

New Series-Expansion Method for the Dimer Problem

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A new series-expansion technique is presented for the grand-partition function for the dimer problem with no attractive interactions. The zeroth-order term in the expansion recovers the Bethe approximation. Higher order corrections involve the weighted summation of closed subgraphs (no vertices of degree one). The weight formula is given and is a simple function of the topological type of the subgraph and the number of edges. From this series expansion, the series in powers of the dimer activity valid at low density of dimers can be recovered. The series expansion is also applicable for high density of dimers. In particular, it provides an improved approximation technique for estimating the molecular freedom per dimer at close packing, as can be seen by comparing the approximate values obtained by other authors and those obtained using this technique with the exact values known for the two dimensional lattices. Finally, this series method is used to discuss the thermodynamic behavior.

I. INTRODUCTION

THE dimer problem arose in connection with theoretical attempts to explain the thermodynamic properties of the adhesion of a gas of diatomic molecules on a surface.^{1,2} The surface may be pictured as a regular lattice which attracts the diatomic molecules (dimers) in such a way that the dimer sits on an edge of the lattice with the atoms on the terminal vertices. Naturally, two dimers cannot occupy adjacent edges since two atoms would then sit on the same vertex. However, attractions might very well exist between atoms in different but neighboring dimers.

The dimer problem has been treated by several authors using essentially the Bethe or random-mixing approximations.^{2,3,4} When there are no attractive interactions, this approximation indicates no anomalous behavior in the thermodynamic functions, and thus there seems to be no phase transition.

More recently, the dimer problem has become of interest because of its connection to the Ising problem.⁵⁻⁷ The Ising problem in two dimensions with no field and the problem of computing the number of ways to fill a two-dimensional lattice with dimers can be solved exactly by the same general method. However, it has not been possible thus far to generalize this method to three-dimensional lattices or to the Ising model with a field or to the dimer problem with no attractive interactions and with a nonzero density of monomers.^{7,8}

In lieu of an exact solution to the Ising-model problem with a field or in three dimensions, various

series expansions have been developed.^{9,10,11} Since much information has been obtained from these series, it seems appropriate to formulate series expansions for the dimer problem. The grand partition function expanded in powers of the dimer activity is the basic low density series. From it the series expansions in powers of either activity or density for the usual thermodynamic functions can be derived by simple algebraic manipulation. The activity series may be formulated quite easily since the n th term is simply related to the number of ways to place n nonoverlapping dimers on a lattice.

Because the number of ways to place n nonoverlapping dimers on the lattice is not easily calculated directly for n greater than three or four, Rushbrooke, Scoins, and Wakefield used the Mayer series expansion technique to provide another way of formulating the basic low-density series.¹² They have given six terms on the square lattice and five terms on the simple cubic lattice. It is unlikely that many more terms could be obtained using this method because of the number and complexity of graph configurations which must be counted. In comparison the series expansion formulation to be discussed in this paper requires fewer graphs of less complexity thereby allowing more terms in the low density series to be obtained more easily than by the earlier technique.

Since the work of Rushbrooke *et al.* it has been found that the number of ways to place n nonoverlapping dimers on the lattice may be found to quite high n as a byproduct of the Ising series.¹³ It is not clear at this time whether this kind of direct calculation or the method presented here will enable more terms to be obtained in the dimer activity series for any given lattice, but the two methods together should provide a useful check on each other. In addition, the series

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¹ R. H. Fowler and G. S. Rushbrooke, *Trans. Faraday Soc.* **33**, 1272 (1937).

² T. S. Chang, *Proc. Roy. Soc. (London)* **A169**, 512 (1939).

³ A. R. Miller, *Proc. Camb. Phil. Soc.* **38**, 109 (1942).

⁴ W. J. C. Orr, *Trans. Faraday Soc.* **40**, 306 (1944).

⁵ P. W. Kasteleyn, *Physica* **27**, 1209 (1961).

⁶ M. E. Fisher, *Phys. Rev.* **124**, 1664 (1961).

⁷ H. S. Green and C. A. Hurst, in *Order-Disorder Phenomena*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1964), Vol. 5.

⁸ P. W. Kasteleyn, *J. Math. Phys.* **4**, 287 (1963).

⁹ C. Domb, *Advan. Phys.* **9**, 149 (1960).

¹⁰ M. E. Fisher, *J. Math. Phys.* **4**, 278 (1963).

¹¹ M. E. Fisher, *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, Colorado, 1965), Vol. VII C.

¹² G. S. Rushbrooke, H. I. Scoins, and A. J. Wakefield, *Discussion Faraday Soc.* **15**, 57 (1953).

¹³ M. F. Sykes (private communication).

method presented here gives some extra information concerning possible anomalies in thermodynamic behavior.

In Sec. II of this paper a series expansion is derived for the grand canonical partition function for the dimer problem when there are no attractive interactions between dimers. Each term in the series expansion corresponds to a subgraph of the original graph (or lattice). The contribution to the series (the weight) of each subgraph is determined by the local degrees of the vertices and the number of edges in the subgraph and is therefore easily calculable. This weight formula is especially well suited to a recent classification of graphs by topological type as is discussed in Sec. IV. Also, the weight of any subgraph with any vertices of degree one is zero. This is a great computational advantage. It also means that the term corresponding to the empty subgraph gives the Bethe approximation and this is explicitly shown in Sec. III. The series for some usual two and three dimensional lattices are presented in Sec. IV. These series will be extended considerably when the lattice data now being obtained by Sykes and his collaborators becomes available, so extensive analysis of these series has not yet been undertaken.¹³ However, the series are long enough to obtain improved approximations to the molecular freedom per dimer at close packing as is shown in Sec. VA. It is shown in Sec. VB that the low density series expansion in powers of the dimer activity valid at low density of dimers can be obtained by rearrangement of the series given in Sec. IV. However, it is perhaps more interesting to consider the series in its original form which is also a low density expansion. Some restrictions on the behavior of the series are derived in Sec. VB. Finally, in Sec. VC the possibility of rearranging the series in a high-density expansion in powers of the monomer activity is discussed. Each term in the high-density series is itself an infinite series which, however, is simply related to the derivatives of the original series in its natural form. This provides a connection between the low-density and high-density series expansions which is useful in discussing a conjecture of Fisher and Stephenson.¹⁴

