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THE STATISTICS OF DIMERS ON A LATTICE

I. THE NUMBER OF DIMER ARRANGEMENTS ON A QUADRATIC LATTICE

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Synopsis

The number of ways in which a finite quadratic lattice (with edges or with periodic boundary conditions) can be fully covered with given numbers of "horizontal" and "vertical" dimers is rigorously calculated by a combinatorial method involving Pfaffians. For lattices infinite in one or two dimensions asymptotic expressions for this number of dimer configurations are derived, and as an application the entropy of a mixture of dimers of two different lengths on an infinite rectangular lattice is calculated. The relation of this combinatorial problem to the Ising problem is briefly discussed.

§ 1. *Introduction.* Combinatorial problems relating to a regular space lattice arise in the theory of various physical phenomena. One of these problems is the "*arrangement problem*", which plays a role in the explanation of the non-ideal thermodynamic behaviour of liquids consisting of molecules of different size with zero energy of mixing (athermal mixtures). In the investigations devoted to this problem (most of which have been discussed critically by Guggenheim¹⁾) much attention has been paid to the so-called quasi-crystalline model. One considers a regular lattice consisting of points (sites, vertices) connected by bonds. This lattice is fully covered with *monomers* (molecules occupying one site) and rigid or flexible *polymers* (molecules occupying several sites connected by bonds); the latter may be dimers, trimers etc., but also "high polymers". If the energy of mixing is zero the thermodynamic properties of this system can be calculated from the *combinatorial factor*, i.e. the number of ways of arranging given numbers of monomers and polymers on the lattice.

The same combinatorial problem arises in the cell-cluster theory of the liquid state²⁾. There one divides the volume of a liquid into a set of cells of which the centres form a regular lattice, and one considers situations in which, by the removal of certain interfaces between cells, a number of double cells, triple cells etc. have been formed. For the calculation of the free energy of the liquid one then has to determine the number of ways in which

a given volume can be divided into given numbers of single, double, triple cells etc.; the equivalence of this combinatorial factor with the former one is obvious.

A two-dimensional form of the arrangement problem is encountered in the theory of adsorption of diatomic, triatomic etc. molecules on a regular surface. The empty sites of the surface then play the role of "monomers".

As in many problems of this sort, it is easy to find the most general solution for a one-dimensional lattice ²⁾, it appears very difficult to find a more or less general solution for two-dimensional lattices, whereas for three dimensions any exact solution seems extremely remote. Therefore one generally uses approximation methods; we refer to the work of Fowler and Rushbrooke ³⁾ (who also made some rigorous calculations on two- and three-dimensional infinite strips of finite width), Chang, Flory, Huggins, Miller, Guggenheim (for detailed references see ref. 1), Orr ⁴⁾, Rushbrooke, Scoins and Wakefield ⁵⁾, and Cohen, De Boer and Salsburg ²⁾. Recently, Green and Leipnik ⁶⁾ claimed to have found a rigorous solution for the case of monomer-dimer mixtures on a two-dimensional lattice, but Fisher and Temperley ⁷⁾, and Katsura and Inawashiro ⁷⁾ proved that their results were not correct.

In this paper we present a rigorous solution to the above-mentioned combinatorial problem for a very special case, viz. that of a *two-dimensional quadratic lattice, completely covered with dimers* (in terms of graph theory we ask for the number of "perfect matchings" of the lattice ⁸⁾). Both the absence of monomers and the dimension of the lattice form serious restrictions, but it is hoped that the present investigation may be useful as a first step. The situation has some resemblance to that of the combinatorial problem connected with the Ising model of cooperative phenomena ⁹⁾, for which an exact solution has been given for an equally special case ¹⁰⁻¹³⁾. It will be shown that the two problems are to a certain extent analogous. In § 2 and § 3 we shall develop the method of solution for the case of a finite lattice imbedded in a plane (i.e. a rectangle with edges), and in § 4 for that of a lattice imbedded in a torus (i.e. with periodic boundary conditions). In § 5 an alternative method will be sketched. As an application, the entropy of a certain mixture of dimers is calculated in § 6.

It is intended to treat in a subsequent paper the statistics of dimers on other two-dimensional lattices, to discuss boundary effects and to make some remarks on three-dimensional lattices.

§ 2. *The planar quadratic lattice.* Consider a planar quadratic $m \times n$ lattice Q_{mn} to which one can attach dimers (figures consisting of two linked vertices) in such a way that every dimer occupies two lattice points connected by a bond. We indicate the lattice points by (i, j) or p ($i = 1, \dots, m$; $j = 1, \dots, n$; $p = 1, \dots, mn$), the number of "horizontal" dimers (occupying

two points (i, j) and $(i + 1, j)$ by N_2 and the number of "vertical" dimers (occupying two points (i, j) and $(i, j + 1)$) by N'_2 . If $g(N_2, N'_2)$ is the *combinatorial factor*, i.e. the number of ways of covering the lattice with dimers so that every site is covered by one and only one dimer vertex, we ask for the *configuration generating function*

$$Z_{mn}(z, z') = \sum'_{N_2, N'_2} g(N_2, N'_2) z^{N_2} z'^{N'_2}, \quad (1)$$

where the sum runs over all combinations N_2, N'_2 satisfying $2(N_2 + N'_2) = mn$; if desired, the counting variables z and z' may be viewed as activities and Z_{mn} as the configurational partition function. At least one of the two numbers m and n has to be even; let m be even. We shall refer to the arrangement of dimers occupying the pairs of sites p_1 and p_2, p_3 and p_4, p_5 and p_6 , etc. as to the *configuration* $C = |p_1; p_2| p_3; p_4| p_5; p_6| \dots |p_{mn-1}; p_{mn}|$. A simple but important configuration is

$$C_0 = |1, 1; 2, 1| 3, 1; 4, 1| \dots |m - 1, 1; m, 1| 1, 2; 2, 2| \dots |m - 1, n; m, n|,$$

which we shall call the *standard configuration* (fig. 1a). We could, however, represent this arrangement of dimers equally well by $|2, 1; 1, 1| 3, 1; 4, 1| \dots$ or by $|4, 1; 3, 1| 1, 1; 2, 1| \dots$ etc. To make the representation unique we order the points of the lattice row after row by choosing the p -numbering as follows:

