Excluded-Volume Problem and the Ising Model of Ferromagnetism

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The relationship between the excluded-volume problem for a discrete random walk on a lattice and the corresponding Ising model of ferromagnetism is investigated. Systematic methods are presented for the construction of rigorous lower bounds to the limit $\mu=\lim_{n\to\infty}(c_{n+1}/c_n)$, where c_n is the number of n-step self-avoiding walks on a given lattice. In this way Temperley's conjecture that $\mu=\coth(J/kT_C)$, where T_C is the Curie temperature of the corresponding Ising-model ferromagnet, is disproved. The series c_n for various two- and three-dimensional lattices have been enumerated exactly for values of n from ten to twenty. Extrapolation of these series, by procedures known to be valid from exact Ising-model results, yields more accurate values of μ than Wall's statistical calculations and also shows that $c_n\sim n^\alpha\mu^n$ where $\alpha\simeq 1/3$ for plane lattices and $\alpha\simeq 1/7$ for three-dimensional lattices. This means that the entropy of the nth "link" of a polymer molecule in solution should vary as $\delta S_n=k\ln\mu+k\alpha/n$. The relevance of these results to the interpretation of the boundary tension of the Ising model, to the critical behavior of gases, and to the mean square size of a polymer molecule is discussed briefly.

1. INTRODUCTION AND SUMMARY

IN this paper we investigate the "excluded volume problem" for discrete random walks on two- and three-dimensional lattices and discuss the relationship of this problem to the configurational properties of the corresponding Ising lattice models of a ferromagnet. In the discrete "excluded volume problem" one studies a random walk of n steps which proceeds from one lattice point to the next via one of the $q=\sigma+1$ "bonds" radiating from each point. (In the simplest cases the bonds are supposed to exist only between lattice points which are geometrical nearest neighbors.) The walk is subject to the restriction that it may pass only once through any lattice point, i.e., it must be *self-avoiding* or *non-self-intersecting*. Interest centers on determining c_n, the total number of self-avoiding walks; u_n, the number of closed, polygonal, self-avoiding walks; and $\langle R_n^2\rangle$, the mean square "size" or "end-to-end length" of all n-step walks with no self-intersections.

The excluded-volume problem is of intrinsic theoretical interest since it represents a stochastic process of a non-Markovian character and relatively little is known about the nature of such processes. Thus, while for any Markovian random walk $\langle R_n^2\rangle/n$ tends to a finite limit as n becomes infinite,[1,2] the true asymptotic behavior of $\langle R_n^2\rangle$ for a self-avoiding walk is not known—although the question has been studied by many authors.[2–12] A non-self-intersecting random walk is a reasonable model of a long-chain polymer molecule in a dilute solution. Knowledge of c_n, the total number of walks, yields information about the configurational entropy of such a molecule,[13] and the asymptotic form of $\langle R_n^2\rangle$ is of great interest in the interpretation of the molecular weight dependence of the viscosity of dilute polymer solutions.[12] The theory of self-avoiding walks is also applicable to a class of Brownian motion and diffusion problems in which the passage of the diffusing particle alters the properties of the medium.

In a recent paper Temperley[14] has drawn attention to the relation between the problem of enumerating non-self-intersecting walks on lattices and the statistical mechanics of lattices with nearest neighbor interactions.[15] More particularly Temperley concluded that there was a close connection between the excluded-volume problem for walks on the plane square lattice and the corresponding Ising model for ferromagnetism[16] whose solution has been elucidated by Onsager.[17] If some such relationship could be established rigorously, there would be hope of a considerable advance in our understanding of the excluded-volume problem since, following Onsager's exact solution, a considerable body of literature on the Ising model for various lattices has grown up.[16–22] Unfortunately, as has been shown in

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the investigations described below, it turns out that the two problems are not nearly as closely related as might have been hoped. Nonetheless, it has proved possible to draw certain further conclusions about the excluded-volume problem, although much still remains to be discovered.

Temperley's main conjecture concerned the value of the "attrition coefficient" or "limiting entropy per step" for a non-self-intersecting walk on the plane square lattice. The "attrition coefficient" was first defined by Wall, Hiller, and co-workers,[3] who have undertaken extensive numerical studies of self-avoiding walks by statistical methods. (Other numerical investigations have been made by Teramoto, by King, and by Rosenbluth and Rosenbluth.[4]) Wall *et al.* observed that the fraction of random walks which survived to n steps without a self-intersection appeared to diminish according to a simple exponential law. The rate constant in this law depended on the lattice and was called the "attrition coefficient." The exponential survival law is equivalent to the statement that the ratio $\nu_n = c_n/c_{n-1}$ of successive total number of walks approaches a finite limit as n tends to infinity. That this should be so is by no means obvious mathematically but Hammersley[23] has been able to justify the assumption rigorously. The limiting ratio,

$$\mu = \lim_{n\to\infty} (c_n/c_{n-1}), \tag{1}$$

represents the average number of allowable next steps for a long walk. Thus on the first step of a walk there are q possibilities, on the second step $\sigma = q-1$ possibilities, and it seems intuitively evident that the mean number of possibilities decreases successively and approaches the limit μ. (In fact, however, the decrease in the ratios ν_n need not be strictly monotonic, and on certain structures ν_n may be less than μ for some n even though ν_n tends to μ in the limit.) By analogy with a polymer molecule Temperley has called the quantity $\delta S_\infty = k \ln\mu$ the "limiting entropy per link,"[13] (k here denotes Boltzmann's constant.) On the basis of the solution of certain combinational problems and a comparison with similar problems arising in the Ising problem, Temperley[14] concluded that the value of μ for a plane square lattice should be exactly $1+\sqrt{2} \simeq 2.4142$. This corresponds to the critical value of the Ising-model "high-temperature counting variable"

$$v = \tanh K = \tanh(J/kT)$$

(in the notation of Newell and Montroll[16]). In general Temperley's conjecture amounts to

$$\mu = \omega, \quad \text{where} \quad \omega = \coth(J/kT_C), \tag{2}$$

and where T_C is the ferromagnetic critical point or Curie temperature for the appropriate Ising lattice.

Now *upper bounds* $\nu_{(k)}$ for the excluded volume limit μ may be obtained by considering restricted random walks which are only allowed to intersect themselves after k steps ($k=2,3,4, \cdots$), i.e., walks with no reversals ($k=2$), with no triangles and no reversals ($k=3$), with no squares, triangles, or reversals ($k=4$), and so on. These limited problems may be solved exactly by the detailed matrix method[2,14] or, more simply, if only the upper bound $\nu_{(k)}$ is required, by direct construction and solution of a recurrence relation for $c_{(k)n}$, the total number of kth-order restricted walks (see Appendix A). The limiting ratio,

$$\nu_{(k)} = \lim_{n\to\infty} (c_{(k)n}/c_{(k)n-1}), \tag{3}$$

is then obtained as the largest root of a characteristic polynomial (of degree at least $k-1$). Evidently

$$\nu_{(k)} \geqslant \mu, \tag{4}$$

since the number of walks with no self-intersections cannot increase at a faster rate than the number of walks in which intersections after k steps are allowed. Each lattice and each value of k must be considered in detail, and the calculations are impractical if k is much greater than 5 although Wakefield[24] has actually constructed the recurrence relations for the square net up to $k=8$, for which case he obtained an equation of 45th order. A modification of the method which avoids the explicit construction of such high-order recurrence relations is explained in Appendix A. It is based on exact enumeration (see below) and has enabled us on the square net to calculate $\nu_{(12)}$ for which the recurrence relations would be of order about 800.[25] The upper bounds obtained in these various ways are quite rigorous and for all lattices they are consistent with the conjecture (2).

Systematic methods for obtaining *lower* bounds to μ, on the other hand, have not previously been developed. In this paper we show how sequences of increasing lower bounds can be obtained in a simple and systematic manner. The method depends on the construction of a subclass of self-avoiding walks whose asymptotic behavior can be calculated exactly. The lower bounds λ_k and $\lambda_{(k)}$ are also then determined as the largest roots of appropriate characteristic polynomials. In this way it has been proved rigorously that the limit μ for the plane square net is greater than the value $\omega = 2.4142$

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[22] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).

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[24] We are indebted to Professor C. Domb for telling us about Wakefield's unpublished work and to Dr. A. J. Wakefield for allowing us to examine his D.Phil. thesis, Oxford, 1951 (unpublished). Wakefield also obtained the lower bound $\lambda = 2.4142$ and the improved lower bound $\lambda = 2.47$ for the square net.

