the statement is consequently correct.

The usefulness of the analogy is unfortunately limited by the fact that for $w_{ij}/z > 1$, one moves out in an unphysical region of the Ising model where J_{ij} has an imaginary part $\frac{1}{2}i\pi$. If the exact solution to the Ising problem is known, this is of course of minor importance; for three-dimensional problems, it seems that one cannot settle the question of phase transition for $w_{ij}/z > 1$ by reference to known results.

4.2. The Hexagonal Lattice

The hexagonal lattice is an example of a planar lattice with coordination number 3 and as such solvable by reformulating the problem as an Ising model on the same lattice. We shall consider the full anisotropic problem. The weights of bonds in the three directions will be w_1 , w_2 , and w_3 , respectively. The pressure p is then given by¹¹

$$p = (1/16\pi^2) \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \log[\Delta(\theta, \phi)] \quad (55)$$

$$\begin{aligned} \Delta(\theta, \phi) = & z^4 + w_1^2 w_2^2 + w_2^2 w_3^2 + w_1^2 w_3^2 \\ & - 2w_1 w_2 (z^2 - w_3^2) \cos(\theta - \phi) \\ & - 2w_1 w_3 (z^2 - w_2^2) (\cos \theta) - 2w_2 w_3 (z^2 - w_1^2) \cos \phi \end{aligned} \quad (56)$$

¹¹ A review of the first solutions of the Ising model for the hexagonal lattice can be found in Ref. 17. We have taken the formula from Ref. 7.

This expression is valid for all values of z , w_1 , w_2 , and w_3 , while it is only when

$$0 \leq w_i/z \leq 1, \quad i = 1, 2, 3 \quad (57)$$

that, as stated above, the result corresponds to a physical region of the Ising model on a hexagonal lattice. Here, this inconvenience can be overcome by transforming to the dual (triangular) lattice. If one numbers the directions in the triangular lattice as the direction in the hexagonal lattice on which they are orthogonal and defines the interactions in the triangular Ising lattice J_1 , J_2 , and J_3 by

$$e^{2J_i} = w_i/z, \quad i = 1, 2, 3 \quad (58)$$

then one can easily check that the grand partition function for the polygon problem $\mathcal{E}_{\text{pol}}(\text{Hex}; z, w_1, w_2, w_3)$ is related to the partition function for the Ising problem $Z_{\text{IS}}(\text{Tri}; J_1, J_2, J_3)$ by

$$\mathcal{E}_{\text{pol}}(\text{Hex}; z_1, w_1, w_2, w_3) = z^N e^{(J_1+J_2+J_3)N} Z_{\text{IS}}(\text{Tri}; J_1, J_2, J_3) \quad (59)$$

The case (57) corresponds to the ferromagnetic case on the triangular lattice, while

$$w_i/z > 1, \quad i = 1, 2, 3 \quad (60)$$

corresponds to the antiferromagnetic case. The two mixed cases

$$w_1/z > 1; \quad w_2/z < 1; \quad w_3/z < 1 \quad (61)$$

and

$$w_1/z < 1; \quad w_2/z > 1; \quad w_3/z > 1 \quad (62)$$

can be transformed to the antiferromagnetic or the ferromagnetic case, respectively, by the transformation

$$w_2 z^{-1} \rightarrow z w_2^{-1}, \quad w_3 z^{-1} \rightarrow z w_3^{-1} \quad (63)$$

which can be achieved by extracting a factor $w_2^2 w_3^2 z^{-4}$ from $\Delta(\theta, \phi)$. One consequently obtains the relation

$$p(z, w_1, w_2, w_3) = p(z, w_1, w_2^{-1}, w_3^{-1}) + \log w_2 + \log w_3 - 2 \log z \quad (64)$$

Stephenson⁽¹⁸⁾ has recently published detailed formulas for the anisotropic triangular lattice and the integral (55) has also been analyzed by Fan and Wu,⁽¹⁹⁾ so we shall here only state the more important result in our

notation. The double integral (55) can be transformed to a single integral

$$p = -\frac{1}{4} \log 2 + (1/8\pi) \int_0^{2\pi} d\theta \log[A_2(\theta) + D_2(\theta)] \quad (65)$$

where

$$A_2(\theta) = z^4 + w_1^2 w_2^2 + w_2^2 w_3^2 + w_1^2 w_3^2 - 2w_1 w_3 (z^2 - w_2^2) \cos \theta \quad (66)$$

$$D_2(\theta) = [z^4 - w_1^2 w_2^2 - w_2^2 w_3^2 + w_1^2 w_3^2 - 2w_1 w_3 (z^2 + w_2^2) \cos \theta]^2 + 16z^2 w_1^2 w_2^2 w_3^2 \sin^2 \theta \quad (67)$$