$$(i, j) \leftrightarrow p = (j - 1)m + i, \quad (2)$$

and we introduce the convention that the points of a configuration shall be indicated in the following ("canonical") order:

$$p_1 < p_2; p_3 < p_4; \dots; p_{mn-1} < p_{mn}; \quad (3a)$$

$$p_1 < p_3 < \dots < p_{mn-1}. \quad (3b)$$

By analogy to the determinantal approach to the Ising problem developed by Kac and Ward¹¹⁾ we shall try to construct a mathematical form consisting of a series of terms each of which corresponds uniquely to one configuration and has the "weight" $z^{N_2} z'^{N'_2}$ of this configuration. The conditions (3) strongly suggest that this form should be a *Pfaffian* rather than a determinant. A Pfaffian is a number attributed to a triangular array of coefficients $a(k; k')$ ($k = 1, \dots, N$; $k' = 1, \dots, N$; $k < k'$; N even) in the following way¹⁴⁾:

$$\text{Pf}\{a(k; k')\} = \sum_P \delta_P a(k_1; k_2) a(k_3; k_4) \dots a(k_{N-1}; k_N), \quad (4)$$

where the sum runs over those permutations k_1, k_2, \dots, k_N of the numbers $1, 2, \dots, N$ which obey

$$k_1 < k_2; k_3 < k_4; \dots; k_{N-1} < k_N; k_1 < k_3 < \dots < k_{N-1}, \quad (3')$$

and where δ_P is the parity of the permutation P , i.e. -1 or $+1$ according

as P is an odd or an even permutation. Pfaffians have been introduced into physics by Caianello and Fubini¹⁵⁾ and in lattice-combinatorial problems by Hurst and Green¹³⁾.

We shall now show that it is possible indeed to define a triangular array of elements $D(p; p')$ so that

$$Z_{mn}(z, z') = \text{Pf}\{D(p; p')\}. \quad (5)$$

We begin by noting that if we define $D(p; p') = 0$ for all pairs of sites $(p; p')$ that are not connected by a bond, all terms in the Pfaffian that would not correspond to a dimer configuration will vanish. Next we put the coefficients $D(p; p')$ corresponding to pairs of sites that are connected by a horizontal or a vertical bond equal, in absolute magnitude, to z and z' , respectively. In this way we get all configurations represented by a term of the proper weight; the conditions (3) and (3') ensure that the correspondence is one-to-one.

Finally, in order that all configurations are counted positively we have to choose the signs of the non-zero elements such that the product $D(p_1; p_2) D(p_3; p_4) \dots$ has the same sign as the parity δ_P . It is evident that the product corresponding to the standard configuration C_0 has to be positive. Now, from C_0 one can obtain any arbitrary configuration C in the following way. We draw a picture of the lattice in which every dimer of the configuration C_0 is represented by a dotted line and every dimer of the configu-

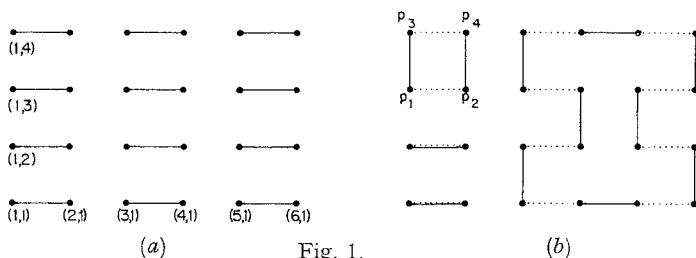


Fig. 1.
(a) The standard configuration C_0 of the planar lattice Q_{64}
(b) The construction of a new configuration C (full lines) from C_0 (dotted lines)

guration C by a full line (fig. 1b). Since any lattice point is the endpoint of just one line of each type the resulting figure consists of: a) pairs of sites connected both by a dotted line and by a full line; b) closed polygons consisting of alternating dotted and full lines (to be called C_0 -bonds and non- C_0 -bonds). If we then take the configuration C_0 and we shift in each of the "alternating" polygons all dimers clockwise or counter-clockwise by one step, C_0 goes over into C .

By analogy to the Ising problem⁹⁾ one might expect that each of the polygons (representing a cyclic permutation of an even number of lattice sites) would contribute a factor -1 to the parity δ_P of the permutation P corresponding to C . In fact, this is true, but owing to the restrictions on

the permutations occurring in a Pfaffian, the proof is not so simple as in the Ising problem. Consider e.g. the small square in fig. 1*b*. According to (3') its vertices occur in the term representing C_0 as ... $D(p_1; p_2)$... $D(p_3; p_4)$... and in the term representing C as ... $D(p_1; p_3)$ $D(p_2; p_4)$ Obviously the change from $p_1 p_2 p_3 p_4$ to $p_1 p_3 p_2 p_4$ is not a cyclic permutation of the four points along the square. It can, however, be considered as the product of the following permutations: $p_1 p_2 p_3 p_4 \rightarrow p_1 p_2 p_4 p_3$ (putting the points into a cyclic order corresponding to the square) $\rightarrow p_2 p_4 p_3 p_1$ (permuting the four points cyclically) $\rightarrow p_2 p_4 p_1 p_3$ (ordering the points p_1 and p_3 according to (3*a*)) $\rightarrow p_1 p_3 p_2 p_4$ (ordering the pairs $(p_1; p_3)$ and $(p_2; p_4)$ according to (3*b*)). The resulting permutation is odd; apparently the parities of the re-ordering permutations just compensate each other.

To show that this is true in general we first take a configuration which differs from C_0 only in the position of the dimers on one polygon. Consider a column of " C_0 -bonds" which is crossed by this polygon. If we describe a closed path along the polygon, we cross this column as many times in the "forward direction" (i.e., in the direction of increasing p) as in the "backward direction". This is true for any column of C_0 -bonds, and therefore, if the path contains r forward steps along C_0 -bonds it must also contain r backward steps along C_0 -bonds. By a similar argument combined with the alternation of the two types of bonds, we can show that it also contains r forward and r backward steps along non- C_0 -bonds. In the terms of the Pfaffian which correspond to C_0 and C , on the other hand, all points of the polygon occur in the order of increasing p . Consequently the permutation which changes the " C_0 -term" into the " C -term" can be considered as the product of: 1) the reversal of the r pairs of sites (C_0 -bonds) for which the canonical order is opposite to the required cyclic order; 2) the rearrangement of the $2r$ C_0 -bonds which is needed to get all polygon vertices in the cyclic order; 3) the cyclic permutation of these $4r$ vertices; 4) the reversal of the r pairs of sites which now violate (3*a*); 5) the rearrangement of the $2r$ pairs which is needed to satisfy (3*b*). Each reversal within a pair contributes a factor -1 to the parity of the resulting permutation, a reshuffling of the pairs a factor $+1$, and the cyclic permutation a factor $(-1)^{4r-1}$. We thus find that the total parity of the permutation is $(-1)^r(+1)(-1)^{4r-1}(+1)(-1)^r = -1$. If there is more than one polygon, we can perform the corresponding permutations consecutively; each polygon then contributes a factor -1 .