[25] This upper bound is less than $e = 2.718$ (see Table V) and so disproves a conjecture of R. S. Lehman and G. H. Weiss [University of Maryland Technical Note BN-115, November, 1957 (unpublished)] to the effect that μ is equal to e on the square net. These authors also discuss the probability of a walk trapping itself.

conjectured by Temperley. In fact we have obtained the bound

$$\mu \geqslant \lambda_{(10)} = 2.5767, \quad \text{(square lattice)}$$

which is more than 6% greater than the Ising-model critical value. The exact critical temperatures are also known for the plane triangular- and hexagonal-lattice Ising models[18,19] and for the Kagomé lattice[20] (in which two triangles and two hexagons meet at each lattice point). In all these cases we have proved rigorously that

$$\mu > \omega. \tag{5}$$

Statistical estimates of the exact limits μ for various lattices have been given by Wall and co-workers.[3] These are somewhat uncertain due to the difficulties of extrapolation and to the sampling errors necessarily involved in the statistical estimation procedure. We have found it possible to obtain considerably more precise estimates for μ by counting exactly the total number of walks c_n for the first ten to twenty values of n. The values of c_n and u_n have been determined for the plane square lattice (to $n=16$), the plane triangular (to $n=10$), the plane hexagonal (to $n=22$), the Kagomé lattice (to $n=13$), and for the simple cubic (to $n=9$), the body-centered cubic (to $n=9$) and the face-centered cubic (to $n=8$). The counting is performed indirectly with the aid of a special theorem, which expresses the series c_n ($n=0,1,2,\cdots$) in terms of a certain restricted class of lattice configurations. A similar theorem holds for the series expansion of the susceptibility of the Ising model[26] which is, in fact, rather similar to the series c_n. Reliable extrapolation procedures have been developed for handling the Ising-model series and these methods have been verified by comparing the extrapolations with the known exact solutions.[22] Application of these procedures to the random walk problem not only yields accurate values of the limiting ratio μ but also enables the asymptotic form of c_n (and u_n) to be determined to the next order of approximation. Thus it transpires that

$$c_n \approx A n^{\alpha} \mu^n, \tag{6}$$

where A is a constant and the index α is about $1/3$ for all the plane lattices and $1/7$ for all the three-dimensional lattices. This result is equivalent to knowing the "entropy per link" as a function of n, the number of steps, the relation being

$$\delta S_n \approx k \ln\mu + k\alpha/n, \tag{7}$$

which shows that the limiting entropy δS_∞ is approached relatively slowly although for $n>30$ the actual magnitude of the correction is negligibly small. The total entropy behaves as $(n \ln\mu + \alpha \ln n)$. In terms of the generating function

$$C(z) = 1 + \sum_{n=1}^{\infty} c_n z^n, \tag{8}$$

the asymptotic form (6) means that $C(z)$ has a singularity at $z=z_c=1/\mu$ of the form

$$C(z) \approx A/(1-\mu z)^{1+\alpha}. \tag{9}$$

Our extrapolated values of μ agree well with Wall's results for three-dimensional lattices but are about 1% lower than Wall's figures for the plane lattices. This is to be expected since Wall's methods overestimate the value of μ to this extent when the index α is appreciable.

The value of the Ising critical parameter ω is not known exactly for three-dimensional lattices but good estimates have been given by Wakefield[21] and by Domb and Sykes.[22] Rigorous lower bounds for μ may also be obtained for three-dimensional lattices but (because of the larger co-ordination number and the smaller value of the index α) they are not as strong as in the case of the plane lattices and, so far, no bounds greater than the corresponding estimated value of ω have been derived. The extrapolated values of μ for these lattices are, however, consistently greater than the values of ω (by 2% or more) and there seems no doubt that in two and three dimensions the excluded-volume limit μ is always greater than the corresponding Ising critical parameter ω. Theoretical arguments in support of this conclusion show rigorously that ω cannot exceed μ. The actual difference between the two parameters is essentially due to a negative contribution from the overlapping of the "separated" lattice configurations (i.e., two or more unconnected polygons or walks) which must be included in the Ising problem.

This general result is also relevant to the interpretation of Onsager's work on the "boundary tension" of the square-net Ising model[17] and to the general problem of the critical behavior of a liquid. Onsager showed analytically that the total free energy associated with a "mismatch seam" between two regions of antiferromagnetic ordering on the square net vanished exactly at the "bulk critical temperature," and so the corresponding "boundary tension" also vanished at this temperature. Now a non-self-intersecting walk on the square net can apparently be regarded as a boundary between two regions of different order. Temperley[14] assumed that the free energy directly associated with such a boundary should vanish at the same temperature as the boundary tension of the corresponding Ising model. This is equivalent to the conjecture $\mu \equiv \omega_{\text{boundary}}$ which seemed to be supported by the discovery of a restricted class of nonintersecting walks ("Onsager boundaries" or "zeroth order progressive walks"—with no "overhangs") for which $\mu' \equiv \omega_{\text{bulk}}$. On the basis of Temperley's argument, the fact that the true value of μ is greater than ω would be taken to imply that the boundary tension vanishes at a temperature *below* the bulk critical temperature. This in turn would seem to support the postulate of Mayer and Mayer[27] that there may be two singularities in the partition function of a

[26] M. F. Sykes and M. E. Fisher, Phys. Rev. Letters **1**, 321 (1958).

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liquid, one corresponding to the vanishing of the surface tension and the other to the vanishing of the density gradient. In fact we feel that our result cannot legitimately be interpreted in such a direct manner since the argument neglects the "loss in bulk free energy due to the presence of the boundary." We hope to consider this problem further in another paper.

The data obtained by enumerating the total number of non-self-intersecting walks c_n and the corresponding number of walks u_n which close on the last step, do not have any direct bearing on the question of the behavior of $\langle R_n^2 \rangle$, the mean square size of a self-avoiding walk. Nonetheless, the ratio u_{n+1}/c_n represents the probability of a random walk returning to its starting point (without actually touching itself) and so must contain some information about the distribution of end points. Our data indicate that the asymptotic behavior of this probability is given by

$$P_n(0) = u_{n+1}/c_n \sim n^{-\beta}, \tag{10}$$

where, for the three-dimensional lattices, β is about 1.81. For a Markovian walk in three dimensions the appropriate value of this index is 3/2. An argument given by Fisher[28] shows that on the assumption that the distribution of end points of a self-avoiding walk attains a limiting shape, a value of $\beta = 1.81$ implies that the mean square size of a self-avoiding walk increases as $n^{1+\delta}$, where δ is about 0.21. (For a Markovian walk the limiting shape is Gaussian and δ is zero.) Wall's direct statistical calculations of $\langle R_n^2 \rangle$ for various walks in three dimensions lead to $\delta = 0.22$ which agrees surprisingly well with the value obtained by merely assuming the existence of a limiting shape and using (8). The argument, however, does not constitute a proof since, even if the assumption of a limiting shape were justified rigorously, it would still be necessary to establish the validity of the extrapolations for β by obtaining strict mathematical bounds.

In the case of the plane lattices, the terms u_n are not very smooth and the extrapolations for β are more difficult to perform. It also seems quite probable that, at least in the case of the square lattice, the distribution does not attain a limiting shape.

The detailed arguments leading to the various conclusions summarized above are presented in the remainder of the paper. The methods for obtaining rigorous lower bounds to the value of μ on the square net are explained in Sec. 2 and the generalizations of the methods for other two- and three-dimensional lattices is outlined in Sec. 3. The techniques used for the exact enumeration of self-avoiding walks are sketched in Sec. 4. The numerical values obtained are presented in Tables I, II, III, and IV. In Sec. 5 the procedure used for extrapolating the series is outlined and its reliability is demonstrated by applying it to similar Ising-model series whose behavior is known exactly. The rigorous bounds and the numerical extrapolations for the five lattices considered are collected together in Table V. Finally, in Sec. 6 the detailed relationship between the Ising model and the excluded volume problem is considered theoretically. Methods for obtaining rigorous upper bounds to μ are explained in Appendix A.

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2. LOWER BOUNDS FOR THE PLANE SQUARE LATTICE

To find lower bounds for the limiting ratio μ we use the following simple lemma:

Lemma.—If the number of n-step walks in a subclass of the total class of non-self-intersecting walks is $d_n \leqslant c_n$, *and if the limiting ratio* $\lambda = \lim_{n\to\infty}(d_{n+1}/d_n)$ *exists, then* λ *is less than or equal to* $\mu = \lim(c_{n+1}/c_n)$. (If μ were less than λ, then eventually the subclass of walks would become dominant so that c_{n+1}/c_n would tend to λ, which would be a contradiction.)