It may also be mentioned that the series-expansion technique used here has been applied to a number of problems in which the interaction consists of a hard core which completely excludes certain configurations.¹⁵

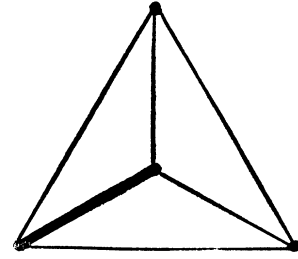
II. DERIVATION OF THE SERIES EXPANSION

The series expansion will be derived for arbitrary linear graphs G which are regular of degree q , that is, each vertex is joined by q edges to other vertices. Infinite regular lattices are a special case. The total

¹⁴ M. E. Fisher and John Stephenson, Phys. Rev. 132, 1411 (1963).

¹⁵ For example, see J. F. Nagle, J. Math. Phys. 7, 1484 and 1492 (1966).

FIG. 1. Tetrahedron graph with one dimer and two monomers.



number of vertices in the graph will be denoted by N and it then follows that there are $\frac{1}{2}qN$ edges. A dimer on G consists of two vertices joined by a distinguished edge and no two dimers have a vertex in common. (See Fig. 1.) Vertices which are not part of any dimer are called monomers. The grand-canonical partition function is defined as

$$\Xi_N(z_1, z_2) = \sum_{\alpha N=0}^N z_1^{\alpha N} z_2^{(1-\alpha)N/2} \sum [\text{states with } \alpha N \text{ monomers and } \frac{1}{2}(1-\alpha)N \text{ dimers}], \quad (1)$$

where z_1 is the activity of a monomer and z_2 is the activity of a dimer. It is also convenient to define $\sigma = q-1$. Then, the series expansion of the grand-canonical partition function is given by the following theorem:

$$\text{Theorem: } \Xi_N(z_1, z_2) = [F(z_1, y_2)]^N \sum_{G' \subseteq G} w(G'), \quad (2)$$

where

$$(i) \quad y_2 = (z_1/2\sigma) [(1+4\sigma z_2/z_1^2)^{1/2} - 1] \quad \text{or} \quad y_2(z_1 + \sigma y_2) = z_2, \quad (3)$$

$$(ii) \quad F(z_1, y_2) = (z_1 + \sigma y_2)^{q/2} / (z_1 + q y_2)^{(q-2)/2}, \quad (4)$$

(iii) The summation is over all subgraphs, $G' \subseteq G$. The null subgraph is required, but subgraphs which differ only by the number of vertices of degree zero (isolated vertices) are considered to be equivalent.

(iv) The weight $w(G')$ of a subgraph G' is given by

$$w(G') = \frac{y_2^e}{(z_1 + \sigma y_2)^e} \prod_{p=0}^q (1-p)^{v(p)}, \quad (5)$$

where e is the number of edges in G' and $v(p)$ is the number of vertices of degree p in G' .

It is convenient to introduce some terminology before deriving the theorem. For each vertex i there are $q+1$ vertex configurations ξ_i , as shown in Fig. 2. The first

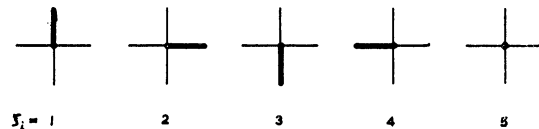


FIG. 2. The vertex configurations for $q=4$.

q vertex configurations have one dimer edge. The $(q+1)$ st vertex configuration has no dimer edge and corresponds to a monomer. Next we define various notions of compatibility of two vertex configurations ξ_i and ξ_j when the vertices i and j are nearest neighbors. ξ_i and ξ_j are called *directly compatible* if both ξ_i and ξ_j have a dimer edge on the edge joining vertices i and j . (Two directly compatible nearest-neighbor vertex configurations may be thought of as a dimer edge.) ξ_i and ξ_j are called *indirectly compatible* if neither ξ_i nor ξ_j has a dimer edge on the edge joining vertices i and j . (Two indirectly compatible nearest-neighbor vertex configurations may be thought of as an empty edge.) Finally, ξ_i and ξ_j are called *incompatible* if one of them has a dimer edge on the edge joining vertices i and j and the other does not. Now, we define a *compatibility function* $A(\xi_i, \xi_j)$ on the vertex configurations ξ_i and ξ_j of neighboring vertices i and j by

$$A(\xi_i, \xi_j) = 1, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are directly or} \\ \text{indirectly compatible} \\ = 0, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are incompatible.} \quad (6)$$

Also, we define a *labeling function* $B(\xi_i)$ by

$$B(\xi_i) = z_1, \quad \text{if } \xi_i = q+1 \\ = z_2^{1/2}, \quad \text{if } \xi_i = 1, 2, \dots, q. \quad (7)$$

Finally, a particular "state" of vertex configurations over the vertices of the entire graph will be called a *vertex complexion*, to be denoted as $\mathbf{C} = (\xi_1, \xi_2, \dots, \xi_N)$, where ξ_i is the vertex configuration of the i th vertex in the complexion \mathbf{C} . Clearly, there are $(q+1)^N$ vertex complexions.