The density of bonds in the direction i , ρ_i , in our notation corresponds to the energy contribution from the direction i in the Ising model. One obtains

$$\rho_2 = w_2 \partial p / \partial w_2 = \frac{1}{4} + (1/8\pi) \int_0^{2\pi} d\theta E_2(\theta) / [D_2(\theta)]^{1/2} \quad (68)$$

with

$$E_2(\theta) = z^4 + w_1^2 w_2^2 + w_2^2 w_3^2 - w_1^2 w_3^2 + 2w_1 w_3 (z^2 + w_2^2) \cos \theta \quad (69)$$

The expressions for ρ_1 and ρ_3 can be obtained by permuting the indices. The density of holes is then given by

$$\rho_h = 1 - \rho_1 - \rho_2 - \rho_3 \quad (70)$$

The critical conditions become

$$z^2 = w_1 w_2 + w_2 w_3 + w_3 w_1 \quad (71)$$

$$z^2 = w_1 w_2 - w_2 w_3 - w_3 w_1 \quad (72)$$

$$z^2 = w_1 w_2 + w_2 w_3 - w_3 w_1 \quad (73)$$

$$z^2 = w_1 w_2 - w_2 w_3 + w_3 w_1 \quad (74)$$

The first condition will admit of a positive solution for z for any (positive) values of w_1 , w_2 , and w_3 ; of the other three, one at most will give a real solution for z . Assuming that

$$w_1 \geq w_2 \geq w_3 \quad (75)$$

one finds that only Eq. (72) can be satisfied for z nonnegative; the condition for solution becomes

$$1 - (w_3/w_1) - (w_3/w_2) > 0 \quad (76)$$

If equality holds in Eq. (76), then $z = 0$ is a solution of Eq. (72).

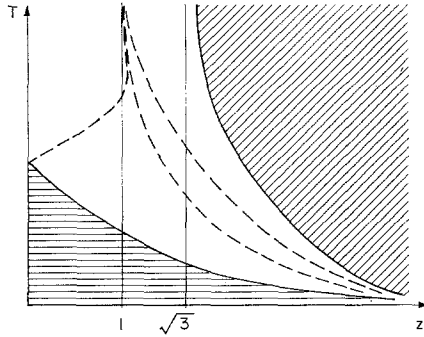


Fig. 3. One of the possible phase diagrams for the polygon model on the hexagonal lattice.

Assuming that w_i , ($i = 1, 2, 3$), depends on temperature in the usual manner

$$w_i = e^{-\beta U_i}, \quad i = 1, 2, 3 \tag{77}$$

one finds the four different T - z phase diagrams shown in Figs. 3-6. Figure 3 is obtained for

$$U_1 + U_2 + U_3 \leq 0$$

Figure 4 is obtained for

$$U_1 < -U_2, \quad U_1 + U_2 + U_3 > 0$$

Figure 5 is obtained for

$$U_1 = -U_2$$

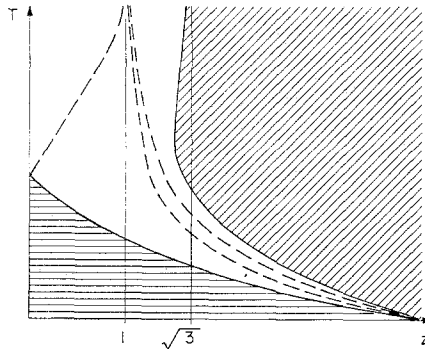


Fig. 4. The second of the possible phase diagrams for the polygon model on the hexagonal lattice.