It shall now be indicated how these factors can be compensated for. First we remark that since no two C_0 -bonds have a point in common, an alternating polygon can neither intersect itself nor cross or touch other polygons. Therefore we shall not encounter such difficulties as arose in the corresponding step of Kac and Ward's method ^{11) 12)}.

Any alternating polygon can be considered as built up from horizontal strips of connected unit squares. From the requirement that during the

cyclic shift the opposite sides of a connected figure are shifted in opposite directions, combined with the alternation of C_0 -bonds and non- C_0 -bonds we conclude that both the numbers of unit squares in a strip and the number of strips are odd (cf. fig. 1b). Consequently, each alternating polygon encircles an odd number of unit squares, and it will be sufficient to choose the signs of the $D(p; p')$ such that among the four bonds bounding a unit square there is an odd number having a negative $D(p; p')$; we have further seen that the standard configuration has to appear with a positive sign. This can be realized e.g. by attributing minus signs to the coefficients of the vertical bonds between lattice sites of odd i . We thus get the following set of coefficients

$$\begin{aligned} D(i, j; i+1, j) &= +z && \text{for } 1 \leq i \leq m-1, 1 \leq j \leq n, \\ D(i, j; i, j+1) &= (-1)^i z' && \text{for } 1 \leq i \leq m, 1 \leq j \leq n-1, \\ D(i, j; i', j') &= 0 && \text{otherwise} \end{aligned} \quad (6)$$

The equations (5) and (6) are sufficient to derive the configuration generating function $Z_{mn}(z, z')$. It should be remarked that throughout this paper we assume that the dimers are symmetric. If they were asymmetric all elements $D(p; p')$ would have to be multiplied by 2, since any pair of sites might then be occupied in two distinguishable ways.

§ 3. *The evaluation of the Pfaffian.* For the evaluation of $\text{Pf}\{D(p; p')\}$ we make use of the property of a Pfaffian that its square is equal to the determinant of the skew-symmetric matrix to which the given triangular array of coefficients can be extended¹⁴). That is, in our case,

$$Z_{mn}^2(z, z') = [\text{Pf } D]^2 = \det D, \quad (7)$$

where D is the matrix given by (6) together with the requirement of skew symmetry:

$$D(i, j; i', j') = -D(i', j'; i, j), \quad (8)$$

and $\text{Pf } D$ stands for $\text{Pf}\{D(p; p')\}$.

If D were a completely periodic matrix, it could easily be brought into a diagonal form, viz. by a Fourier-type similarity transformation⁹), and the calculation of the determinant would be straightforward. However, the truncated edges of the lattice Q_{mn} disturb the periodicity of the matrix. Fortunately, it is still possible to bring it into a "nearly diagonal" form. We write D as the sum of two direct products of a $m \times m$ matrix and $n \times n$ matrix:

$$D = z(Q_m \times E_n) + z'(F_m \times Q_n), \quad (9)$$

where E is the unit matrix,

$$Q = \begin{bmatrix} 0 & 1 & 0 & 0 & \dots & 0 & 0 \\ -1 & 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & -1 & 0 & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 0 & 1 \\ 0 & 0 & 0 & 0 & \dots & -1 & 0 \end{bmatrix}, F = \begin{bmatrix} -1 & 0 & 0 & \dots & 0 & 0 \\ 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & 0 & -1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & -1 & 0 \\ 0 & 0 & 0 & \dots & 0 & 1 \end{bmatrix}, \quad (10)$$

and the indices indicate the order of the matrices. It can be verified that Q_n can be diagonalized by a similarity transformation $\tilde{Q}_n = U_n^{-1} Q_n U_n$ with the matrix U_n given by

$$\begin{aligned} U_n(l; l') &= \{2/(n+1)\}^{\frac{1}{2}} i^l \sin \{l' \pi / (n+1)\}, \\ U_n^{-1}(l; l') &= \{2/(n+1)\}^{\frac{1}{2}} (-i)^{l'} \sin \{l \pi / (n+1)\}; \end{aligned} \quad (11)$$

the diagonal elements of \tilde{Q}_n are the eigenvalues $2i \cos \{l \pi / (n+1)\}$ of Q_n ($l = 1, \dots, n$). On the other hand, this transformation obviously leaves E_n invariant. Q_m can be diagonalized analogously by a transformation with U_m , but this transformation disturbs the diagonal form of F_m , although not seriously. Transforming D with the direct product $U = U_m \times U_n$ we find that $\tilde{D} = U^{-1} D U$ has the following elements:

$$\begin{aligned} \tilde{D}(k, l; k', l') &= 2iz \delta_{k, k'} \delta_{l, l'} \cos \{k \pi / (m+1)\} - 2iz' \delta_{k+k', m+1} \delta_{l, l'} \\ &\quad \times \cos \{l \pi / (n+1)\}; \end{aligned}$$

i.e. the only non-zero elements are grouped in 2×2 blocks along the diagonal. Thus the determinant is readily found:

$$\det D = \det \tilde{D} = \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n \begin{vmatrix} 2iz \cos \frac{k\pi}{m+1} & -2iz' \cos \frac{l\pi}{n+1} \\ -2iz' \cos \frac{l\pi}{n+1} & -2iz \cos \frac{k\pi}{m+1} \end{vmatrix}, \quad (12)$$

and, from (7) and (12), we find the following expression for the configuration generating function of the lattice Q_{mn} :

$$\begin{aligned} Z_{mn}(z, z') &= \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n 2 \left[z^2 \cos^2 \frac{k\pi}{m+1} + z'^2 \cos^2 \frac{l\pi}{n+1} \right]^{\frac{1}{2}} = \\ &= \begin{cases} 2^{\frac{1}{2}mn} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^{\frac{1}{2}n} \left[z^2 \cos^2 \frac{k\pi}{m+1} + z'^2 \cos^2 \frac{l\pi}{n+1} \right], & (n \text{ even}) \\ 2^{\frac{1}{2}m(n-1)} z^{\frac{1}{2}m} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^{\frac{1}{2}(n-1)} \left[z^2 \cos^2 \frac{k\pi}{m+1} + z'^2 \cos^2 \frac{l\pi}{n+1} \right]. & (n \text{ odd}) \end{cases} \end{aligned} \quad (13)$$