The following identity, which is easily verified from (1), (6), and (7), is the starting point of the derivation.

$$\Xi_N(z_1, z_2) = \sum_{\mathbf{C}} \prod_{\substack{nn \\ i < j}} A(\xi_i, \xi_j) \prod_{i=1}^N B(\xi_i), \quad (8)$$

where the summation is over all $(q+1)^N$ vertex complexions, the first product is over all pairs of nearest-neighbor vertices, and the second product is over all vertices.

The idea is to transform the simple expression for the grand-partition function in (8) by rewriting each compatibility function essentially as a sum of a constant and a new compatibility function, i.e., $A(\xi_i, \xi_j) \sim (K + a(\xi_i, \xi_j))$. (This step is reminiscent of the Ursell-Mayer treatment of the classical gas problem.) The resulting expression for $\Xi_N(z_1, z_2)$ may then be expanded in powers of the new compatibility functions. Each product of new compatibility functions defines a subgraph of the basic graph in question under the one-to-one correspondence between $a(\xi_i, \xi_j)$ and the edge joining vertices i and j . The result of summation over vertex complexions of a product of new compatibility functions is called the *weight* of the corresponding

subgraph. Now, it is desirable that the $a(\xi_i, \xi_j)$ satisfy two conditions. First, if the new compatibility function is factorable,

$$a(\xi_i, \xi_j) = c_{ij}(\xi_i)c_{ji}(\xi_j); \quad (9)$$

then, as will be seen in the sequel, the computation of the graph weights becomes straightforward. Second, if

$$\sum_{\xi_i=1}^{q+1} c_{ij}(\xi_i)b(\xi_i) = 0, \quad (10)$$

where $b(\xi_i)$ is a new labeling function associated with the new compatibility function, then it will also be seen in the sequel that all graphs with any vertices of degree one have zero weight.

We define two parameters y_1 and y_2 which will shortly be related to z_1 and z_2 . Then, the definition of the new compatibility function is

$$a(\xi_i, \xi_j) = (y_1 + \sigma y_2)^2, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are directly} \\ \text{compatible;} \\ = -y_2(y_1 + \sigma y_2), \quad \text{if } \xi_i \text{ and } \xi_j \text{ are incom-} \\ \text{patible;} \\ = y_2^2, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are indirectly} \\ \text{compatible.} \quad (11)$$

This definition satisfies (9) as follows:

$$c_{ij}(\xi_i) = -(y_1 + \sigma y_2), \quad \text{if } \xi_i \text{ has a dimer edge on the} \\ \text{edge joining vertices } i \text{ and } j. \\ = y_2 \quad \text{otherwise.} \quad (12)$$

Let us also define

$$\varphi(\xi_i, \xi_j) = (y_1 + \sigma y_2)(y_1 + q y_2), \quad \text{if } \xi_i \text{ and } \xi_j \text{ are} \\ \text{directly compatible;} \\ = y_2(y_1 + q y_2), \quad \text{if } \xi_i \text{ and } \xi_j \text{ are} \\ \text{indirectly compatible;} \\ = 1, \quad \text{if } \xi_i \text{ and } \xi_j \text{ are} \\ \text{incompatible.} \quad (13)$$

Then, we may check that

$$A(\xi_i, \xi_j) = [y_2(y_1 + \sigma y_2) + a(\xi_i, \xi_j)] / \varphi(\xi_i, \xi_j). \quad (14)$$

From (8), (13), and (14), it follows that

$$\Xi_N(z_1, z_2) = \sum_{\mathbf{C}} \prod_{nn} [y_2(y_1 + \sigma y_2) + a(\xi_i, \xi_j)] \\ \times \prod_{i=1}^N [B(\xi_i) / y_2^{(q-\rho)/2} (y_1 + q y_2)^{q/2} (y_1 + \sigma y_2)^{\rho/2}], \quad (15)$$

where $\frac{1}{2}\rho N$ is defined as the number of dimers present, and equals the number of directly compatible φ factors. Since ρ is an implicit function of z_1 and z_2 , it will be removed by absorbing it into a new labeling function.¹⁶

¹⁶ In the first derivation by this author, ρ was kept explicit, which led to a series expansion for the entropy, which for infinite lattices was evaluated by the method of steepest descents. The author is deeply indebted to M. E. Fisher for suggesting the step performed here which allows us to use grand-canonical methods.

Let us define

$$\begin{aligned} b(\xi_i) &= z_1, & \text{if } \xi_i = q+1; \\ &= z_2^{1/2} y_2^{1/2} / (y_1 + \sigma y_2)^{1/2}, & \text{if } \xi_i = 1, \dots, q. \end{aligned} \quad (16)$$

Then, (15) becomes

$$\begin{aligned} \Xi_N(z_1, z_2) &= \sum_C \prod_{nn} [y_2(y_1 + \sigma y_2) + a(\xi_i, \xi_j)] \\ &\quad \times \prod_{i=1}^N [b(\xi_i) / y_2^{q/2} (y_1 + q y_2)^{q/2}]. \end{aligned} \quad (17)$$

Alternatively, the new labeling function could be defined as

$$\begin{aligned} b'(\xi_i) &= z_1 (y_1 + \sigma y_2)^{1/2} / y_2^{1/2}, & \text{if } \xi_i = q+1; \\ &= z_2^{1/2}, & \text{if } \xi_i = 1, \dots, q. \end{aligned} \quad (18)$$