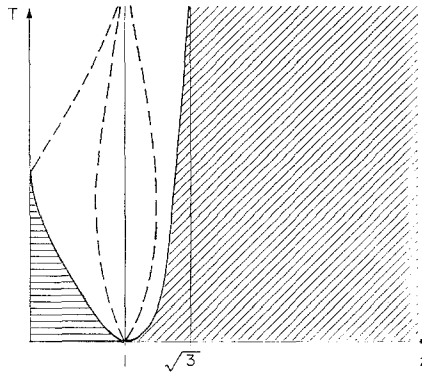


Fig. 5. The third of the possible phase diagrams for the polygon model on the hexagonal lattice.

Figure 6 is obtained for

$$U_1 > -U_2$$

The horizontally shaded area corresponds to an ordered phase with long chains and few bonds in the least favored direction, 3. The oblique shaded area corresponds to an ordered phase with few bonds, the bonds being arranged in small polygons. The unshaded area corresponds to a disordered phase.

There is a certain interest connected with the case when $D(\theta)$ [eq. (67)] is a perfect square (i.e., a square of a linear function of $\cos \theta$). This occurs when

$$z^2 = w_1 w_2 + w_2 w_3 - w_1 w_3 \tag{78}$$

$$z^2 = w_1 w_2 - w_2 w_3 + w_1 w_3 \tag{79}$$

$$z^2 = -w_1 w_2 + w_2 w_3 + w_1 w_3 \tag{80}$$

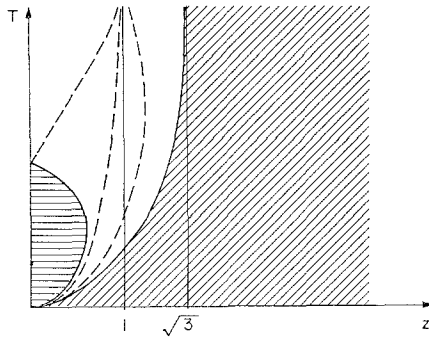


Fig. 6. The fourth of the possible phase diagrams for the polygon model on the hexagonal lattice.

It is easily seen that the values of z^2 given by Eqs. (78) and (79) fall between the values given by Eqs. (71) and Eq. (72). While the condition (80) coincides with (72) for $z = 0$. The three lines defined by Eqs. (78), (79), and (80) are shown as dashed lines in Figs. 3–6. The curve crosses the line $z = 1$ if, respectively,

$$\text{sign}(U_2) \cdot \text{sign}(U_1 + U_2) = -1 \quad (81)$$

$$\text{sign}(U_1) \cdot \text{sign}(U_1 + U_2) = -1 \quad (82)$$

$$\text{sign}(U_3) < 0 \quad (83)$$

If $z = 0$, then $D(\theta)$ will also be a perfect square. Since the phase transition then occurs at the crossing of another line for which $D(\theta)$ is a perfect square, one might expect peculiar behavior; in fact, one finds behavior similar to the modified KDP model on a square lattice.^(20,21)¹² For T less than the critical temperature, one finds that the free energy is given by

$$p = \frac{1}{2} \log(w_1 w_2) \quad (84)$$

and the density of bonds in the i 'th direction is consequently constant:

$$\rho_1 = \rho_2 = \frac{1}{2}; \quad \rho_3 = 0 \quad (85)$$

The densities for T above T_c are given by

$$\rho_i = (\theta_i/\pi) - \frac{1}{4}, \quad i = 1, 2 \quad (86a)$$

$$\rho_3 = \frac{3}{2} - [(\theta_1 + \theta_2)/\pi] \quad (86b)$$

$$\theta_1 = \cos^{-1}[-(w_1^2 w_2^2 + w_1^2 w_3^2 - w_2^2 w_3^2)/(2w_2 w_3 w_1^2)] \quad (87a)$$

$$\theta_2 = \cos^{-1}[-(w_1^2 w_2^2 - w_1^2 w_3^2 + w_2^2 w_3^2)/(2w_1 w_3 w_2^2)] \quad (87b)$$

where θ_1 and θ_2 should be chosen in the interval between 0 and π ; actually, one has

$$\frac{2}{3}\pi \leq \theta_i \leq \pi, \quad i = 1, 2 \quad (88)$$

The compressibility will show a square-root divergence as T approaches T_c from above.