In writing down the expression valid for odd n use has been made of the relation

$$\prod_{k=1}^{\frac{1}{2}m} 2 \cos \{k \pi / (m+1)\} = 1,$$

which is a particular case of the identity

$$\prod_{k=1}^{\frac{1}{2}m} 4 \left[u^2 + \cos^2 \frac{k\pi}{m+1} \right] \equiv \frac{[u + (1 + u^2)^{\frac{1}{2}}]^{m+1} - [u - (1 + u^2)^{\frac{1}{2}}]^{m+1}}{2(1 + u^2)^{\frac{1}{2}}}; \quad (14)$$

this identity holds (for even m) because the two members represent two polynomials in u of the same degree m , with the same zeros, and with equal coefficients of the leading term. For numerical calculations it is sometimes useful to perform, with the aid of (14), the product over k in (13). In this way we find

$$Z_{mn}(z, z') = z^{\frac{1}{2}mn} \prod_{l=1}^{[\frac{1}{2}n]} \frac{\left\{ \left[\zeta \cos \frac{l\pi}{n+1} + \left(1 + \zeta^2 \cos^2 \frac{l\pi}{n+1} \right)^{\frac{1}{2}} \right]^{m+1} - \left[\zeta \cos \frac{l\pi}{n+1} - \left(1 + \zeta^2 \cos^2 \frac{l\pi}{n+1} \right)^{\frac{1}{2}} \right]^{m+1} \right\}}{2 \left(1 + \zeta^2 \cos^2 \frac{l\pi}{n+1} \right)^{\frac{1}{2}}}, \quad (15)$$

where $\zeta = z'/z$ and $[\frac{1}{2}n] = \frac{1}{2}n$ or $\frac{1}{2}(n-1)$ according as n is even or odd.

In the limit $m \rightarrow \infty$, i.e. for *infinitely long strips* of finite width n , we get

$$Z_n(z, z') = \lim_{m \rightarrow \infty} \{Z_{mn}(z, z')\}^{1/m} = z^{\frac{1}{2}n} \prod_{l=1}^{\frac{1}{2}n} \left[\zeta \cos \frac{l\pi}{n+1} + \left(1 + \zeta^2 \cos^2 \frac{l\pi}{n+1} \right)^{\frac{1}{2}} \right]. \quad (16)$$

Finally we have, in the limit of an *infinitely large lattice*:

$$\begin{aligned} Z(z, z') &= \lim_{m, n \rightarrow \infty} \{Z_{mn}(z, z')\}^{1/mn} = \\ &= \exp \left\{ \pi^{-2} \int_0^{\pi/2} d\omega \int_0^{\pi/2} d\omega' \ln 4[z^2 \cos^2 \omega + z'^2 \cos^2 \omega'] \right\} = \\ &= z^{\frac{1}{2}} \exp \left\{ \pi^{-1} \int_0^{\pi/2} d\omega \ln [\zeta \cos \omega + (1 + \zeta^2 \cos^2 \omega)^{\frac{1}{2}}] \right\}. \end{aligned} \quad (17)$$

For $|z'| \leq |z|$ we may expand the latter integrand in terms of ζ , integrate term by term, and sum the resulting series, which gives:

$$\begin{aligned} \ln Z(z, z') &= \frac{1}{2} \ln z + \pi^{-1} \sum_{j=0}^{\infty} (-1)^j (2j+1)^{-2} \zeta^{2j+1} = \\ &= \frac{1}{2} \ln z + \pi^{-1} \int_0^{\zeta} dx x^{-1} \arctan x = \\ &= \frac{1}{2} \ln z' + \pi^{-1} \int_0^{1/\zeta} dx x^{-1} \arctan x. \end{aligned} \quad (18)$$

From the equivalence of the last two expressions (which is easily proved) and the analogous derivation in the case $|z'| \geq |z|$ it follows that either of them may be used for all values of z and z' . Using the relation $\arctan x = (2i)^{-1}[\ln(1+ix) - \ln(1-ix)]$ and introducing the function

$A_2(x) = (2i)^{-1}[L_2(ix) - L_2(-ix)]$, where $L_2(u) = -\int_0^u dx x^{-1} \ln(1-x)$ is Euler's dilogarithm¹⁶⁾, we finally arrive at the following expressions for the limit of the configurational partition function per site:

$$\boxed{\begin{aligned} \ln Z(z, z') &= \frac{1}{2} \ln z + \pi^{-1} A_2(z'/z) \\ &= \frac{1}{2} \ln z' + \pi^{-1} A_2(z/z'). \end{aligned}} \quad (19)$$

By substituting $z = z' = 1$ in equations (13) or (15), (16) and (19) we immediately find the *total number of dimer arrangements*, $g(\frac{1}{2}mn)$, and its asymptotic behaviour. One is sometimes interested in the "molecular freedom" φ_2 of the dimers defined³⁾ as the number of arrangements per dimer:

$$\varphi_2 = \{g(\frac{1}{2}mn)\}^{2/mn} = \{\sum'_{N_2, N_2'} g(N_2, N_2')\}^{2/mn} = \{Z_{mn}(1,1)\}^{2/mn}. \quad (20)$$

In particular, for the infinite lattice we find

$$\boxed{\varphi_2^{(\infty)} = Z^2(1,1) = \exp\{2\pi^{-1}A_2(1)\} = \exp\{2G/\pi\} = 1.791\,622\,812\, \dots} \quad (21)$$

where

$$G = 1^{-2} - 3^{-2} + 5^{-2} - 7^{-2} + \dots = 0.915\,965\,594\, \dots \text{ (Catalan's constant).}$$

Several approximate values for $\varphi_2^{(\infty)}$ have, in more or less explicit form, been given in the literature. From Flory's theory of polymers¹⁷⁾ one can derive a value which corresponds to a "Bragg-Williams" or "random mixing" approximation, Chang¹⁸⁾ and Cohen *et al.*²⁾ used a "1st Bethe-Kikuchi" or "quasi-chemical" approximation, Orr⁴⁾ worked out a "2nd Bethe approximation", Miller¹⁹⁾ calculated a lower bound, and Fowler and Rushbrooke³⁾ obtained a very close estimate by extrapolating their exact results for infinite quadratic strips of widths up to 8*) (which are, of course, included as special cases in our expression (16)). The various results are summarized in table II (p. 1220).