An obvious subclass of self-avoiding walks are those walks which always proceed in the same direction, but this merely shows that $\mu \geqslant 1$. To improve on this we consider a "progressive walk of zero order" which (on the square net) consists only of steps in the $+X$ direction or in the $\pm Y$ directions, (the $+Y$ and $-Y$ steps being always separated by at least one $+X$ step). Such a walk can never "double back" so as to intersect itself but merely progresses further and further along the positive X axis. After n steps suppose that the total number of walks of this type which end in a $+X$ step is a_n, while the total number ending in a $+Y$ or $-Y$ step is b_n. Now a $+X$ step may be followed by another X step or by a $+Y$ or $-Y$ step, but a Y step must be followed by a similar Y step or by a $+X$ step. Thus we have

$$\begin{aligned} a_{n+1} &= a_n + b_n, \\ b_{n+1} &= 2a_n + b_n. \end{aligned} \tag{11}$$

These recurrence relations may be solved in the standard way, say by assuming $a_n = A\lambda^n$ and $b_n = B\lambda^n$. The asymptotic behavior is determined by the largest root of the characteristic equation

$$\begin{vmatrix} 1-\lambda & 1 \\ 2 & 1-\lambda \end{vmatrix} = 0, \tag{12}$$

which reduces to the simple quadratic equation

$$\lambda^2 - 2\lambda - 1 = 0, \tag{13}$$

with roots $\lambda = 1 \pm \sqrt{2}$. This yields the first lower bound for the plane square lattice, namely

$$\mu \geqslant \lambda_0 = 1 + \sqrt{2} = 2.4142. \tag{14}$$

By coincidence this happens to be identical with the corresponding Ising-model limit $\omega = 1 + \sqrt{2}$. Temperley called this zeroth order progressive walk an "Onsager boundary" and the coincidental equality of λ and ω seems, unfortunately, to have confirmed his impression

that μ was also equal to ω. To show that this is not so, we must consider the next significant order of progressive walk. This is the third-order walk which arises when we allow a simple "kink" or "double-back" consisting of the sequence of steps $(+X)$, $+Y$, $-X$, $+Y$, $+X$ [see Fig. 1(a)]. Any zeroth order progressive walk ending in a $+X$ step can be continued in the form of this kink in at least one way without making a self-intersection [see Fig. 1(b)], although if the penultimate step is a $-Y$ step the kink must be inverted [Fig. 1(c)]. [If the penultimate step also is a $+X$ step, the kink can be added in two ways, upright or inverted, Fig. 1(d); by neglecting one of these, as we shall do now for simplicity, we will merely obtain a somewhat weaker lower bound.] After completing the kink in four steps, the walk may take either a $+X$ step or a suitable Y step and the argument then proceeds as before just as though the kink had not occurred. The recurrence relation (11) must thus be modified to

$$\begin{aligned} a_{n+1}&=a_n+b_n+a_{n-4},\\ b_{n+1}&=2a_n+b_n+a_{n-4}. \end{aligned} \tag{15}$$

The corresponding characteristic equation may be written

$$\lambda^2-2\lambda-1=1/\lambda^3, \tag{16}$$

and the largest root is

$$\lambda_3=2.43839. \tag{17}$$

This is greater than $1+\sqrt{2}$, which proves directly that the limit μ for the plane square lattice is greater than the Ising parameter ω.

To obtain stronger lower bounds one must include the possibility of successively more complicated "kinks" which take five or more steps to be completed. The new types which arise in the fourth order, fifth order, and sixth order progressive walks are shown in Fig. 2. The details of the general argument are rather involved but the basic principle is quite simple. The characteristic equation derived from the recurrence relations for the kth order progressive walk is

$$\lambda^2-2\lambda-1=S_k(\lambda), \tag{18}$$

where $S_k(\lambda)$ is a polynomial of kth degree in the inverse

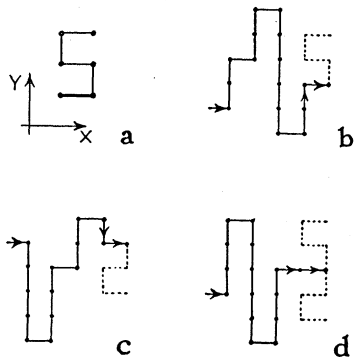

FIG. 1. A simple "kink" on the plane square lattice (a), and its addition to a zeroth-order progressive walk (b), (c), and (d).

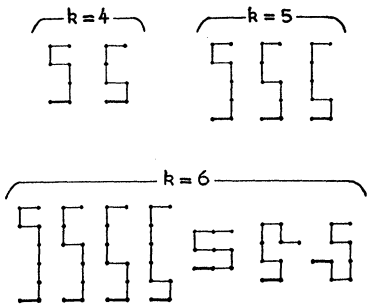

FIG. 2. The sequence of higher order "kinks" which arise in the fourth-, fifth- and sixth-order progressive walks on the plane square lattice.

powers of λ, namely

$$S_k(\lambda)=\sum_{j=1}^{k} s_j\lambda^{-j}=\frac{1}{\lambda^3}+\frac{3}{\lambda^4}+\frac{5}{\lambda^5}+\frac{11}{\lambda^6}+\cdots. \tag{19}$$

The coefficients s_j are determined by the new types of "kink" which arise at the jth stage. The various types of kink have to be subclassified according to the number of ways they can be added to a walk and according to how many Y steps they can be followed by. The enumeration, however, is quite straightforward and the first half-dozen coefficients s_j are easily determined. All the coefficients are positive and so the greatest roots λ_k of Eqs. (18) form a strictly increasing sequence of lower bounds to μ. The coefficients s_j have been evaluated up to s_{11} and thus the bounds $\lambda_{10}=2.533$ and $\lambda_{11}=2.539$ have been obtained.

The decreasing sequence of upper bounds $\nu_{(k)}$ obtained by excluding reversals, reversals and triangles, etc., will certainly tend to a limit ν_∞ which will be the same as the excluded volume limit μ. (Hammersley[23] has stated this theorem but does not offer a formal proof.) On the other hand, it is not obvious that the limit of the lower bounds $\lambda_\infty=\lim\lambda_k$ $(k\to\infty)$ should be the same as μ. This point has not yet been decided by rigorous argument and we defer discussion of the numerical evidence to Sec. 5 below.

An alternative method of discussing the higher order progressive walks is in terms of generating functions. For the same amount of labor this yields rather stronger bounds. If the number of walks of a certain type, with l X-steps (plus or minus) and m Y-steps, is p_{lm}, then the generating function is defined by

$$P(x,y)=\sum_{l,m=0}^{\infty} p_{lm}x^l y^m. \tag{20}$$

On setting $x=y=z$ this becomes $P(z)$, the generating function for $p_n=\sum_{l+m=n} p_{lm}$, the number of walks of n steps of either kind. The asymptotic behavior of p_n is then determined by the singularity of $P(z)$ which is nearest to the origin. If this singularity occurs at $z=z_c$, then $p_n\sim\lambda^n$ $(n\to\infty)$, where $\lambda=1/z_c$. For the zeroth order progressive walk, the method has been illustrated by Temperley.[14] The generating function for a walk consisting of one $+X$ step followed by any number of Y steps is

$$\phi=x+2xy+2xy^2+2xy^3+\cdots=x(1+y)/(1-y), \tag{21}$$

and so the generating function for a zeroth order progressive walk or "Onsager boundary" is

$$1+x\frac{1+y}{1-y}+x\frac{1+y}{1-y}x\frac{1+y}{1-y}+\cdots=\sum_{r=0}^{\infty}\phi^r=1/(1-\phi), \quad (22)$$

which becomes singular when

$$\phi=x(1+y)/(1-y)=1. \quad (23)$$

On setting $x=y=1/\lambda$ this reduces to (13), with the root $\lambda_0=1+\sqrt{2}$. To include the simple "kink" of Fig. 1, we must modify (21) to

$$\begin{aligned}\phi&=x(1+y)/(1-y)+xyxyx(1+y+y^2+\cdots)\\&=x(1+y)/(1-y)+x^3y^2/(1-y),\end{aligned} \quad (24)$$

where the factor $xyxyx=x^3y^2$ in the second term accounts for the steps $+X$, $+Y$, $-X$, $+Y$, $+X$, forming the kink, and the factor $1+y+y^2+\cdots=(1-y)^{-1}$ allows for any number of $+Y$ steps following the kink before the next $+X$ step occurs. On using (24) with $x=y=1/\lambda$ the characteristic equation $\phi=1$ reduces, as expected, to (16). However, it is very easy to generalize (24) to allow for simple kinks in which the "vertical arms" consist of any number of Y steps, and also to allow for the fact (neglected before) that after a $+X$ step the kink may be added in *two* ways. The result is simply

$$\phi=x\frac{(1+y)}{1-y}+x\frac{y}{1-y}x\frac{y}{1-y}x\frac{1}{1-y}+x^2\frac{y}{1-y}x\frac{y}{1-y}x\frac{1}{1-y}, \quad (25)$$

which leads to the characteristic equation

$$\lambda^2-2\lambda-1=(\lambda+1)/\lambda^2(\lambda-1)^2. \quad (26)$$

This has the solution

$$\lambda_{(3)}=2.4997, \quad (27)$$

which is a considerably better lower bound than the original bound (17). The method may be extended systematically by successively including the new shapes of kink that arise with 4,5,6, . . . steps. Evidently the next three new shapes are those illustrated in Fig. 2, corresponding to $k=6$. The corresponding terms in ϕ may be written down immediately and are

$$x^2\frac{y}{1-y}x^2\frac{y}{1-y}x^2\frac{1}{1-y}(1+x)+x\frac{y}{1-y}x\frac{y}{1-y}\frac{yxy}{1-y^2}x\frac{1+y}{1-y}(1+x)+2x\frac{yxy}{1-y^2}\frac{y}{1-y}x\frac{y}{1-y}x\frac{1}{1-y}.$$