It is interesting to notice that the case $z = 0$ is also in another respect similar to the ice-rule models on the square lattice, insofar as the isotropic

¹² It is not very surprising that the modified KDP model and the polygon covering of the hexagonal lattice show the same behavior, since both can be reformulated as the dimer covering problem on the hexagonal lattice. For the polygon covering, one merely makes an interchange of covering and noncovering of the edges; for the modified KDP model, one can find the rewriting in Ref. 21.

case shows a residual entropy. This was calculated by Wannier⁽²²⁾ to be, per site,

$$s = (3/\pi) \int_0^{\pi/6} \ln(2 \cos \theta) d\theta = 0.32206 \quad (89)$$

Aside from the special case $z = 0$, then, the phase transition will always be accompanied by a logarithmic divergence in the compressibility.

4.3. The Square Lattice

The general polygon model on the square lattice corresponds to the eight-vertex problem⁽⁶⁾ (see Fig. 7), with the following relations for the weights of the vertex configurations $\omega_i, i = 1, 2, \dots, 8$,

$$\omega_1 = z, \quad \omega_2 = 0, \quad \omega_5 = \omega_6, \quad \omega_7 = \omega_8 \quad (90)$$

If one only distinguishes between bond directions and not between valence angles, then one further gets

$$\omega_3 = w_v, \quad \omega_4 = w_h, \quad \omega_5 = \omega_6 = \omega_7 = \omega_8 = (w_h w_v)^{1/2} \quad (91)$$

with w_h for the weight of a horizontal bond and w_v for the weight of a vertical bond.

Unfortunately, neither the general case (90) nor the more special case (91) has known solutions except if one includes further assumptions. This is caused by the necessity for the assumption $\omega_1 \neq \omega_2$.¹³ The special case $z = 0$, which is closely related to the well-known ferroelectric problems, will be discussed briefly at the end of the section. The only case with $z \neq 0$ for which a solution has been published is the case

$$\omega_7 = \omega_8 = 0 \quad (92)$$

which is Wu's modified KDP model.^(20,21) Since this model conserves the

¹³ It is essential for application of the analogy between the "ferroelectric" models and the one-dimensional anisotropic Heisenberg model that one has $\omega_1 = \omega_2$ and $\omega_3 = \omega_4$.⁽²³⁾

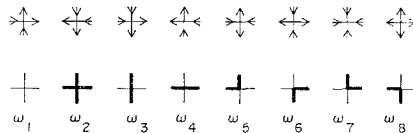


Fig. 7. The eight different vertices of the ferroelectric problem together with the corresponding configuration of bonds in the polygon model.

number of polymers proceeding in the diagonal direction from lower left to upper right and thus does not allow closed polygons or *s*-shaped wiggles, it is of interest primarily as a limiting case.

If one imposes the restriction

$$\omega_3\omega_4 = \omega_5\omega_6 + \omega_7\omega_8 \quad (93)$$

in addition to Eq. (90), then the model can be solved by the Pfaffian technique, a fact first observed by Fan and Wu.⁽¹⁹⁾ The condition (93) will not hold for all temperatures if one assumes the normal temperature dependence

$$\omega_i = e^{-\beta U_i}, \quad i = 3, 4, 5, 6, 7, 8 \quad (94)$$

This difficulty can be overcome either by introducing the condition (92) or by assuming another temperature dependence. The simplest possibility seems to be inclusion of entropy factors; (93) will then be satisfied if one assumes

$$\begin{aligned} \omega_i &= 2e^{-\beta U_i}, & i &= 3, 4 \\ \omega_i &= 2e^{-\beta U_i}, & i &= 5, 6, 7, 8 \\ U_3 + U_4 &= U_5 + U_6 = U_7 + U_8 \end{aligned} \quad (95)$$

or

$$\omega_3\omega_4 = 2\omega_5\omega_6 = 2\omega_7\omega_8 \quad (96)$$

We shall, for the sake of generality, investigate the full problem with only the restriction (93) added to (90). The integral formula for the pressure can be found in Fan and Wu's paper⁽¹⁹⁾ and we shall not rederive it here. We would, however, like to point out that the assumption $\omega_2 = 0$ implies that we can perform the analogous dimer covering problem on a simpler lattice, namely the bathroom-tile lattice with one diagonal in the squares (see Fig. 8). The formula for the pressure becomes

$$p = (1/8\pi^2) \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \log[\Delta(\theta, \phi)] \quad (97)$$

$$\begin{aligned} \Delta(\theta, \phi) &= z^2 + \omega_3^2 + \omega_4^2 + 2z\omega_3 \cos \theta + 2z\omega_4 \cos \phi \\ &+ 2(\omega_3\omega_4 - \omega_5^2) \cos(\theta - \phi) + 2(\omega_3\omega_4 - \omega_7^2) \cos(\theta + \phi) \end{aligned} \quad (98)$$