Then, (15) would become

$$\begin{aligned} \Xi_N(z_1, z_2) &= \sum_C \prod_{nn} [y_2(y_1 + \sigma y_2) + a(\xi_i, \xi_j)] \\ &\quad \times \prod_{i=1}^N [b'(\xi_i) / y_2^{\sigma/2} (y_1 + q y_2)^{q/2} (y_1 + \sigma y_2)^{1/2}]. \end{aligned} \quad (19)$$

The remainder of the derivation is much the same whether $b(\xi_i)$ or $b'(\xi_i)$ is used, and the final series expansions will be shown to be equivalent. Therefore, it is sufficient to consider only (16) and (17). To satisfy (10) now requires

$$\begin{aligned} b(\xi_i) &= y_1 & \text{if } \xi_i = q+1 \\ &= y_2 & \text{if } \xi_i = 1, \dots, q. \end{aligned} \quad (20)$$

Thus, from (16) and (20),

$$y_1 = z_1 \quad \text{and} \quad y_2 = z_2^{1/2} y_2^{1/2} / (y_1 + \sigma y_2)^{1/2}, \quad (21)$$

in accordance with (3) in the statement of the theorem.

As was mentioned earlier, the series expansion is in powers of the $a(\xi_i, \xi_j)$ compatibility functions and each product of the $a(\xi_i, \xi_j)$ compatibility functions corresponds to a subgraph of the original graph. The first term of the series is defined as the one with no $a(\xi_i, \xi_j)$ factors. This term will be denoted as $[F(z_1, y_2)]^N$ and is easily calculated from (17) to be

$$F(z_1, y_2) = (z_1 + \sigma y_2)^{q/2} / (z_1 + q y_2)^{(q-2)/2}, \quad (22)$$

in agreement with the notation of (4) in the statement of the theorem. It is desirable to factor $[F(z_1, y_2)]^N$ from the series so that the first term of the final series is unity. Therefore, from (22) and (17), we have

$$\begin{aligned} \Xi_N(z_1, z_2) &= [F(z_1, y_2)]^N \sum_C \prod_{nn} [y_2(z_1 + \sigma y_2) + a(\xi_i, \xi_j)] \\ &\quad \times \prod_{i=1}^N [b(\xi_i) / y_2^{q/2} (z_1 + \sigma y_2)^{q/2} (z_1 + q y_2)]. \end{aligned} \quad (23)$$

The final step in the proof of the theorem is to find the weights of subgraphs corresponding to products of

one or more $a(\xi_i, \xi_j)$ compatibility functions. From (2) and (23) we see that $w(G')$ is defined by

$$\begin{aligned} w(G') &= \sum_C [y_2(z_1 + \sigma y_2)]^{-e} \prod_{nn \text{ in } G'} a(\xi_i, \xi_j) \\ &\quad \times \prod_{i=1}^N b(\xi_i) / (z_1 + q y_2), \end{aligned} \quad (24)$$

where each $a(\xi_i, \xi_j)$ corresponds to one of the e edges of G' . Next, perform a partial vertex complexation summation in (24) over all vertices not contained in G' . Then,

$$\begin{aligned} w(G') &= [y_2(z_1 + \sigma y_2)]^{-e} \sum_{\xi_i \text{ in } G'} \prod_{nn \text{ in } G'} a(\xi_i, \xi_j) \\ &\quad \times \prod_{i \text{ in } G'} b(\xi_i) / (z_1 + q y_2), \end{aligned} \quad (25)$$

where the summation is now over all vertex complexions of G' and the second product is over all vertices in G' . Because of the dependence of the $a(\xi_i, \xi_j)$ on both ξ_i and ξ_j , the summation in (25) is "cooperative." However, it is possible to perform this summation over each vertex independently because the $a(\xi_i, \xi_j)$ as defined by (11) and (12) are factorable. Therefore,

$$\begin{aligned} w(G') &= [y_2(z_1 + \sigma y_2)]^{-e} \prod_{i \text{ in } G'} \sum_{\xi_i=1}^{q+1} \frac{b(\xi_i)}{(z_1 + q y_2)} \\ &\quad \times \prod_j c_{ij}(\xi_i), \end{aligned} \quad (26)$$

where the j index runs over all nearest neighbors of i in G' , and the summation is only over the vertex configurations of vertex i . This single-vertex summation is easily performed for an arbitrary vertex in G' . Let vertex i have degree p in G' , which means that there will be p factors, $c_{ij}(\xi_i)$. Now for $\xi_i = q+1$, which is the vertex configuration corresponding to a monomer, all p of the $c_{ij}(\xi_i)$ equal y_2 and $b(\xi_i)$ equals z_1 . The remaining q vertex configurations have a dimer edge and $b(\xi_i)$ equals y_2 . Of these q vertex configurations, p have their dimer edge in G' and for these one of the $c_{ij}(\xi_i)$ equals $-(z_1 + \sigma y_2)$ and the other $(p-1)$ equal y_2 . The remaining $(q-p)$ vertex configurations do not have their dimer edge in G' , and for these all the $c_{ij}(\xi_i)$ equal y_2 . Thus,

$$\begin{aligned} w(G') &= [y_2(z_1 + \sigma y_2)]^{-e} \\ &\quad \times \prod_{i \text{ in } G'} \frac{z_1 y_2^p - p y_2^p (z_1 + \sigma y_2) + (q-p) y_2^{p+1}}{z_1 + q y_2} \\ &= \left[\frac{y_2}{z_1 + \sigma y_2} \right]^e \prod_{p=0}^q (1-p)^{v(p)}, \end{aligned} \quad (27)$$

where to obtain the last equality, use has been made of

the fact that the sum of the local vertex degrees equals twice the number of edges in a graph and $v(p)$ is defined to be the number of vertices of degree p in G' in accordance with (5) in the statement of the theorem. This completes the proof of the theorem.