This procedure has been extended to include all the new types that occur up to $k=10$. (If some possibilities are omitted in such an enumeration, the only result is to lower somewhat the resulting bound.) Solution of the characteristic equations then leads to

$$\lambda_{(9)}=2.5725, \quad \lambda_{(10)}=2.5767. \quad (28)$$

This latter bound is the strongest that has been obtained so far although it could be improved further if required. The best upper bound to μ at present available is

$$\nu_{12}=2.712. \quad (29)$$

The derivation of this bound is discussed in the Appendix.

3. LOWER BOUNDS FOR OTHER LATTICES

We now consider lower bounds for other two- and three-dimensional lattices. The calculations have not been pushed as far as for the square net since the main objects were, in the case of the plane lattices, to demonstrate that μ was greater than ω, and in the case of the three-dimensional lattices to illustrate how the method could be adapted.

Consider firstly the plane triangular lattice and take the Y axis along one of the lattice directions. The other two lattice directions have components along the X axis and the corresponding steps may, for the purpose of obtaining bounds, be considered simply as "X steps." Thus in the zeroth order progressive walk on the triangular lattice there are two possible "X steps" at each stage and the corresponding "column" generating function is

$$\phi=2x(1+y)/(1-y), \quad (30)$$

which leads to the characteristic equation

$$\lambda^2-3\lambda-2=0. \quad (31)$$

This equation yields the bound

$$\textit{Triangular lattice:}\quad \lambda_0=\tfrac{1}{2}(3+17^{\frac{1}{2}})=3.5616, \quad (32)$$

which is actually lower than the corresponding Ising parameter[18,19]

$$\textit{Triangular lattice:}\quad \omega=2+\sqrt{3}=3.7321. \quad (33)$$

To obtain a stronger lower bound, it is only necessary to include the various simple kinks which have one $-X$ step. The extra term in ϕ is

$$x^3(1+y)(1-y^4)(1+2x)/(1-y)^4,$$

and the bound obtained from the corresponding characteristic equation is

$$\textit{Triangular lattice:}\quad \lambda_{(2)}=3.8404. \quad (34)$$

This is well above the Ising value (33).

The plane hexagonal or honeycomb lattice is topologically equivalent to the "brick" lattice which is obtained by deleting every other X bond of the plane

square lattice. Using this form of the lattice and considering only walks with an even number of steps, the generating function for the zeroth order progressive walks is easily seen to be

$$\phi=2yx/(1-y^2), \tag{35}$$

which leads to the simple characteristic equation

$$\lambda^2-3=0. \tag{36}$$

The corresponding lower bound happens, as for the square net, to coincide with the Ising parameter[18,19]; i.e.,

$$\textit{Honeycomb:}\quad \omega=\lambda_0=\sqrt{3}=1.7321. \tag{37}$$

Inclusion of the simplest kinks with one $-X$ step, however, yields the stronger bound

$$\textit{Honeycomb:}\quad \lambda_{(4)}=1.7872, \tag{38}$$

which is again greater than the Ising value.

The Kagomé lattice[20] may be treated in the same way as the triangular lattice but successive columns of Y steps are now separated by two X steps so that the "column" generating function is

$$\phi=2x^2(1+y)/(1-y). \tag{39}$$

This leads to a cubic equation whose greatest root,

$$\textit{Kagomé:}\quad \lambda_0=2.2695, \tag{40}$$

is lower than the appropriate Ising parameter[20]

$$\textit{Kagomé:}\quad \omega=2.2966. \tag{41}$$

As in the previous cases, inclusion of the simplest kinks leads to a stronger bound,

$$\textit{Kagomé:}\quad \lambda_{(2)}=2.4453, \tag{42}$$

which is greater than the Ising value.

The lower bounds for all these plane lattices can easily be improved by including further shapes of kink as was done for the square net. The procedure for three-dimensional lattice is, however, rather more complicated. Firstly the lattice is divided into parallel layers and the progressive walk moves on from one layer to the next. Before progressing to the next layer, however, the walk may follow any non-self-intersecting path on the plane lattice forming the layer. These paths are treated as progressive walks on the corresponding plane lattice. Consider, for example, the simple cubic lattice. On entering a layer for the first time there are four possible first steps in the layer and altogether twelve distinct second steps. Each of these second steps may be regarded as the initial X step of a zeroth order progressive walk on the plane square lattice for which the total generating function is

$$x\frac{1+y}{1-y}\left(1-x\frac{1+y}{1-y}\right)^{-1}.$$

The complete zeroth-order "layer" generating function for the simple cubic lattice is thus

$$\phi=z\left[1+4x+12x^2\frac{1+y}{1-y}\left(1-x\frac{1+y}{1-y}\right)^{-1}\right]. \tag{43}$$

The corresponding characteristic equation, $\phi=1$, reduces to

$$\lambda^4-3\lambda^3-3\lambda^2-3\lambda-8=0. \tag{44}$$

Solution of this quartic equation gives the lower bound

$$\textit{Simple cubic:}\quad \lambda_0=4.0456. \tag{45}$$

The Ising parameter for the simple cubic lattice is not known exactly but extrapolation of the series for the susceptibility, etc. (see references 21 and 22 and Sec. 3 below) shows that ω is about 4.58, which is well above λ_0.

To improve the bound (45), the effects of simple kinks must be included. The kinks may lie within a layer, in which case the argument used for the plane square net applies, or the kinks may lie perpendicular to the layer, thereby carrying the walk back to the previous layer. This leads to considerable complication although no essential difficulty arises. Solution of the corresponding characteristic equation yields the improved bound

$$\textit{Simple cubic:}\quad \lambda_{(3)}=4.225. \tag{46}$$

This result is appreciably stronger than (45) but still quite a long way below the extrapolated value of ω. Although, as shown by the numerical evidence of Sec. 5, the limit μ is certainly greater than the Ising value ω, the labor which would be required to obtain a rigorous lower bound exceeding 4.58 is quite prohibitive with the present methods.

Similar procedures may be applied to the body-centered and face-centered cubic lattices. Due mainly to the higher coordination number, the bounds so obtained are relatively weaker than those for the simple cubic lattice. The upper bounds derived by eliminating only squares and reversals and triangles and reversals, respectively, are correspondingly stronger. The best available lower and upper bounds for these two lattices and for the others discussed above, are tabulated in Table V, together with the corresponding exact or extrapolated values of the Ising parameter ω. Except for the square lattice, all the upper bounds quoted in this table have been calculated by solving the explicit recurrence relations. By using the alternative method described in Appendix A, appreciably stronger bounds could be obtained for these lattices. To Table V might be added the first lower bound for the tetrahedral or diamond lattice which is

$$\textit{Tetrahedral:}\quad \lambda_0=(3+2\sqrt{3})^{\frac{1}{2}}=2.5325, \tag{47}$$

and the best available upper bound

$$\textit{Tetrahedral:}\quad \nu_{(10)}=2.923, \tag{48}$$

which was obtained by Wakefield.[25]

4. EXACT ENUMERATION OF SELF-AVOIDING WALKS

More precise numerical estimates of the limiting ratio μ and further information about the asymptotic behavior of c_n, the total number of self-avoiding walks, and of u_n, the number of closed self-avoiding walks, can be obtained by actual enumeration of c_n and u_n for as many values of n as feasible. There are two approaches: on the one hand, there is the *statistical* or *Monte Carlo* method employed by Hammersley and Morton[23] with hand calculations, and, very extensively, by Wall and others[3,4] with high-speed electronic digital computers. On the other hand, there is the method of *exact enumeration* which, for this problem, has not previously received much attention. With the Monte Carlo method, quite long walks (50 to 100 steps or more) can be sampled but the data are necessarily subject to statistical uncertainty, and this increases with the number of steps. Exact enumeration becomes difficult for walks much longer than 10 to 20 steps but, since they are not subject to error, the data may be extrapolated by more refined and precise methods. In fact, as we show below, the method of exact enumeration leads to estimates of μ which are considerably more accurate than the statistical estimates (about 0.1% as against 1%) and, more importantly, the method also yields the second approximation to the asymptotic behavior of c_n and u_n. (Parenthetically, it might be remarked that exact enumeration is more economical than the Monte Carlo method although, of course, the direct statistical procedures used by Wall and others also yield data about the mean square size and other details of the complete distribution.) In this section we discuss briefly the techniques used for the exact enumeration of non-self-intersecting walks and in the following section we consider the extrapolation of the resulting series and discuss the figures obtained.