§ 4. *The toroidal quadratic lattice.* In this section we shall investigate the changes brought forward by introducing *periodic boundary conditions*, i.e. by winding the lattice on a torus. We shall call the toroidal $m \times n$ lattice $Q_{mn}^{(t)}$ and the corresponding generating functions $Z_{mn}^{(t)}(z, z')$, $Z_n^{(t)}(z, z')$ and $Z^{(t)}(z, z')$.

One difference with the case of a planar lattice is that $D(m, j; 1, j)$ and $D(i, n; i, 1)$ should no longer be taken to be zero but equal, in absolute

*) Miller's criticism¹⁹⁾ of the calculations of Fowler and Rushbrooke rests on a wrong interpretation of the method and is therefore not valid.

magnitude, to z and z' , respectively; we can still choose the signs of these elements. Further we have now to distinguish four classes of configurations. The first class comprises those configurations that can be derived from the standard configuration (which we take identical to that of § 2) by cyclic shifts along polygons not looping the torus either in horizontal or in vertical direction, or, more generally, looping the torus an even number of times in both directions; let us call them (e, e) configurations. In an analogous

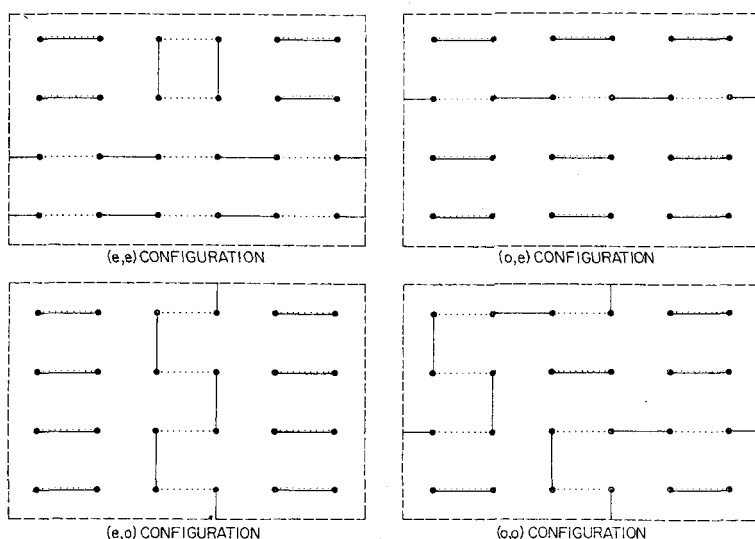


Fig. 2. Configurations from the four configuration classes of the toroidal lattice $Q_{64}^{(t)}$

way we define (o, e), (e, o) and (o, o) configurations (cf. fig. 2; e = even, o = odd, first symbol refers to horizontal loops). If we define, for $1 \leq i \leq m$, $1 \leq j \leq n$,

$$D(m, j; 1, j) = +z; D(i, n; i, 1) = (-1)^i z', \quad (22.1)$$

i.e. if we make the matrix, now to be called D_1 , periodical in both directions, it can be shown that $\text{Pf } D_1$ counts only the (e, e) configurations correctly; the others are counted with the wrong sign. In order to get all configurations correctly counted we use a device introduced by Potts and Ward²⁰⁾ in their treatment of the corresponding Ising problem. We define three other matrices:

$$D_2 \text{ with } D(m, j; 1, j) = +z; D(i, n; i, 1) = (-1)^{i+1} z', \quad (22.2)$$

$$D_3 \text{ with } D(m, j; 1, j) = -z; D(i, n; i, 1) = (-1)^i z', \quad (22.3)$$

$$D_4 \text{ with } D(m, j; 1, j) = -z; D(i, n; i, 1) = (-1)^{i+1} z', \quad (22.4)$$

and we remark that $\text{Pf } D_2$ counts all configurations correctly except those from the class (o, e), $\text{Pf } D_3$ all configurations except the class (e, o) and

$\text{Pf } D_4$ all configurations except the class (0, 0). These counting rules are summarized in table I:

TABLE I

Counting of configurations on a toroidal lattice				
Class of configurations	Sign of corresponding terms in $\text{Pf } D_\mu$			
	D_1	D_2	D_3	D_4
(e, e)	+	+	+	+
(o, e)	-	-	+	+
(e, o)	-	+	-	+
(o, o)	-	+	+	-

It is evident from this table that if we put

$$Z_{mn}^{(t)}(z, z') = \frac{1}{2}(-\text{Pf } D_1 + \text{Pf } D_2 + \text{Pf } D_3 + \text{Pf } D_4), \quad (23)$$

all configurations are counted with the right sign so that we have obtained the analogue of eq. (5) for a toroidal quadratic lattice.

The evaluation of eq. (23) runs parallel to that of eq. (5), the only difference being the occurrence of the matrices

$$\begin{bmatrix} 0 & 1 & 0 & 0 & \dots & 0 & -1 \\ -1 & 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & -1 & 0 & 1 & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \dots & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \dots & 0 & 1 \\ 1 & 0 & 0 & 0 & \dots & -1 & 0 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 1 & 0 & 0 & \dots & 0 & 1 \\ -1 & 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & -1 & 0 & 1 & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \dots & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \dots & 0 & 1 \\ -1 & 0 & 0 & 0 & \dots & -1 & 0 \end{bmatrix}$$

instead of Q (cf. eq. (9) and (10)). They can be diagonalized successively by a transformation with the matrices

$$\begin{aligned} V(l, l') &= (1/n)^{\frac{1}{2}} \exp \{2ll' \pi i/n\}, \\ V^-(l, l') &= (1/n)^{\frac{1}{2}} \exp \{l(2l' - 1) \pi i/n\}. \end{aligned} \quad (24)$$