The alternative derivation based on (18) and (19) yields the following modification which may be easily proved in the same way as the theorem. Modification:

$$\Xi_N(z_1, z_2) = [F(y_1, z_2)]^N \sum_{G' \subseteq G} w(G'), \quad (28)$$

where

$$(i) \quad y_1 = (\sigma^{1/2} z_1 / z_2^{1/2}) (z_2 + z_1^2 / 4\sigma)^{1/2} + z_1^2 / 2z_2^{1/2},$$

or

$$y_1^2 = z_1^2 (y_1 + \sigma z_2^{1/2}) / z_2^{1/2}; \quad (29)$$

$$(ii) \quad F(y_1, z_2) = z_2^{1/4} (y_1 + \sigma z_2^{1/2})^{\sigma/2} / (y_1 + q z_2^{1/2})^{(q-2)/2}. \quad (30)$$

(iii) (Same as in condition (iii) in the statement of the theorem).

(iv) The weight $w(G')$ of a subgraph G' is given by

$$w(G') = [z_2^{1/2} / (y_1 + \sigma z_2^{1/2})]^e \prod_{p=0}^q (1-p)^{v(p)}. \quad (31)$$

This modification is just the theorem disguised by an algebraic transformation of variables, as may be seen by the following equivalence of the series parameters.

$$\begin{aligned} y_2 / (z_1 + \sigma y_2) &= [(1 + (4\sigma z_2 / z_1^2))^{1/2} - 1] / \\ &\quad \sigma [1 + (4\sigma z_2 / z_1^2)]^{1/2} + 1] \\ &= (4z_2 / z_1^2) / [2 + (4\sigma z_2 / z_1^2) \\ &\quad + 2(1 + (4\sigma z_2 / z_1^2))^{1/2}] \\ &= z_2^{1/2} / (y_1 + \sigma z_2^{1/2}). \end{aligned} \quad (32)$$

It may also be easily shown that $F(z_1, y_2) = F(y_1, z_2)$.

III. RECOVERY OF THE BETHE APPROXIMATION

One of the advantages of series expansions in which the weights of all graphs with any vertices of degree one is zero is that the term corresponding to the null subgraph should give the same result as the Bethe approximation. This follows because the Bethe approximation is exact for lattices with no cycles (polygonal paths), and for this kind of lattice (Bethe lattice) all subgraphs except the null subgraph have some vertices of degree one.¹⁷

First, let us rederive the Bethe approximation for the dimer problem. Assume that the number of dimers

¹⁷ Imposing the customary periodic boundary conditions on a lattice results in some subgraphs with no vertices of degree one which "loop the torus." For ordinary lattices, these can be neglected as a surface effect as $N \rightarrow \infty$. Formally, there is some difficulty in imposing periodic boundary conditions on the Bethe lattice, because the surface of a Bethe lattice is not negligible compared to the volume as $N \rightarrow \infty$. However, this complication does not seem to affect the validity of the statements made in the text, as will be seen in the sequel.

is $\frac{1}{2}N\rho$, so the number of dimer vertices is $N\rho$ and the number of monomer vertices is $N(1-\rho)$. Then, the number of ways, $W_N(\rho)$, to arrange $\frac{1}{2}N\rho$ dimers can be written approximately

$$W_N(\rho) = \left[\binom{N}{N\rho} q^{N\rho} \right] \left[\left(\frac{\rho}{q} \right)^{1/2} \left(1 - \frac{\rho}{q} \right)^{\sigma/2} \right]^{N\rho} \times \left[\left(1 - \frac{\rho}{q} \right)^{q/2} \right]^{N(1-\rho)}. \quad (33)$$

The first square bracket in (33) gives the number of ways to arrange $N\rho$ dimer vertex configurations on the lattice. The second square bracket in (33) is the square root of the probability (disregarding correlations around cycles) of a dimer vertex configuration being compatible with all its nearest-neighbors' vertex configurations. (For example, ρ/q is the probability that the dimer edge meets another dimer edge and $[1 - (\rho/q)]$ is the probability that an empty edge meets an empty edge.) The third square bracket in (33) is the square root of the probability of a monomer vertex configuration being compatible with all its nearest-neighbors' vertex configurations. The square roots are taken since the probabilities would otherwise be computed twice, once from each vertex at the end of each edge.

From (33) we may compute the entropy as a function of density. To compute the grand potential Γ as a function of z_2 we may use the following equations, which are valid for purely hard-core systems:

$$N \ln z_2^{1/2} = - (d/d\rho) \ln W_N(\rho), \quad (34)$$

$$(1/N) \Xi_N = \Gamma = (1/N) [\ln W_N - \rho (d/d\rho) \ln W_N(\rho)]. \quad (35)$$

(These may be derived from $S/k = -F/kT = -\rho \ln z + \Gamma$, and $\rho = z(d/dz)\Gamma$. $z_2^{1/2}$ appears in (34) because ρ is defined as twice the density of dimers.) From (33) and (34) we obtain

$$z_2^{1/2} = \rho^{1/2} (q - \rho)^{1/2} / (1 - \rho)q, \quad (36)$$

or

$$\rho = q(1 + 2qz_2 - (1 + 4\sigma z_2))^{1/2} / 2(1 + q^2 z_2), \quad (37)$$

and from (33), (35), and (36) we obtain

$$\begin{aligned} \Gamma_B(z_2) &= (q/2) \ln [1 + 2q\sigma z_2 + (1 + 4\sigma z_2)^{1/2}] \\ &\quad - \ln [q(1 + 4\sigma z_2)^{1/2} - (\sigma - 1)] \\ &\quad - \frac{1}{2} (q-2) \ln 2(1 + q^2 z_2), \end{aligned} \quad (38)$$

where the subscript B refers to the Bethe approximation.