Evaluation of the series c_n and u_n ($n=1,2,3,\cdots$) is a special case of the general problem of determining the number of ways in which a given "configuration" of n bonds can be placed on a specified lattice (without using any lattice point more than once). By a "configuration" we here mean a set of "points" and "bonds" joining them together (i.e., an abstract linear graph). If all the points of a configuration can be reached via the bonds from any starting point, we say the configuration is "connected"; otherwise we refer to a "separated" configuration. If all the points of a configuration are joined to other points by at least two bonds, we say the configuration is "closed." A polygon of n bonds is the simplest type of closed configuration; some more complicated types are shown in Fig. 3. An "open" configuration has "loose ends," the simplest example being the chain of $n+1$ points (and n bonds). For a given number of bonds, the number of ways an open configuration can be placed on a lattice is usually considerably greater than the number of ways available for a closed configuration. In particular the total number of self-avoiding walks (chains) of n steps is much greater than the corresponding number of closed self-avoiding walks (polygons). From the computational viewpoint this is important since, at least for the plane lattices, it is not too difficult to determine the number of n-bond polygons up to, say $n=8$ or 9, by actually drawing the different possibilities and taking advantage of the symmetry of the lattice. As regards enumerating the chains c_n, however, this direct method is quite impractical since, for example, on the triangular lattice $c_9=964134$. (The use of symmetry effectively reduces this figure but only by a factor of about 12.) To overcome this difficulty a theorem has been devised which expresses the number of chains on a lattice in terms of the number of certain closed configurations or, more specifically, in terms of the number of polygons and the number of "figure eights" of the general type shown in Fig. 3. The proof of this theorem and the discussion of the detailed enumeration of the necessary restricted configurations are being published elsewhere. The proof proceeds essentially by analyzing the configurations produced when further links are added to the two ends of a non-

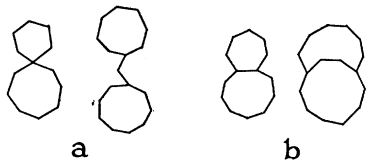

FIG. 3. Some closed connected lattice configurations. Two types of "figure eight"; in the sense of R. J. Riddell and G. E. Uhlenbeck [J. Chem. Phys. **21**, 2056 (1953)], those of type (a) are "generalized trees" and those of type (b) are "stars."

self-intersecting chain. The result is most conveniently stated in terms of the generating function $C(z)$ for the series c_n [defined in (8)], the generating function $U(z)$ for the series u_n, and the corresponding generating function $G(z)$ for the figure-eights. If $\sigma+1$ is the coordination number of the lattice, we have

$$C(z)=(1-\sigma z)^{-2}[1-(\sigma-1)z - \sigma z^2-(1-z)U(z)+G(z)], \quad (49)$$

which means that the c_n can be calculated recursively in terms of the u_n and the g_n. A very similar, but more complicated theorem holds for the susceptibility of an Ising lattice when this is expressed in terms of the variable $v=\tanh(J/kT)$.[26] In that case the generating function $U(z)$ corresponds to the configurational energy of the lattice, and the function $G(z)$ enumerates closed configurations similar to those of Fig. 3 except that they are not necessarily connected (see also Sec. 6 below).

Techniques for the evaluation of g_n and the numbers of other closed connected configurations which occur on various lattices have been described by Domb and Sykes.[29] By symbolic analysis many of these "lattice

[29] C. Domb and M. F. Sykes, Phil. Mag. **2**, 733 (1957).

constants" can be "reduced" and expressed in terms of a relatively few "irreducible lattice constants" corresponding, generally, to more closely packed configurations. The number of polygons (closed walks u_n) can be determined in terms of these constants, together with q_n, the number of closed random walks with no immediate reversals (but with higher order self-intersections being allowed). Closed expressions for the distributions of random walks with restricted reversals have been derived by Domb and Fisher[30] and, consequently, even for a lattice as complex as the face-centered cubic, it has proved possible to calculate u_n up to $n=9$. For other lattices the enumeration can be carried further. Present results are tabulated in Tables I to IV. They do not represent the limit of what could be achieved (indeed sufficient lattice constants are available to add two terms to the series for the plane lattices but

TABLE I. The values of c_n, the total number of nonintersecting walks of n steps, for various two-dimensional lattices.

n \ Lattice	Square	Triangular	Honeycomb	Kagomé
1	4	6	3	4
2	12	30	6	12
3	36	138	12	32
4	100	618	24	88
5	284	2730	48	240
6	780	11 946	90	652
7	2172	51 882	174	1744
8	5916	224 130	336	4616
9	16 268	964 134	648	12 208
10	44 100	4 133 166	1218	32 328
11	120 292		2328	85 408
12	324 932		4416	224 608
13	881 500		8388	588 832
14	2 374 444		15 780	
15	6 416 596		29 892	
16	17 245 332		56 268	
17			106 200	
18			199 350	
19			375 504	
20			704 304	

the calculations have not yet been finally checked). Nonetheless, with present methods it would not be possible to extend the series by a factor as great as 2 or 3, the main limitation being the difficulty of determining some of the higher order irreducible lattice constants.

5. EXTRAPOLATION OF THE SERIES

The numbers c_n and u_n are conveniently regarded as the coefficients of the power series expansions of the generating functions $C(z)$ and $U(z)$. The limit $\lim(c_{n+1}/c_n)=\mu$ determines the position, $z=z_c$, of the singularity of $C(z)$ nearest to the origin, by $z_c=1/\mu$. Furthermore, it is easily seen that the nature of this singularity is related to the asymptotic behavior of the coefficients c_n. Thus if

$$C(z)\approx A/(1-\mu z)^{1+\alpha}, \quad (z\sim 1/\mu) \tag{50}$$

[30] C. Domb and M. E. Fisher, Proc. Cambridge Phil. Soc. **54**, 48 (1958).

TABLE II. The values of u_n, the number of closed nonintersecting walks of n steps, for various two-dimensional lattices. (The values u_0, u_1, and u_2 must be determined by a convention and it is convenient to put $u_0=u_1=u_2=0$.)

n \ Lattice	Square	Triangular	Honeycomb	Kagomé
3	0	12	0	4
4	8	24	0	0
5	0	60	0	0
6	24	180	6	4
7	0	588	0	28
8	112	1968	0	80
9	0	6840	0	120
10	560	24 240	30	120
11	0		0	264
12	2976		24	1080
13	0		0	3120
14	16 464		168	
...				
16	94 016		288	
...				
18	549 648		1170	
...				
20			2760	

application of the binomial theorem and Stirling's asymptotic formula shows that

$$c_n\approx Bn^{\alpha}\mu^n, \quad (n\to\infty) \tag{51}$$

where A and B are constants. The case $\alpha=-1$ corresponds to a logarithmic singularity in $C(z)$. If $C(z)$ has the form (50), then (by the binomial theorem) the ratios $\nu_n=c_n/c_{n-1}$ are given by

$$\nu_n=\mu(1+\alpha/n), \tag{52}$$

so that a plot of ν_n against $1/n$ is a straight line of slope α which intercepts the ν axis at $\nu_\infty=\mu$. If $C(z)$ is

TABLE III. The values of c_n for various three-dimensional lattices.

n \ Lattice	Simple cubic	Body-centered cubic	Face-centered cubic
1	6	8	12
2	30	56	132
3	150	392	1404
4	726	2648	14 700
5	3534	17 960	152 532
6	16 926	120 056	1 573 716
7	81 390	804 824	16 172 148
8	387 966	5 351 720	165 697 044
9	1 853 886	35 652 680	

TABLE IV. The values of u_n for various three-dimensional lattices.[a]

n \ Lattice	Simple cubic	Body-centered cubic	Face-centered cubic
3	0	0	48
4	24	96	264
5	0	0	1680
6	264	1776	11 640
7	0	0	86 352
8	3312	43 776	673 104
9	0	0	5 424 768
10	48 240	1 237 920	
...			
12	762 096		

[a] We are indebted to Professor G. S. Rushbrooke for pointing out a small error in our original calculation of u_{12}.