As usual, one can carry out one integration which gives the expression

$$p = -\frac{1}{2} \log 2 + (1/4\pi) \int_0^{2\pi} d\theta \log[A(\theta) + D(\theta)] \quad (99)$$

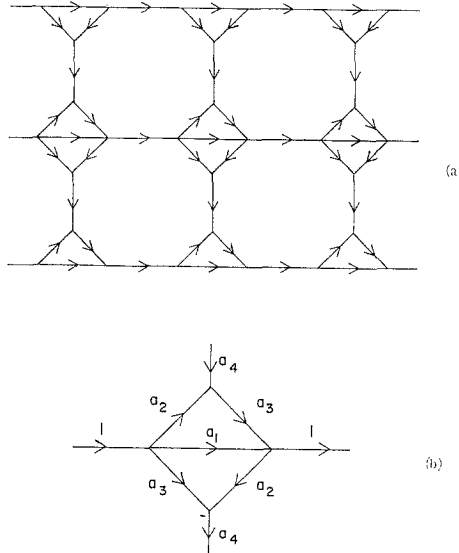


Fig. 8. (a) The bathroom-tile lattice with a correct arrow assignment for the Pfaffian method. (b) The unit cell, with bond weights shown. For the *general model*, $\omega_1 = a_1 a_4$, $\omega_2 = 0$, $\omega_3 = a_2^2 + a_3^2$, $\omega_4 = a_4$, $\omega_5 = a_3 a_4^{1/2}$, $\omega_7 = a_2 a_4^{1/2}$. For the *staggered Wu model*, a factor z_1^N has been extracted from the partition function. Then, $a_1 = 0$, $a_2 = w_h/z$, $a_3 = w_v/z$, $a_4 = 1$.

with

$$A(\theta) = z^2 + \omega_3^2 + \omega_4^2 + 2z\omega_3 \cos \theta \quad (100)$$

$$D(\theta) = (z^2 + \omega_3^2 - \omega_4^2 + 2z\omega_3 \cos \theta)^2 + 16\omega_5^2 \omega_7^2 \sin^2 \theta \quad (101)$$

This expression for p is, as can be seen, rather similar to that which obtains for the hexagonal lattice. The critical conditions for the present case are

$$z = \omega_3 + \omega_4 \quad (102)$$

$$z = \omega_3 - \omega_4 \quad (103)$$

or

$$z = \omega_4 - \omega_3 \quad (104)$$

As for the hexagonal lattice, we find one phase transition, (102), for all values of ω_3 and ω_4 and one more in the anisotropic case, $\omega_3 \neq \omega_4$. It is interesting to notice that the values of ω_5 and ω_7 do not enter the critical conditions.

The conditions for $D(\theta)$ to be a perfect square are

$$z^2 = (\omega_3 - \omega_4)^2 + 4\omega_5^2 \quad (105)$$

$$z^2 = (\omega_3 - \omega_4)^2 + 4\omega_7^2 \quad (106)$$

It is easily seen that only for $\omega_5 = 0$ or $\omega_7 = 0$ it is possible to have one of the critical conditions (102)–(104) satisfied simultaneously with $D(\theta)$ being a perfect square. We consequently have that the phase transition is accompanied by a logarithmic singularity in the compressibility, except when $\omega_5 = 0$ or $\omega_7 = 0$.

Earlier in this section, the unphysical aspect of the polymer interpretation of the Wu-modified KDP model was described. In fact, there are two equivalent versions of the Wu model: either $\omega_5 = \omega_6 = 0$ or $\omega_7 = \omega_8 = 0$. Closed polygons in the interior of the lattice may be allowed simply by introducing the *staggered Wu model*, in which the weights alternate on the two sublattices of the square lattice, as shown in Table I.