Proceeding as in § 3 we find

$$\begin{aligned} Z_{mn}^{(t)}(z, z') &= -\frac{1}{2} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n 2[z^2 \sin^2 \{2k\pi/m\} + z'^2 \sin^2 \{2l\pi/n\}]^{\frac{1}{2}} + \\ &+ \frac{1}{2} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n 2[z^2 \sin^2 \{2k\pi/m\} + z'^2 \sin^2 \{(2l - 1) \pi/n\}]^{\frac{1}{2}} + \\ &+ \frac{1}{2} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n 2[z^2 \sin^2 \{(2k - 1) \pi/m\} + z'^2 \sin^2 \{2l\pi/n\}]^{\frac{1}{2}} + \\ &+ \frac{1}{2} \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^n 2[z^2 \sin^2 \{(2k - 1) \pi/m\} + z'^2 \sin^2 \{(2l - 1) \pi/n\}]^{\frac{1}{2}}. \end{aligned} \quad (25)$$

The first term of the right-hand member is easily seen to be equal to zero.

If desired, this equation can be put into a form analogous to (15) with the aid of the following identities, valid for even m and non-negative values of u :

$$\prod_{k=1}^{\frac{1}{2}m} 2[u^2 + \sin^2\{2k\pi/m\}]^{\frac{1}{2}} \equiv [u + (1 + u^2)^{\frac{1}{2}}]^{\frac{1}{2}m} - [-u + (1 + u^2)^{\frac{1}{2}}]^{\frac{1}{2}m}, \quad (26)$$

$$\prod_{k=1}^{\frac{1}{2}m} 2[u^2 + \sin^2\{(2k-1)\pi/m\}]^{\frac{1}{2}} \equiv [u + (1 + u^2)^{\frac{1}{2}}]^{\frac{1}{2}m} + [-u + (1 + u^2)^{\frac{1}{2}}]^{\frac{1}{2}m}.$$

For $m \rightarrow \infty$, i.e. for *infinite cylindrical strips*, the second and fourth term of eq. (25) can be shown to be dominant and equal, and we find

$$Z_n^{(t)}(z, z') = z^{\frac{1}{2}n} \prod_{l=1}^{[\frac{1}{2}n]} \left[\zeta \sin \frac{(2l-1)\pi}{n} + \left(1 + \zeta^2 \sin^2 \frac{(2l-1)\pi}{n} \right)^{\frac{1}{2}} \right], \quad (27)$$

which is to be compared with eq. (16), valid for planar strips. In the limit $n \rightarrow \infty$ we finally obtain eq. (17) again. The values for the molecular freedom φ_2 in cylindrical strips of widths up to 8 calculated by Fowler and Rushbrooke³⁾ can be found as special cases from eq. (27). In table II we list the various values of φ_2 (exact and approximate) calculated for strips and for the infinite lattice.

TABLE II

The molecular freedom φ_2 for planar and toroidal quadratic $\infty \times n$ lattices					
n	planar lattice		toroidal lattice	method	
1	1.000		—	Fowler and Rushbrooke ³⁾ and this paper (in those cases where ref. 3 gave no or less accurate results, those of the present method have been recorded)	
2	1.618		2.414		
3	1.551		1.686		
4		1.685	1.932		
5	1.658		1.754		
6		1.716	1.849		
7	1.701		1.772		
8		1.732	1.823		
∞		1.471		Flory ¹⁷⁾	} approximate
		1.687		Chang ¹⁸⁾	
		1.736		Orr ⁴⁾	
		1.63		Miller ¹⁹⁾	
		1.8		Fowler and Rushbrooke ³⁾	
		1.791 623 ...		this paper	

§ 5. *Alternative approaches.* We saw in § 2 that the number of dimer configurations on a lattice is equal to the number of alternating polygons (defined with respect to a standard configuration) on that lattice. The strong analogy with the Ising problem suggests that a solution of the present problem is possible which follows more closely the method of Kac and Ward referred to above. This can indeed be developed, and again one obtains the configuration generating function Z_{mn} as the square root of a determinant.

We shall not go into details but instead mention another closely related method for calculating Z_{mn} .

It follows from the considerations of § 2 that there is a one-to-one correspondence between alternating polygons on Q_{mn} and closed paths on a corresponding *oriented lattice* Q_{mn}^{or} , sketched in fig. 3. In this lattice any bond may be traversed in only one direction: the C_0 -bonds in the direction of increasing (decreasing) i for odd (even) values of j , the non- C_0 -bonds in the direction from the "head" of a C_0 -bond to the "tail" of another C_0 -bond.

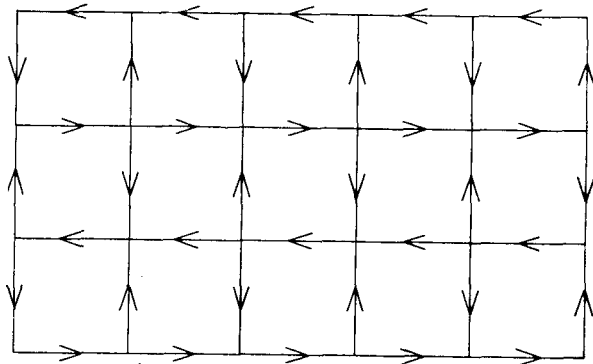


Fig. 3. The oriented lattice Q_{64}^{or} .

We now form a $mn \times mn$ matrix d whose rows and columns correspond to the sites of Q_{mn}^{or} . We define, for all combinations of indices which represent lattice points,

$$\begin{aligned} d(i, j; i, j) &= 1 \\ d(i, j; i+1, j) &= y \quad \text{for } j \text{ odd,} \\ d(i, j; i-1, j) &= y \quad \text{for } j \text{ even,} \\ d(i, j; i, j+1) &= \begin{cases} +y' & \text{for } i \text{ even, } j \text{ odd,} \\ -y' & \text{for } i \text{ odd, } j \text{ even,} \end{cases} \\ d(i, j; i, j-1) &= \begin{cases} +y' & \text{for } i \text{ even, } j \text{ odd,} \\ -y' & \text{for } i \text{ odd, } j \text{ even,} \end{cases} \\ d(i, j; i', j') &= 0 \quad \text{otherwise,} \end{aligned} \quad (28)$$