TABLE V. Comparison of bounds, extrapolations, etc., for various two- and three-dimensional lattices.[a]

Lattice	Square	Triangular	Honeycomb	Kagomé	Simple cubic	Face-centered cubic	Body-centered cubic
Coordination number, $q=\sigma+1$	4	6	3	4	6	12	8
Ising singularity, ω	2.41421	3.73205	1.73205	2.29663	4.58±1	9.816±5	6.41±3
Upper bound, $\nu_{(k)}$	2.712	4.508	1.9276	2.6968	4.8646	10.6569	6.7829
Lower bound, $\lambda_{(k)}$	2.5767	3.8404	1.7872	2.4453	4.225	7.644	5.187
Extrapolated walk singularity, μ	2.639±3	4.152±6	1.845±15	2.555±15	4.69±2	10.05+2	6.54±1
Excess $\mu/\omega-1$, %	9.3	11.3	6.5	11.2	2.4	2.4	2.0
Index for c_n, α	0.33±2	0.33±2	0.33±6	0.33±3	0.145±10	0.140±5	0.142±6
Index for u_{n+1}/c_n, β	1.75±10	1.45±10	...	...	1.810±7	1.810±5	1.810±7

[a] The uncertainties quoted are in the last decimal place in each case.

not merely a simple binomial expression, then (52) will contain higher powers of $1/n$ so that the ν_n *versus* $1/n$ plot will be somewhat curved. Also the points may oscillate slightly about the straight line. In practice it is found that the series c_n and most Ising-model high-temperature expansions give very good straight lines after the fourth or fifth terms, and consequently consistent extrapolations for μ and α can be obtained from the formulas

$$\mu_{\text{ext}}=(n\nu_n-m\nu_m)/(n-m), \tag{53}$$

and

$$\alpha_{\text{ext}}=n(\nu_n-\mu_{\text{ext}})/\mu_{\text{ext}}. \tag{54}$$

The ratios for the series u_n (closed walks) and for low-temperature Ising expansions tend to be rather more irregular but with care these can also be extrapolated reliably.

The extrapolation procedure outlined above was introduced (in a slightly different form) for the Ising problem by Domb.[31] It has been used by Domb and Sykes[22] to obtain, from the high-temperature series, the critical parameters for three-dimensional Ising lattices which are quoted in Table V. A related extrapolation method has been discussed by Park.[32] It leads to very similar results but is not so well suited to the series c_n and the high-temperature susceptibility series.

The reliability of the extrapolation formulas (53) and (54) may be gauged by applying them to series for various plane Ising lattices for which exact solutions are available. As an example, consider the high-temperature series for the susceptibility of the plane triangular lattice. From the first ten terms of this series we may calculate the first ten ratios, $\nu_1=6.000\,000$ to $\nu_{10}=4.006\,286$. Sequences of estimates for the limit ω may then be obtained from (53) by evaluating the intercept defined by the first and third ratios, by the second and fourth ratios and so on. The last few extrapolants obtained in this way are 3.7683, 3.7673, 3.7529, 3.7414, 3.7401, and 3.7401. The exact value[18,19] of ω is $2+\sqrt{3}=3.7321$ and the last two estimates differ from this only by about 0.2%. If the exact value had not been known, the extrapolation would probably have been quoted as $\omega=3.737\pm6$ (since the successive estimates are diminishing). The uncertainty quoted here (and in the similar extrapolations in Table V) is not, of course, a rigorous bound; rather it indicates the degree of consistency of the extrapolations and represents a reasonable confidence range. (It is evident that the extrapolated value of ω is slightly too high and this is probably so for other plane lattices as well.)

The ratios obtained from the self-avoiding walk series c_n behave in a manner very similar to that illustrated above, and consequently we may infer that the extrapolated values of the limit μ are accurate to a similar degree. It is found that for lattices with a high coordination number the ratios are very smooth, whereas for a lattice like the plane hexagonal (honeycomb) lattice the extrapolations are more difficult to perform. To a large extent, however, this difficulty is compensated by the fact that many more terms of the series c_n can be obtained for a lattice of low coordination number. The values of μ obtained by extrapolating the series given in Tables I and III are tabulated in Table V. In all cases the estimates are consistent with the rigorous upper and lower bounds. It has been noticed, furthermore, that the upper bounds $\nu_{(k)}$, corresponding to walks with no kth order or lower self-intersections, are very close to the corresponding ratios $\nu_k=c_k/c_{k-1}$ (see Appendix A). Consequently the upper bounds can be extrapolated in the same manner as the ratios. On the plane square net, for example, the second and third bounds, $\nu_{(4)}$ and $\nu_{(6)}$, yield the extrapolant 2.664 which is only 1% greater than the preferred value, 2.639. In the same way it can be seen that to obtain a rigorous upper bound for the triangular lattice equal to 4.30, it is necessary to calculate the asymptotic behavior of a walk in which self-intersections are only allowed after nine steps. The sequences of lower bounds λ_k and $\lambda_{(k)}$ (described in Sec. 2) may be extrapolated in a similar way to yield estimates for λ_∞. The data for the square net suggest that λ_∞ is about 2.615, which seems to be significantly lower than the estimate of μ. We conclude tentatively that λ_∞ will generally be smaller than μ.

The index α in the expression (51) for the asymptotic behavior of c_n may be estimated from the slope of the ν_n *versus* $1/n$ plot by (54). Because the numerator of (54) is the difference between two roughly equal ratios, the estimates of α are subject to greater uncertainty

[31] C. Domb, Proc. Roy. Soc. (London) **A199**, 199 (1949).
[32] D. Park, Physica **22**, 932 (1956).

than are those for μ. Fortunately it is again possible to verify the method by applying it to a similar series for which α is known exactly. Such a series is the low-temperature expansion for the magnetization of the plane square Ising lattice. This is a series of even terms only, somewhat analogous to the series u_n (polygons). The appropriate coefficients b_n have been given by Domb[31] up to the term in z^{18}, and from the exact solution obtained by Yang[33] it is known that $\alpha=9/8=1.125$. Since only even terms are available the ratios are taken as $\nu_n=(b_{n+1}/b_{n-1})^{\frac{1}{2}}$, ($n$ odd). Extrapolation using (53) suggests $\omega=2.415\pm2$ (actually $\omega=1+\sqrt{2}=2.4142$), and using this value in (54) gives for α the successive estimates 1.120, 1.1281, 1.1296, 1.1282, 1.1276. These values are falling, so the estimate for α would probably have been quoted as $\alpha=1.126\pm8$ where the uncertainty takes account of possible error in ω. If the coefficients had been available only up to the term in z^{14}, the result would have been rather more uncertain, say $\alpha=1.13\pm2$. In either case the estimates are very reasonable approximations to the exact value 1.125. Corresponding extrapolations for the walk series c_n are presented in Table V. For all plane lattices the index α is close to 0.33 while for all the three-dimensional lattices α is near 0.142. We conjecture that for plane lattices α is exactly 1/3 and for three-dimensional lattices exactly $1/7=0.14286$. (Similarly for the susceptibility of all plane Ising lattices, α seems to be exactly 3/4, while for all three-dimensional Ising lattices it seems to be exactly 1/4.[22,32]) As pointed out in Sec. 1, the asymptotic form (51) implies that the additional configurational entropy contributed by the nth link of a polymer molecule may be written

$$\delta S_n \simeq k \ln\mu + k\alpha/n. \tag{55}$$

The estimates of the limit μ obtained by Wall and his co-workers[3] for the plane lattices are about 1% higher than our figures. Wall's values were obtained from the gradient of the plot of $\ln c_n$ *versus* n, for values of n up to about 50. According to our analysis the gradient of this plot should be

$$\frac{\partial}{\partial n}\ln c_n \approx \ln\mu + \alpha/n. \tag{56}$$

On substituting the values $\alpha=1/3$ and $n\simeq40$, this shows that Wall's values of μ should, indeed, be expected to be about 1% greater than the true limit. [Compare also with (52)]. For the three-dimensional lattices, (56) indicates that Wall's estimates should be about 0.3% too high and comparison with our extrapolations again seems to bear this out.