It may be noticed that in the preceding derivation of the Bethe approximation we have neglected to include z_1 , the monomer activity. It is not essential to include it, since it is the ratio of activities, or in this case z_2/z_1^2 , which appears nontrivially in all quantities, as may be seen from (1). This may also be verified for the theorem and its modification in Sec. II. Now from

(2) and (35) the zeroth-order approximation is

$$\Gamma_0(z_1, z_2) = \ln F(z_1, y_2) = \ln z_1 + \frac{1}{2}q \ln \frac{1}{2}[(1+4\sigma z_2')^{1/2} + 1] - \frac{1}{2}(q-2) \ln(1/2\sigma) \times [\sigma - 1 + q(1+4\sigma z_2')^{1/2}], \quad (39)$$

where $z_2' = z_2/z_1^2$. To compare (37) with (38), set $z_1 = 1$ and therefore $z_2' = z_2$. The equivalence of (38) and (39) now follows easily from the following identities.

$$4\sigma(1+q^2 z_2) = [q(1+4\sigma z_2)^{1/2} + \sigma - 1] \times [q(1+4\sigma z_2)^{1/2} - (\sigma - 1)],$$

$$2[1+2q\sigma z_2 + (1+4\sigma z_2)^{1/2}] = [1 + (1+4\sigma z_2)^{1/2}] \times [q(1+4\sigma z_2)^{1/2} - (\sigma - 1)]. \quad (40)$$

IV. GRAPH DATA AND THE SERIES

To obtain higher approximations than the zeroth order or Bethe approximation, one must know the number of ways closed subgraphs (no vertices of degree one) may occur on the graph. In the case of infinite lattices one first takes $\lim_{N \rightarrow \infty} (1/N) \ln(\text{series})$. This is accomplished formally by retaining only the coefficients of N in the series.⁹

In the derivation and often in the application of lattice data, it is convenient to classify graphs by topological type.¹⁸⁻²⁰ Some particular topological types required for the dimer series are shown in Fig. 3. A particular graph may be obtained from its topological type by the insertion of zero or more vertices of degree two. This classification of graphs by topological type is particularly well suited to the dimer series derived in Sec. II since all graphs with the same topological type and the same number of edges have the same weight. Furthermore, the dependence of the graph weight on the number of edges is particularly simple. Let us define the *specific weight* $y(G')$ of a graph G' with e edges by

$$y(G') = e^{-\epsilon w(G')}, \quad (41)$$

where x is the expansion variable in the series given by

$$x = y_2 / (z_1 + \sigma y_2). \quad (42)$$

Let T denote the topological type of G' . Then, considering T also as a particular graph with $e(T)$ edges, we have

$$y(G') = (-1)^{e-e(T)} y(T), \quad (43)$$

where, of course, $y(T)$ does not depend on e .

The problem of obtaining lattice data has been considered in detail by Sykes¹³ and his collaborators and data for the major lattices will shortly become available which will enable the computation of many more terms in the dimer series than are presented here.

¹⁸ J. F. Nagle, *J. Math. Phys.* **7**, 1588 (1966).

¹⁹ B. R. Heap, *J. Math. Phys.* **7**, 1582 (1966).

²⁰ M. F. Sykes, J. W. Essam, B. R. Heap, and B. J. Hiley, *J. Math. Phys.* **7**, 1557 (1966).

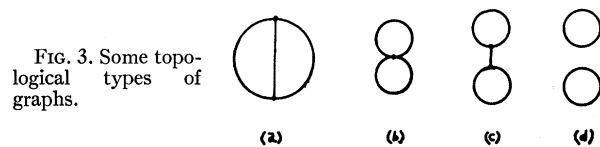


FIG. 3. Some topological types of graphs.

Most of the lattice data used in this paper have been obtained from Sykes prior to publication or from the review article by Domb.⁹ The following series are given in powers of the variable x defined in (42), and the series give $\Gamma - \Gamma_0 = (1/N) \ln \Xi_N - \ln F(z_1, y_2)$:

honeycomb lattice

$$(1/2)x^6 + (3/2)x^{10} + 6x^{11} - (3/4)x^{12} + \dots, \quad (44)$$

square lattice (sq)

$$x^4 + 2x^6 + 8x^7 - (7/2)x^8 + 80x^9 - 44x^{10} + 392x^{11} + \dots, \quad (45)$$

diamond lattice

$$2x^6 + 3x^8 + 72x^{11} - 11x^{12} + 720x^{13} - 1002x^{14} + 3712x^{15} - 9568\frac{1}{2}x^{16} + \dots, \quad (46)$$

triangular lattice

$$-2x^3 + 3x^4 + 6x^5 - 73x^6 + 360x^7 - 1348\frac{1}{2}x^8 + \dots, \quad (47)$$

simple-cubic lattice (sc)

$$3x^4 + 22x^6 + 72x^7 - 559\frac{1}{2}x^8 + 2016x^9 - 3612x^{10} + \dots, \quad (48)$$

face-centered-cubic lattice (fcc)

$$-8x^3 + 33x^4 - 24x^5 - 1534x^6 + \dots. \quad (49)$$

V. DISCUSSION OF THE SERIES AND SOME PRELIMINARY RESULTS

A. Entropy at Close Packing of Dimers

To obtain the limit of close packing of dimers we may set $z_1 = 0$ and $z_2 = 1$. Then, the grand potential $\Gamma(0,1)$ equals $(1/N) \ln W_N(\rho=1)$, where $W_N(1)$ is the number of ways to arrange dimers on the lattice when the lattice is completely filled with dimers. The series for $(1/N) \ln W_N(1)$ have been approximated in two ways in this paper. First, the series have been truncated after the last term. Second, the Padé approximants to the series have been formed²¹ and the values obtained from the last three near diagonal approximants $[(n,n), (n \pm 1, n), \text{ and } (n, n \pm 1)]$ have been averaged. In the case of the honeycomb lattice, the series is so erratic that only the last three terms have been treated using the Padé approximant.