The grand canonical pressure is readily obtained as a dimer covering by the Pfaffian technique. It is curious that we again obtain a covering of the bathroom-tile lattice shown in Fig. 8(a), with translationally invariant dimer weights. The basic unit cell is shown in Fig. 8(b).

The grand canonical pressure in the thermodynamic limit is given by

$$p = (1/4\pi)^2 \int_0^{2\pi} d\theta \int_0^{2\pi} d\phi \log \Delta(\theta, \phi) \quad (107a)$$

where

$$\Delta(\theta, \phi) = z^4 + (w_h^2 + w_v^2)^2 - 2z^2[w_h^2 \cos(\theta - \phi) + w_v^2 \cos(\theta + \phi)] \quad (107b)$$

The integral (107a) is closely related to the one obtained by Onsager⁽¹⁾ for the rectangular Ising model. Clearly, $\Delta(\theta, \phi) \geq 0$; equality is obtained when both $\theta = \phi = 0$, and

$$w_h^2 + w_v^2 = z^2 \quad (108)$$

This, then, is the critical condition. It is to be noted that the introduction of anisotropy ($w_h \neq w_v$) does not give rise to an additional transition, unlike the previous model. This feature can be readily understood from an intuitive point of view.

By inspection of (107a), it is easy to see that the z density is continuous

Table I. Vertex Weights for the Staggered Wu Model

Sublattice	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
<i>A</i>	z	0	w_v	w_h	$(w_v w_h)^{1/2}$	$(w_v w_h)^{1/2}$	0	0
<i>B</i>	z	0	w_v	w_h	0	0	$(w_v w_h)^{1/2}$	$(w_v w_h)^{1/2}$

at the critical point given by (108), but that the z compressibility has a logarithmic singularity there, independent of the degree of anisotropy.

Finally, we shall consider the polygon covering case, $z = 0$, for the square lattice. With $\omega_1 = \omega_2 = 0$, the model reduces to the six-vertex problem. However, the most general polygon covering of the square lattice with translationally invariant weights corresponds to a *staggered* ferroelectric problem. Since the staggered ferroelectric problem has not yet been solved, except for rather special cases, we are still forced to place a further restriction on the weights. The most interesting case obtains when

$$\omega_3 = \omega_4 = \omega_s \quad (109a)$$

$$\omega_5 = \omega_6 = \omega_7 = \omega_8 = \omega_b \quad (109b)$$

This corresponds to the F -model,⁽²⁴⁾ which has an infinite-order phase transition at

$$\omega_t = 2\omega_b \quad (110)$$

The low-temperature, ordered state favors vertices 3 and 4.

4.4. Discussion

The rigorous results obtained above for the hexagonal lattice and the square lattice seem to indicate the following general behavior of the polygon model for lattices of dimensions greater than one:

The model has always a second-order (?) phase transition for a relatively large value of z (and low density of bonds), with the ordered state having few bonds.

If the lattice is anisotropic or if a particular valence angle is favored, then another phase transition might occur at low values of z (and high density of bonds), with the ordered state having long polymer chains where the favored bond direction (valence angle) dominates.

The first of these two possible phase transitions seems to have little physical significance, since it occurs under circumstances where the total exclusion of free ends appears to be a very unreasonable assumption.

The second phase transition may well be of greater physical significance. The low density of holes gives the model a reasonable resemblance to amorphous polymers, in which case the phase transition should correspond to the glass transition. There are, however, two obvious objections to this interpretation. The glass transition is not connected with anisotropy of the system, which leaves only the possibility of a favored valence angle, a case which has only vague support in the obtained rigorous result (the polygon covering of the square lattice). More serious is the fact that the model does not conserve

the length of the polygons, which is equivalent to the molecular weight of the polymers; actually, there does not even seem to be any way of obtaining information about the distribution of polygon sizes. The phase transition might therefore very well be accomplished primarily by breaking of bonds and change in the molecular weight distribution.

APPENDIX: NOTE ADDED AFTER COMPLETION OF WORK

C. Gruber and H. Kunz have kindly drawn our attention to the possible application of their general theory of polymers⁽²⁵⁾ to the present case. We shall start by defining a polymer in our sense.