i.e. we attach weight factors y and $\pm y'$ to horizontal and vertical oriented bonds, respectively, and a factor 1 to each lattice site on its own. Thus in $\det d$ each term will correspond to a configuration of closed paths on Q_{mn}^{or} (cf. ref. 9). A term representing a permutation consisting of ν cycles (each permuting an even number of points) occurs with a factor $(-1)^\nu$; since in a determinant, as contrasted with a Pfaffian, there is no restriction on the order of the indices of the elements, the difficulty mentioned in § 2 does not arise here. The argument of § 2 shows again that the difference in sign between permutations consisting of odd and even numbers of cycles is compensated for by the negative signs attributed to the vertical bonds between sites with odd values of i . So $\det d$ is just the path generating

function $H_{mn}(y, y')$ for the lattice Q_{mn}^{or} :

$$\det d = \sum_M \sum_{M'} h(M, M') y^M y'^{M'} = H_{mn}(y, y'),$$

$h(M, M')$ being the number of ways of combining M horizontal and M' vertical steps to closed paths. According to § 2 such a combination may be considered as representing a configuration of M' vertical dimers, and hence $\frac{1}{2}mn - M'$ horizontal dimers. It follows that

$$\begin{aligned} Z_{mn}(z, z') &= \sum_{M'} g(\tfrac{1}{2}mn - M', M') z^{\frac{1}{2}mn - M'} z'^{M'} = \\ &= z^{\frac{1}{2}mn} \sum_{M'} \sum_M h(M, M') \zeta^{M'} = z^{\frac{1}{2}mn} \det(d)_{y=1, y'=\zeta}. \end{aligned} \quad (29)$$

This is confirmed by an evaluation of $\det d$. For an infinite lattice e.g. one finds

$$\begin{aligned} H(y, y') &= \lim_{m, n \rightarrow \infty} \{H_{mn}(y, y')\}^{1/mn} = \\ &= \exp\left\{\pi^{-2} \int_0^{\pi/2} d\omega \int_0^{\pi/2} d\omega' \ln [(1 - y^2)^2 + 4y^2 \cos^2 \omega + 4y'^2 \cos^2 \omega']\right\}; \end{aligned} \quad (30)$$

multiplication by $z^{\frac{1}{2}}$ and substitution of $y = 1$, $y' = \zeta$, immediately lead to (17). This result is noteworthy in that Z_{mn} itself is expressed as a determinant rather than its square. The origin of this possibility lies in the fact that the quadratic lattice can, in the well-known way, be divided into two sublattices, that of the "odd" and that of the "even" sites (or, in terms of graph theory, that it is "dichromatic" 8)); this ensures the possibility of working with the oriented lattice Q_{mn}^{or} . The algebraic root lies in the possibility of writing certain Pfaffians as a determinant (cf. Muir ¹⁴), vol. IV p. 263). For the triangular lattice, on the other hand, the method of this section cannot be used, whereas that of § 2 still works, as we hope to show in the envisaged sequel to this paper.

§ 6. *The entropy of a system of dimers on a rectangular lattice.* Consider a planar rectangular $m \times n$ lattice, i.e. a lattice whose horizontal and vertical bonds differ in length. Let the lattice be covered entirely by two sorts of dimers: N_2 dimers which fit only into horizontal positions (i.e. which can occupy two sites (i, j) and $(i + 1, j)$), and N'_2 dimers fitting only into vertical positions. If the energy of mixing of these dimers is zero, the configurational free energy of the mixture is completely determined by the *entropy of mixing*, i.e. by the combinatorial factor $g(N_2, N'_2)$. This quantity can be calculated from the configuration generating function with the aid of Cauchy's formula:

$$g(N_2, N'_2) = (2\pi i)^{-1} \oint d\zeta \zeta^{-(N'_2+1)} Z_{mn}(1, \zeta), \quad (31)$$

where the path of integration encircles the origin but excludes the singularities of $Z_{mn}(1, \zeta)$. We shall introduce $x = N_2/\frac{1}{2}mn$ and $x' = N'_2/\frac{1}{2}mn = 1 - x$.

For large m and n we can evaluate (31) by the saddle-point method. We find

$$\lim_{m, n \rightarrow \infty} \{g(\frac{1}{2}mnx, \frac{1}{2}mnx')\}^{1/mn} = \gamma(x), \quad (32)$$

where $\gamma(x)$ is given by the following two equivalent expressions:

$$\begin{aligned} \ln \gamma(x) &= \pi^{-1} A_2(\tan \frac{1}{2}\pi x) - \frac{1}{2}x \ln(\tan \frac{1}{2}\pi x) = \\ &= \pi^{-1} A_2(\tan \frac{1}{2}\pi x') - \frac{1}{2}x' \ln(\tan \frac{1}{2}\pi x'). \end{aligned} \quad (33)$$

In fig. 4 the reduced entropy per dimer of this "interlocking mixture", $\sigma = S/\frac{1}{2}mnk = 2 \ln \gamma(x)$, which corresponds to Flory's "entropy of disorientation" ¹⁷), is plotted against x . For comparison we have also plotted the entropy of mixing for an "ideal" or "random mixture", i.e. of a system where to each single lattice site a horizontal dimer (available fraction: x) or a vertical dimer (fraction: $x' = 1 - x$) is attached in a random manner,

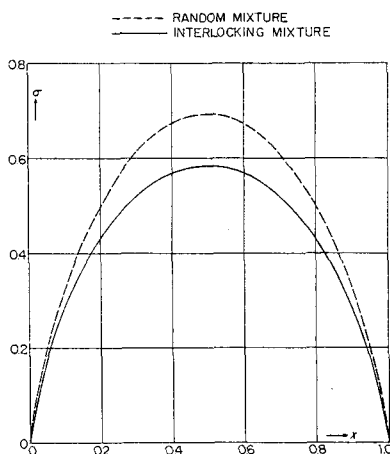


Fig. 4. The reduced entropy per dimer of a mixture of horizontal and vertical dimers as a function of x (fraction of horizontal dimers).

without paying attention to possible hindrances. This quantity is equal to $-x \ln x - x' \ln x'$. The difference between the two entropies is a measure of what might be called the *order of interlocking*.