It has been customary in the literature to quote the value of $[W_N(1)]^{2/N}$, called the molecular freedom per dimer. The approximant evaluations of the molecular freedom per dimer computed from the above approximations of $(1/N) \ln W_N(1)$ are given in Table I, along with the approximations given by other authors and

²¹ G. A. Baker, *Phys. Rev.* **129**, 99 (1963).

TABLE I. Values of W^2 , the molecular freedom per dimer at close packing, for some major lattices.

	Honeycomb	Square	Diamond	Triangular	S. C.	F. C. C.
Fowler & Rushbrooke ^a		1.8	1.8	2.3 also 2.38	2.38	
Miller ^b & Chang ^c Bethe approx.	1.3333	1.6875	1.6875	2.4113	2.4113	4.6079
Rushbrooke ^d		1.78		2.36	2.46	4.57
This paper Truncated series	1.3659	1.7694	1.7007	2.3519	2.4420	4.5642
This paper Padé ^e series	1.3659 ^e	1.7905	1.7004	2.3562	2.4423	4.5693
Exact ^f	1.3814	1.7916		2.3565		

^a Reference 1.
^d Reference 23.

^b Reference 3.
^e See text.

^c Reference 2.
^f See Refs. 8 and 15.

the exact results known for two-dimensional lattices. Since the zeroth-order term of the series presented here is the (first-order) Bethe approximation, one is not surprised that the approximations of this paper are better than those of Chang and Miller.^{2,3} An entirely different method used by Fowler and Rushbrooke is to compute the exact values of $W_N(1)$ for finite strips of lattice and extrapolate the width of the strips to infinity.¹ (This method is now being used by Runnels²² for the intermediate-density problem.) Although this method has given very good results for various problems in two dimensions, it is too laborious to apply to three-dimensional lattices. Finally, the series of Rushbrooke, Scoins and Wakefield may be used to obtain extrapolated approximations which are quite good.²³ This reflects the fact that not many terms are needed in the basic low density series in order to obtain adequate approximations to the molecular freedom per dimer.

Fowler and Rushbrooke¹ suggested that the molecular freedom per dimer might be primarily dependent on coordination number, and this is true in the Bethe approximation. However, it is not true for the series corrections. These are of opposite sign for the triangular and simple-cubic lattices largely because the first term is negative for close-packed lattices and positive for loose-packed ones. The square lattice and the diamond lattice also have the same coordination number and both are loose packed, but the diamond lattice has fewer short cycles, so the series correction to the Bethe approximation is smaller than for the square lattice. Since there is no reason to believe that this approximation method is any less accurate in three dimensions than in two dimensions, we conclude that the three-dimensional Padé approximations in Table I are probably quite close to the exact values and are certainly better than previous approximations.

²² L. K. Runnels (private communication).

²³ G. S. Rushbrooke (private communication). It may be noted that Professor Rushbrooke's choice of quoting only three significant figures imposes a somewhat larger error on his estimates than might be reasonably inferred from his series, especially for the close-packed lattices.

A. Low-Density Series Expansions

We may set $z_1=1$ for the low-density series since only the ratio z_2/z_1^2 is physically significant. The series parameter x given by (42) may be expanded in terms of z_2 as

$$x = z_2 - 2\sigma z_2^2 + 5\sigma^2 z_2^3 - 14\sigma^3 z_2^4 + \dots \quad (50)$$

Because this expansion has no constant term, the first n terms in the expansion of $\Gamma(1, z_2)$ in powers of z_2 can be found from the first n terms in the expansion of Γ in powers of x . Since the series in powers of z_2 is also being obtained in another way (see Introduction and Ref. 24), we will not discuss it further.

We may also examine the series expanded in the natural parameter x . This is also a low-density expansion since x increases as z_2 increases. $x = \sigma^{-1}$ is the close-packing limit. Equation (42) implies

$$y_2 = x/(1 - \sigma x),$$

and then (21) yields

$$z_2 = x/(1 - \sigma x)^2 \quad \text{and} \quad dz_2/dx = (1 + \sigma x)/(1 - \sigma x)^3. \quad (51)$$

Using (51) the density of dimers, ρ_2 , and the isothermal compressibility K_T are

$$\rho_2 = z_2(d\Gamma/dz_2) = [x(1 - \sigma x)/(1 + \sigma x)](d\Gamma/dx), \quad (52)$$

and

$$kT\rho K_T = d\rho/d\Gamma = (d\rho/dx)/(d\Gamma/dx)$$

$$= \frac{1 - 2\sigma x - (\sigma x)^2}{(1 + \sigma x)^2} + \frac{x(1 - \sigma x)(d^2\Gamma/dx^2)}{(1 + \sigma x)(d\Gamma/dx)}. \quad (53)$$

Also, in terms of x , the Bethe approximation is

$$\Gamma_B(x) = -\ln(1 - \sigma x) - \frac{1}{2}(q - 2)\ln(1 + x). \quad (54)$$

The total Γ is given as $\Gamma = \Gamma_B + \Gamma_s$ where the $\Gamma_s(x)$ are given in Sec. IV.