Definition. A polymer is a set of monomer units which are connected by bonds and which are not connected by bonds to any monomer units outside the set. A polymer can be viewed in graph terminology as any connected subgraph of the lattice. It should be noted that the bonds are sufficient to specify the polymer, while the placement of the monomer units on the lattice does not necessarily specify the polymer. If P is a polymer, then we write $[P]$ for the set of vertices in P . If j is a vertex in P , $j \in [P]$, then we write $z(j)$ for the fugacity of the monomer unit on that vertex $[z(j)]$ given in accordance with the definition of the branching-polymer model or the chain-polymer model by the number of bonds in P which are connected to the monomer unit]. We then get the total fugacity $\phi(P)$ of the polymer P from

$$\phi(P) = \prod_{j \in [P]} z(j) \quad (\text{A.1})$$

The polymer concept introduced here is not the same as the concept given by Gruber and Kunz. They associate a fugacity $\check{\phi}(S)$ with any subset of vertices S and consider any subset with nonzero fugacity as a polymer. However, making the connection

$$\check{\phi}(S) = \sum_{[P]=S} \phi(P) \quad (\text{A.2})$$

it is easily seen that their theory applies also to polymers as defined in this paper. Following Gruber and Kunz, one then consider the conditions

$$S_j(\xi) = \sum_{[P] \ni j} |\phi(P)| \xi^{N(P)} - z_0 \xi \quad (\text{A.3})$$

$$|1 + z_0| > \sup_j \{(1/\xi)[1 + S_j(\xi)]\} \quad (\text{A.4})$$

where the sum runs over all polymers which contains the vertex j and the contribution from the monomer is subtracted; $N(P)$ is the number of vertices

in P . If there exist a positive, real ξ such that $S_j(\xi)$ is finite for all j and the condition (A.4) is fulfilled, then one has existence and analyticity of the pressure and correlation functions in the thermodynamic limit; i.e., the same type of result which we obtained in Section 2 by applying Ruelle's theory for the solubility of the Kirkwood-Salsburg equations to the trimer version.

The problem is then to work out an upper bound on the sum $S(\xi)$ in terms of the variables z_0, z_1, \dots, z_q using the structure of the lattice. For the chain-polymer model it is fairly easy to get a crude estimate. If q is the coordination number of the lattice, then the number of chains of length $n + 2$ starting at a fixed point is bounded by $q(q - 1)^n$, while the number of polygons of length $n + 2$ which include a given point is bounded by $\frac{1}{2}q(q - 1)^n$. Assuming

$$\alpha = \xi z_2(q - 1) < 1 \quad (\text{A.5})$$

one then finds that $\hat{S}(\xi)$ given by

$$\hat{S}(\xi) = \frac{q}{2} \left[\frac{z_1}{z_2(q - 1)} \right]^2 \frac{3\alpha^2 - 2\alpha^3}{(1 - \alpha)^2} + \frac{q}{2} \frac{1}{(q - 1)^2} \frac{\alpha^2}{1 - \alpha} \quad (\text{A.6})$$

is an upper bound on $S(\xi)$. One consequently has that the condition (A.4) is fulfilled if

$$|1 + z_0| > (1/\xi)[1 + \hat{S}(\xi)] \quad (\text{A.7})$$

and ξ satisfies (A.5). The value of ξ which gives the lowest bound on $|1 + z_0|$ can be found by minimizing the right-hand side of (A.7); since this involves solving a third-degree equation, we shall not pursue the case further. Better bounds on the number of self-avoiding walks and polygons for particular lattices can be found in the literature.⁽²⁶⁾

For the branching-polymer model, a similar method can be applied to estimate $S(\xi)$. The configuration of bonds at the initial (j th) vertex is specified first; this gives rise to a total contribution of

$$\eta_1 = \sum_{j=1}^q z_j \binom{q}{j} \quad (\text{A.8})$$

Subsequently, one specifies the configuration at each of the vertices where the bonds from the initial vertex end. This can at most give rise to a contribution

$$\eta = \sum_{j=1}^q z_j \binom{q-1}{j-1} \quad (\text{A.9})$$

for each vertex. In the following generations one will still at most get a factor η per vertex, and one then ends up with

$$\tilde{S}(\xi) = \xi^2 \eta_1 / (1 - \xi \eta) \quad (\text{A.10})$$

as an upper bound on $S(\xi)$ for the branching-polymer model. The minimum value of $\xi^{-1} + \xi^{-1}\alpha(\xi)$ is obtained for

$$\xi = [\eta + (\eta\eta_1)^{1/2}]^{-1} \quad (\text{A.11})$$

and one gets the bound

$$|1 + z_0| > \eta + 2(\eta\eta_1)^{1/2} \quad (\text{A.12})$$

sufficient to satisfy (A.4).