As noted above, the direct extrapolations of the polygon series u_n are not as reliable as those for the total walks series c_n. It seems fairly certain on physical grounds, however, that the limit[34]

$$\mu_u=\lim_{n\to\infty}(u_{n+1}/u_n) \tag{57}$$

is identical with the limit $\mu=\lim(c_{n+1}/c_n)$. Although this conclusion is well borne out by extrapolations of the u_n series, it should be stated that neither the existence of the limit (57) nor its identity with μ has, so far, been established rigorously. If μ_u exists, it follows immediately that it cannot exceed μ [since the class of closed $(n+1)$-step walks is essentially a subclass of all non-self-intersecting walks of n steps]. Consequently upper bounds for μ are also upper bounds for μ_u. Lower bounds for μ_u can be obtained by constructing "snake-like" polygons similar to the progressive walks but these bounds are rather poor. The best direct result available derives from Temperley's exact solution of the problem of enumerating those polygons (or domains) on the square lattice which can be formed by placing single columns of arbitrary length side by side.[14] This yields the lower bound

$$\textit{Square lattice:}\quad \mu_u \geqslant 1+\sqrt{2}, \tag{58}$$

which again happens to coincide with the appropriate Ising value, and was interpreted by Temperley as meaning that $\mu_u\equiv\omega$. Equation (66) of the next section, however, shows quite generally that the Ising parameter ω is always a lower bound to μ_u and hence, also, to μ.

The ratio,

$$P_n(0)=u_{n+1}/c_n, \tag{59}$$

represents the probability that a self-avoiding walk of n steps returns to the origin, or more precisely, returns as closely as possible without actually touching itself. If $\mu_u\equiv\mu$, the limit as $n\to\infty$ of the ratio $P_{n+1}(0)/P_n(0)$ is exactly unity. With the aid of this assumption, fairly accurate estimates of the asymptotic behavior of the probability $P_n(0)$ can be obtained. The data indicate that

$$P_n(0)\simeq A/n^{\beta},$$

where A is a constant and where the extrapolations for β are given in Table V. For the three-dimensional lattices, the estimates of β are all near to 1.810 which is significantly greater than the value 1.500 appropriate to a Markovian walk in three dimensions. The initial sequence of ratios for the plane lattices are somewhat erratic, but it is clear that the value of β is again greater than the Markovian value $\beta=1.000$. As mentioned in Sec. 1, an argument given by Fisher[28] suggests that the figures for β might throw some light on the asymptotic behavior of the mean square size of a self-avoiding walk, but this point will not be pursued further in this paper.

[33] C. N. Yang, Phys. Rev. **85**, 808 (1952).

[34] In the case of loose-packed lattices, such as the square net, on which $u_{2m+1}\equiv0$ ($m=1,2,\ldots$) this limit must be suitably redefined, for example as $\lim(u_{2m+2}/u_{2m})^{\frac{1}{2}}$ ($m\to\infty$). In the arguments following, the modifications necessary to cover loose-packed lattices will not be mentioned explicitly since they are essentially trivial.

6. RELATION TO THE ISING PROBLEM

In this section we discuss the relationship between the configurational problems of the Ising model and the excluded-volume problem in greater detail, and try to understand the reason why μ is greater than ω.

In terms of the variable $v=\tanh K$, the relevant part of the total partition function for an Ising model with N spins can be written[16]

$$\Lambda(N,v)=1+\sum a_n(N)v^n, \tag{60}$$

where $a_n(N)$ is the number of distinct closed graphs of n bonds which can occur on the lattice, each graph having an even number of bonds meeting at each lattice point. The partition function per spin,

$$\Lambda(v)=1+\sum a_n v^n, \tag{61}$$

is given by the Nth root of (60) (strictly, in the limit $N\to\infty$). The coefficients a_n in (61) correspond to the same configurations as in (60) but are counted *per spin*. The critical point of the lattice is fixed by the limits[35]

$$1/v_c=\lim_{n\to\infty}(a_{n+1}/a_n)=\lim_{\substack{n\to\infty\\N\to\infty}}[a_{n+1}(N)/a_n(N)]=\omega. \tag{62}$$

Now each allowed configuration of bonds on an Ising lattice can be decomposed into a superposition of simple polygons. Different polygons may overlap but they must have no bonds in common. Thus a_8, for example, enumerates the number of octagons on the lattice, plus the number of pentagons with a triangle, separated or touching at a vertex, plus the number of pairs of squares separated or overlapping without common bonds. This decomposition into simple polygons naturally suggests that the series for $\Lambda(v)$ should be compared with the "polygon series"

$$1+\sum p_n z^n, \quad p_n=u_n/2n. \tag{63}$$

p_n is the "number of polygons per site"; the factor $1/2n$ arises because on any polygon a starting point for a non-self-intersecting random walk may be chosen in n ways, while the sense of the walk can be chosen in two ways. The singularity of the polygon series (63) corresponds to the excluded-volume limit or, more precisely, to the limit μ_u, i.e.,

$$1/z_c=\lim_{n\to\infty}(p_{n+1}/p_n)=\mu_u. \tag{64}$$

Now it follows from the multinomial theorem that the coefficient $\pi_n(N)$ in the expansion

$$(1+\sum p_n z^n)^N=1+\sum \pi_n(N)z^n \tag{65}$$

counts the number of configurations, on a lattice of N points, which can be formed from all possible superpositions of polygons with a total of n bonds. Thus π_n will count all the configurations in which the polygons have common bonds and it will count all other overlapping configurations more than once (since the decomposition of such configurations into a superposition of polygons is never unique). Consequently, for $n\geqslant 2h$, where h is the number of bonds in the smallest polygon on the lattice, we see that

$$\pi_n(N)>a_n(N), \tag{66}$$

and so as $n\to\infty$, $a_n(N)$ cannot increase at a faster rate than $\pi_n(N)$. It follows immediately that

$$\omega\leqslant\mu_u\leqslant\mu, \tag{67}$$

which means that the Ising parameter ω can never exceed the excluded-volume limit μ.

The difference coefficient,

$$d_n(N)=\pi_n(N)-a_n(N), \tag{68}$$

enumerates all overlapping configurations with common bonds and all the allowed overlapping configurations which are overcounted in (65). Now d_n cannot increase faster than π_n, i.e., not faster than the number of polygons, but d_n includes, for example, the number of $(n-3)$-bond polygons which have a common bond with a triangle. The number of such configurations must increase asymptotically at least at the same rate as the polygons themselves, and so

$$\lim_{n\to\infty}(d_{n+1}/d_n)=\mu_u. \tag{69}$$

Consequently the Ising coefficient $a_n(N)$ is the difference between two quantities, π_n and d_n, both of which increase at a similar rate and this is why it is *possible* for the Ising limit ω to be smaller than the polygon limit μ_u. To prove that ω is actually smaller than μ_u obviously requires a more subtle analysis. The result seems to depend to quite an important extent on the dimensionality of the lattice. From Table V it can be seen that μ is of the order of 10% greater than ω for all the plane lattices but only about $2\frac{1}{2}\%$ greater for the three-dimensional lattices. This indicates that in two and three dimensions the overlapping configurations in (65) become overwhelmingly important for large n although the effect is smaller the higher the number of dimensions. This is reminiscent of other random walk theorems which show that in three dimensions an indefinitely long walk is relatively unlikely to intersect itself whereas in two dimensions self-intersection is "almost certain." On these grounds one might conjecture that in four or some higher number of dimensions the two limits μ_n and ω would in fact become identical.

Many properties of two-dimensional Ising models have been obtained in closed form[16–20] and this raises the hope that similar solutions for the excluded-volume problem might be found in the case of plane lattices. This hope is supported by the exact expressions which

[35] The precise manner of taking the second (double) limit is, in general, a delicate manner. However, if as is usually supposed, the lattice is wrapped on a torus and if "edge effects" are consistently neglected, then $\Lambda(N,v)$ is the exact Nth power of $\Lambda(v)$. It then follows from Abel's theorem on the product of two series and from the positiveness of the coefficients a_n, that $\lim[a_{n+1}(N)/a_n(N)]=\lim(a_{n+1}/a_n)$ $(n\to\infty)$ for all N so that it is actually unnecessary to make $N\to\infty$.

have been found for the square-net generating functions

$$R(z)=\sum r_n z^n \quad \text{and} \quad Q(z)=\sum q_n z^n, \tag{70}$$

where r_n is the number of n-step unrestricted closed random walks and q_n is the corresponding number of closed walks with no immediate reversals.[30] In fact,

$$R(z)=(2/\pi)K(4z), \tag{71}$$

and

$$Q(z)=\frac{1-3z^2}{1+3z^2}\frac{2}{\pi}K\left(\frac{4z}{1+3z^2}\right)-\frac{1-3z^2}{1-z^2}, \tag{72}$$

where $K(k)$ is the complete elliptic integral of modulus k. These expressions are remarkably similar to Onsager's expression for the configurational energy of the square net[17] which also involves the complete elliptic integral. Furthermore the energy is essentially the derivative of $\Lambda(v)$ with respect to v so that its expansion is closely related to the series u_n for the closed self-avoiding walks. So far, however, we have not made any progress towards an exact solution. Investigation shows that the limits μ are probably *not* the roots of relatively simple algebraic equations as are the Ising parameters ω, and this suggests that the excluded-volume problem is essentially less tractable than the Ising model.