§ 7. *Concluding remarks.* We have seen that the generating function $Z_{mn}(z, z')$ for dimer configurations on a planar quadratic lattice can be written in the form of a Pfaffian. The corresponding skew-symmetric matrix could by a similarity transformation be brought into a nearly diagonal form, and its determinant, which is the square of the Pfaffian, evaluated. The asymptotic behaviour of $Z_{mn}(z, z')$ for large lattices was found to be described by equation (17), which can also be written as

$$Z(z, z') = \exp\left\{(2\pi)^{-2} \int_0^\pi d\omega \int_0^\pi d\omega' \ln 2[z^2 + z'^2 + z^2 \cos \omega + z'^2 \cos \omega']\right\}. \quad (34)$$

The same result was found when periodic boundary conditions were introduced. The effect of boundary conditions is, however, not entirely trivial and will be discussed in more detail in a subsequent paper.

The right-hand member of (34) has a remarkable resemblance to Onsager's expression for the partition function per spin of a rectangular Ising system ^{9)10) *)}. A more detailed examination reveals that $Z(z, z')$ as a function of $\zeta = z'/z$ has no singular points on the real positive axis; it corresponds to Onsager's partition function at the critical point (or critical line, if the strengths of the horizontal and vertical interactions vary with respect to each other). This fact might tempt one to conjecture that the more general problem of monomer-dimer mixtures would be the analogue of the Ising problem at arbitrary temperatures, and hence rigorously solvable. However, this is not the case. It is easy to see that the true analogue of the partition function of an Ising system is the generating function $H_{mn}(y, y') = \det d$ for closed paths on the lattice Q_{mn}^{or} ; for an infinite lattice, the function $H(y, y')$ given by (30) has a singularity at $y = 1$, which is just the value of interest for the dimer problem.

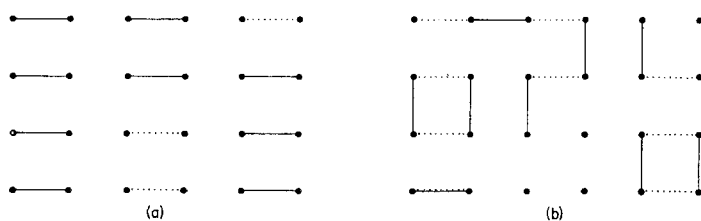


Fig. 5. The construction of a monomer-dimer configuration from the standard configuration by (a) the omission of bonds and (b) the shift of dimers along chains of bonds.

A monomer-dimer mixture, on the other hand, has more resemblance to an Ising ferromagnet in an external field ⁹⁾: the various configurations can be derived from the standard configuration C_0 by the omission of a number of bonds (fig. 5a) followed by the shift of dimers along certain chains of bonds, *which need no longer be closed* (fig. 5b). The contribution to the combinatorial factor from open chains increases with the ratio of the activity of two monomers to that of a dimer, whereas in the Ising case it increases with the ratio of the activity of $+$ spins to that of $-$ spins, i.e. with the magnetic field. Since this general Ising problem has as yet resisted all attempts at a rigorous solution one suspects that the monomer-dimer problem will also be very hard to solve. On the other hand, a better insight into the latter problem might throw some new light on the former.

*) In this connection it may be remarked that the algebraic introduction which Hurst and Green ¹³⁾ need for re-deriving Onsager's results by the Pfaffian method can be avoided by deriving them along the lines of the present paper.

Note added in proof.

After the submission of this paper the author received preprints of a short communication by H. N. V. Temperley and M. E. Fisher (to be published in *Phil. Mag.*) and of an article by M. E. Fisher (to be published in *Phys. Rev.*), both on the statistics of dimers on a quadratic lattice. Following the lines used by Hurst and Green¹³) in the discussion of the Ising problem, the authors obtain results identical to those of the present paper. They discuss in more detail the asymptotic behaviour of these results for large lattices, and in addition make some remarks on monomer-dimer mixtures. On the other hand, they restrict themselves to planar quadratic lattices, and their method – although formally equivalent to that developed above – seems less suited to generalization to other two-dimensional lattices. We hope to comment upon these papers in more detail later on.

Received 28-6-61

REFERENCES

- 1) Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford (1952) Chapter X.
- 2) Cohen, E. G. D., De Boer, J. and Salsburg, Z. W., *Physica* **21** (1955) 137.
- 3) Fowler, R. H. and Rushbrooke, G. S., *Trans. Faraday Soc.* **33** (1937) 1272.
- 4) Orr, W. J. C., *Trans. Faraday Soc.* **40** (1944) 306.
- 5) Rushbrooke, G. S., Scoins, H. I. and Wakefield, A. J., *Discussions Faraday Soc.* **15** (1953) 57.
- 6) Green, H. S. and Leipnik, R., *Rev. mod. Phys.* **32** (1960) 129.
- 7) Fisher, M. E. and Temperley, H. N. V., *Rev. mod. Phys.* **32** (1960) 1029.
Katsura, S. and Inawashiro, S., *Rev. mod. Phys.* **32** (1960) 1031.
- 8) Berge, C., *Théorie des graphes et ses applications*, Dunod, Paris (1958) 175, 30.
- 9) Newell, G. F. and Montroll, E. W., *Rev. mod. Phys.* **25** (1953) 352.
Domb, C., *Adv. in Phys.* **9** (1960) 149, in particular § 3.
- 10) Onsager, L., *Phys. Rev.* **65** (1944) 117.
- 11) Kac, M. and Ward, J. C., *Phys. Rev.* **88** (1952) 1332.
- 12) Sherman, S., *J. math. Phys.* **1** (1960) 202.
- 13) Hurst, C. A. and Green, H. S., *J. chem. Phys.* **33** (1960) 1059.
- 14) Muir, T., *Contributions to the History of Determinants*, London (1930).
Scott, R. F. and Mathews, G. B., *Theory of Determinants*, Cambridge University Press, New York (1904) 93.
- 15) Caianello, E. R. and Fubini, S., *Nuovo Cimento* **9** (1952) 1218.
- 16) Gröbner, W. and Hofreiter, N., *Integraltafel II*, Springer Verlag, Wien & Innsbruck (1950) 72.
- 17) Flory, P. J., *J. chem. Phys.* **10** (1942) 51.
- 18) Chang, T. S., *Proc. roy. Soc., London, A* **169** (1939) 512.
- 19) Miller, A. R., *Proc. Camb. phil. Soc.* **38** (1942) 109.
- 20) Potts, R. B. and Ward, J. C., *Progr. theor. Phys.* **13** (1955) 38.