We will now investigate the permissible behavior of $\Gamma_s(x)$ and its derivatives. Let us allow $d^2\Gamma_s/dx^2$ to have a pole of order $(x_c - x)^{-\gamma}$ where x_c is the critical value of x . If $\gamma > 1$, then the dominant part of $d\Gamma_s/dx$ at x_c

goes as $(x_c - x)^{1-\gamma}$, and if $\gamma > 2$, then the dominant part of Γ_s at x_c goes as $(x_c - x)^{2-\gamma}$. It should be noted that for the Bethe approximation, $\Gamma_B(x)$, in (54), $\gamma = 2$, and $x_c = \sigma^{-1}$. There are two interesting cases to consider.

(a). Assume $x_c < \sigma^{-1}$. Since there is no singularity in the Bethe approximation for such an x_c , (52) implies that $\gamma < 1$ since ρ_2 cannot exceed $\frac{1}{2}$. The fact that the series for the molecular freedom per dimer, which is just $\exp 2\Gamma_s(x = \sigma^{-1})$, behaves so well suggests that γ is not too large and that x_c is not too far from σ^{-1} .

(b). Assume $x_c = \sigma^{-1}$. Using only Γ_B in (52) gives $\rho_c = \frac{1}{2}$. Therefore, $d\Gamma_s/dx$ must be less singular than $d\Gamma_B/dx$, so that $\gamma < 2$. This also follows from the series analysis of the molecular freedom per dimer. Thus, in this case the singularities in Γ and its derivatives are dominated by the Bethe approximation. However, non-Bethe-like behavior may exist in the rates at which $\rho_c - \rho$ and K_T approach zero as $x \rightarrow x_c$. Consider

$$\rho_c - \rho = \frac{1 - \sigma x}{1 + \sigma x} \left[\frac{1}{2} + \frac{(q-2)x}{2(1+x)} - x(d\Gamma_s/dx) \right]. \quad (55)$$

A not too obvious possibility is for

$$d\Gamma_s/dx = (\sigma^2/q) - d(1 - \sigma x)^\alpha + \dots, \quad (56)$$

where $\alpha > 0$, and d is a constant. Then, the asymptotic behavior as $x \rightarrow \sigma^{-1}$ of (55) is

$$\rho_c - \rho \sim (1 - \sigma x)^{1+\alpha}. \quad (57)$$

This kind of behavior with $\alpha \sim 1/7$ agrees with a preliminary analysis performed by Gaunt²⁴ using a rearrangement of the low-density series for Γ in powers of z_2 for the sq lattice. If (56) is valid, then $\gamma = 1 - \alpha < 1$.

C. High-Density Series Expansion

Next, we ask if a high-density series expansion can be found. Let us set $z_2 = 1$ and expand in powers of z_1 . The relevant formulas are obtained most easily from the modification to the theorem, Eqs. (29), (30), and (31):

$$x = \sigma^{-1}(1 - \sigma^{-\frac{1}{2}}z_1 + \sigma^{-1}z_1^2/2 + \dots), \quad (58)$$

and

$$\Gamma_B = -\frac{1}{2} \ln x - \frac{1}{2}(q-2) \ln(1+x). \quad (59)$$

Because there is a constant term in (58), each graph will contribute to the coefficient of each power of z_1 .

Thus, formally,

$$\Gamma(z_1, 1) = \Gamma(0, 1) + a_1 z_1 + a_2 z_1^2 + \dots, \quad (60)$$

where $\Gamma(0, 1)$, a_1 , and a_2 are each an infinite series. $\Gamma(0, 1)$ was evaluated approximately in the discussion of the entropy at close packing. By taking the coefficients of z_1 and z_1^2 in the expansion of x^n , it is easily verified from (58), (59), (42), and (5) that

$$a_1 = (\sigma^{1/2}/q) - \sigma^{-3/2}(d\Gamma_s/dx)|_{x=\sigma^{-1}} \quad (61)$$

$$a_2 = (q-2)/2q^2 + \frac{1}{2}\sigma^{-2}\partial\Gamma_s/\partial x|_{x=\sigma^{-1}} + \frac{1}{2}\sigma^{-3}\partial^2\Gamma_s/\partial x^2|_{x=\sigma^{-1}}. \quad (62)$$

The first terms come from the Bethe approximation and the terms in the series are simply related to the derivatives of Γ_s evaluated at close packing.

This formal connection between the coefficients of the high-density series and the derivatives of the low-density series leads to the following observation: If Eq. (56) is valid, then $a_1 = 0$ and for $\alpha < 1$, a_2 is a divergent sum. This behavior for the series in (60) has been suggested by Fisher and Stephenson¹⁴ in their study of the monomer correlation coefficients for the sq lattice. They felt that this behavior indicates an incipient phase transition at close packing. Since (56) is also suggested by otherwise independent work, this is strong presumptive evidence that $\gamma < 1$ and $x_c = \sigma^{-1}$.

However, preliminary studies of the series for $d\Gamma_s/dx$ and $d^2\Gamma_s/dx^2$ using the Padé approximant tend to suggest that $\gamma > 1$ or $x_c < \sigma^{-1}$ for the sq lattice. (In contrast, there is no evidence of any physical singularities in Γ_s or any of its derivatives for the triangular lattice.) Still, the series are not yet very long and sequences of Padé approximants are erratic, so this evidence is far from conclusive. It is hoped that when the lattice data become available, analysis of the longer series will resolve the outstanding questions concerning the thermodynamic behavior.

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²⁴ D. S. Gaunt (private communication).