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APPENDIX A

In this appendix we outline the way in which recurrence relations may be constructed for $c_{(k)n}$, the total number of n-step walks in which kth order and lower order self-intersections are forbidden. These relations determine the limiting ratios

$$\nu_{(k)}=\lim_{n\to\infty}\nu_{(k)n}, \quad \nu_{(k)n}=c_{(k)n}/c_{(k)n-1}, \tag{A.1}$$

which are upper bounds to μ. We go on to indicate how the limits $\nu_{(k)}$ can be calculated in a way which avoids explicitly determining and solving the recurrence relations.

Consider the simple cubic lattice and its d-dimensional generalization. To find a recurrence relation for $c_{(4)n}$, the number of walks with no reversals and no squares, we write

$$c_{(4)n}=a_n(1)+a_n(2)+a_n(3), \tag{A.2}$$

where $a_n(\alpha)$ is the number of n-step walks of this type which require at least α extra steps in order to close a square. Thus $a_n(1)$ enumerates those walks which end end in three steps forming a "hook" of the type $\ldots X,Y,-X$; $a_n(2)$ enumerates those walks ending in a bend which does not form a hook, e.g., $\ldots X,Y,X$; and $a_n(3)$ enumerates those walks in which the last two steps are in the same direction, e.g., $\ldots X,Y,Y$. Now the addition of a further step to a walk of type $\{a_n(1)\}$ in $2d$ possible ways leads either to a forbidden reversal or closure of a square, or to a new walk of type $\{a_{n+1}(2)\}$ or type $\{a_{n+1}(3)\}$. Thus each $\{a_n(1)\}$ gives rise to $2d-3$ walks of type $\{a_{n+1}(2)\}$ and to one of type $\{a_{n+1}(3)\}$. Considering in a similar way the addition of a step to the types $\{a_n(2)\}$ and $\{a_n(3)\}$ leads to the recurrence relations

$$\begin{aligned}
a_{n+1}(1)&= a_n(2),\\
a_{n+1}(2)&=(2d-3)a_n(1)+(2d-3)a_n(2)+(2d-2)a_n(3),\\
a_{n+1}(3)&= a_n(1)+ a_n(2)+ a_n(3).
\end{aligned} \tag{A.3}$$

These have the solutions

$$a_n(\alpha)=\sum_{i=1}^{3} A_i(\alpha)\theta_i^n, \tag{A.4}$$

where the θ_i are the roots of the determinantal equation

$$\begin{vmatrix} -\theta & 1 & 0 \\ 2d-3 & 2d-3-\theta & 2d-2 \\ 1 & 1 & 1-\theta \end{vmatrix}=0, \tag{A.5}$$

which reduces to the cubic characteristic equation

$$\theta^3-2(d-1)\theta^2-2(d-1)\theta-1=0. \tag{A.6}$$

The $A_i(\alpha)$ are constants determined by the initial conditions of the walk. Equations (A.4) imply that the total number of walks is

$$c_{(4)n}=\sum_{i=1}^{3} C_i\theta_i^n, \tag{A.7}$$

where the C_i are constants. If θ_1 is the root of largest modulus, we have

$$\nu_{(4)n}=\theta_1[1+O\{(\theta_2/\theta_1)^n\}], \quad (n\to\infty), \tag{A.8}$$

so that

$$\nu_{(4)}=\theta_1. \tag{A.9}$$

In the case of the plane square lattice, solution of (A.6) yields $\nu_{(4)}=2.8312$.

To eliminate hexagons as well as squares and reversals, the walks must be subclassified into classes $\{a_n(\alpha,\beta)\}$, where β is the least number of further steps required to close a hexagon. The maximum value of β (after the initial steps) is $(6/2)+1=4$ so that apparently there are $3\times4=12$ classes. On the plane square net, however, the combination $(\alpha=1,\beta=4)$ cannot occur so that the recurrence relations are only of eleventh order: they yield the root $\nu_{(6)}=2.7756$. In three and more dimensions, on the other hand, further subclassification is necessary because the hexagon need not lie in a plane and on the addition of a further step, different configurations then yield different types of walk.

The appropriate general procedure is now evident. For loose-packed lattices like the square net the number of different classes, and hence the order of the

recurrence relations, will be roughly of magndeitu

$$N\sim\left(\frac{k}{2}+1\right)\left(\frac{k-2}{2}+1\right)\cdots 5\times 4\times 3 = \tfrac{1}{2}\left(\frac{k+2}{2}\right)!, \quad \text{(A.10)}$$

while for a close-packed lattice the rough magnitude is

$$N\sim\tfrac{1}{2}\left[\left(\frac{k+1}{2}\right)!\right]^2, \quad k \text{ odd},$$
$$\sim\frac{k+2}{4}\left[\left(\frac{k}{2}\right)!\right]^2, \quad k \text{ even}. \quad \text{(A.11)}$$

The rapid increase of N with k shows that the task of obtaining the recurrence relations for higher values of k soon becomes hopeless. An alternative procedure for calculating the largest roots θ_1 is based on the following considerations. The required root is in fact the largest eigenvalue of the matrix of the recurrence relation coefficients. Accordingly instead of multiplying out the characteristic determinant, θ_1 may be calculated by the standard matrix iterative method,[36] in which an arbitrary initial vector is repeatedly premultiplied by the matrix. The ratio of corresponding components of the successive iterated vectors then tends to the required largest eigenvalue. With the appropriate choice of initial vector this method is quite equivalent to the direct use of the recurrence relations to calculate $a_n(\alpha)$ and $c_{(k)n}$, the eigenvalue θ_1 then being determined from the successive ratios $c_{(k)n}/c_{(k)n-1}$. Thus the bound $\nu_{(k)}=\theta_1$ is calculated directly from the values of $c_{(k)n}$ so that, if the $c_{(k)n}$ can be determined in some other way, there is no need to make explicit use of the recurrence relations.

Now as a by-product of the enumeration of chains with no self-intersections it is not difficult to evaluate the $c_{(k)n}$ directly for the same values of n. In fact for $n\leqslant k$, $c_{(k)n}\equiv c_n$ while the values of $c_{(k)k+1}$, $c_{(k)k+2},\cdots$ can be derived from c_{k+1}, $c_{k+2}\cdots$ by adding to these the relatively few configurations which have self-intersections of order $k+1, k+2,\cdots$. On using this procedure and evauating the successive ratios $\nu_{(k)n}$ it is found that for $n\geqslant k$ the ratios very rapidly approach their limit. Thus on the square net the fifth and following ratios for $k=4$ are 2.8400, 2.8310, 2.8308, 2.8313, 2.8312, 2.8312, The last two ratios agree exactly with the root calculated from the characteristic equation (A.6). For $k=6$ the seventh and following ratios are 2.7846, 2.7753, 2.7757, 2.7753, 2.7757 while the corresponding exact root is $\nu_{(6)}=2.7756$. In this way the following improved upper bounds for the square net have been obtained: $\nu_{(8)}=2.7443$, $\nu_{(10)}=2.7250$, $\nu_{(12)}=2.712$. The characteristic equation determining this last bound is of degree about 800 and consequently this bound would be quite beyond the reach of the normal recurrence relation method.*

[36] D. R. Hartree, *Numerical Analysis* (Oxford University Press, Oxford, 1952), Sec. 8.6.

* *Note added in proof.*—In a recent paper Wall and Erpenbeck [J. Chem. Phys. **30**, 634 (1959)] have described a method of sampling much longer walks than previously, in fact up to $n=800$. On this basis they re-estimate the attrition coefficient for the square net. In our notation their new estimate is $\mu=2.6395\pm 15$ whereas previously Wall's estimate was 2.66. This new estimate falls in the center of the range of our estimate as would be predicted from Eq. (56) above. (We have since improved our estimate to $\mu=2.6395\pm 10$.) The agreement is gratifying confirmation of the validity of our extrapolation technique and shows that the correct asymptotic behavior is clearly indicated by the first ten to twenty exact terms.