ACKNOWLEDGMENT

It is the authors' pleasure to thank Professor E. H. Lieb for stimulating comment.

REFERENCES

1. L. Onsager, *Phys. Rev.* **65**:117 (1944).
2. P. W. Kasteleyn, *Physica* **27**:1209 (1961); H. N. V. Temperley and M. E. Fisher, *Phil. Mag.* **6**:1061 (1961); M. E. Fisher, *Phys. Rev.* **124**:1664 (1961).
3. R. L. Dobrushin, *Theoret. Prob. Appl.* **13**:201 (1968); *Funct. Anal. Appl.* **2**(4):31, 44 (1968).
4. J. L. Lebowitz and G. Gallavotti, "Phase transitions in binary lattice gases," preprint.
5. O. J. Heilmann and E. H. Lieb, *Phys. Rev. Letters* **24**:1412 (1970); "Theory of monomer-dimer systems," to be published.
6. E. H. Lieb and F. Y. Wu, in *Encyclopedia of Statistical Mechanics*, C. Domb and H. S. Green, eds., Academic Press, New York, to be published.
7. H. S. Green and C. A. Hurst, *Order-Disorder Phenomena* (Vol. 5 of Monographs in Statistical Physics and Thermodynamics), Interscience, New York, 1964, p. 95.
8. S. Levine and J. W. Perram, in *Hydrogen-Bonded Solvent Systems*, A. K. Covington and P. Jones, eds., Taylor and Francis, London, 1968, p. 115.
9. N. Obreschhoff, *Verteilung und Berechnung der Nullstellen reeler Polynome*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1963, Sections 5.4, 5.22.
10. D. Ruelle, *Ann. Phys.* **25**:109 (1963); *Rev. Mod. Phys.* **36**:580 (1964). See also O. Penrose, *J. Math. Phys.* **4**:1312 (1963).
11. D. Ruelle, *Statistical Mechanics*, Benjamin, New York, 1969, Chapter 4.2.
12. G. Gallavotti, S. Miracle-Sole, and D. W. Robinson, *Phys. Letters* **25A**:493 (1967); G. Gallavotti and S. Miracle-Sole, *Commun. Math. Phys.* **7**:274 (1968).
13. M. E. Fisher, *Arch. Rat. Mech. Anal.* **17**:377 (1964).
14. D. Ruelle, *Helv. Phys. Acta* **36**:183, 789 (1963).
15. J. W. Essam and M. E. Fisher, *Rev. Mod. Phys.* **42**:271 (1970).
16. J. Ginibre, *Phys. Letters* **24A**:223 (1967).
17. C. Domb, *Advan. Phys.* **9**:149 (1960).
18. J. Stephenson, *Can. J. Phys.* **47**:2621 (1969).
19. C. Fan and F. Y. Wu, *Phys. Rev.* **2B**:723 (1970).
20. F. Y. Wu, *Phys. Rev. Letters* **18**:605 (1967).

21. F. Y. Wu, *Phys. Rev.* **168**: 539 (1968).
22. G. H. Wannier, *Phys. Rev.* **79**:357 (1950).
23. B. Sutherland, *J. Math. Phys.* **11**:3183 (1970).
24. E. H. Lieb, *Phys. Rev. Letters* **18**:1046 (1967).
25. C. Gruber and H. Kunz, "General Properties of Polymer Systems," to appear in *Commun. Math. Phys.*
26. J. M. Hammersley, *Sankhya* **25A**:29, 269 (1963); H. Kesten, *J. Math. Phys.* **5**:1128 (1964); M. E. Fisher and M. F. Sykes, *Phys. Rev.* **114**:45 (1959); M. F. Sykes, *J. Math. Phys.* **2**:52 (1961); J. F. Hiley and M. F. Sykes, *J. Chem. Phys.* **34**:1531 (1961); J. W. Essam and M. F. Sykes, *Physica* **29**:378 (1963); M. F. Sykes, *J. Chem. Phys.* **39**:410 (1963).