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Self-avoiding walks on irregular networks

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Abstract. Exact numerical data on self-avoiding walks are presented for the irregular network studied by Finney in connection with the Bernal model of a liquid and for a face-centred cubic lattice with randomly removed bonds. Averages for the total number of walks $\bar{C}_n$, and polygonal closures $\bar{U}_n$, are defined and found to be consistent with $\bar{C}_n \sim \mu^n n^g$, $\bar{U}_n \sim \mu^n n^h$ where the critical parameters g and h have the same values as those obtained from the regular lattices. The mean-square end-to-end distances $\langle R_n^2 \rangle$ are also studied and the critical parameter θ is found to have the usually accepted value of 6/5. Our results add further support to the conjecture that these exponents depend only on the dimensionality and are not affected by the irregularity of the network.

1. Introduction

Much of the recent work on phase transitions has been directed towards a study of the critical exponents and their inter-relationship. The similarity in the magnitude of corresponding exponents obtained from widely different physical processes suggests that there are some aspects of phase transitions that are independent of the detailed nature of the individual processes. However, there are notable differences and one of the main problems is to find which features have a significant effect. Some understanding of what is involved comes from a detailed study of simplified theoretical models. For example, in the case of the liquid–gas transition the failure of the classical van der Waals method has led to an extensive study of the lattice gas. Although the results obtained from this model compare favourably with the experimental values of the critical exponents, there are small but significant differences (see Kadanoff *et al* 1967).

Unfortunately, one of the unsatisfactory features of the lattice gas is that it imposes a long-range spatial order on the 'liquid' state. Real liquids do not possess such an order and it has been suggested that this lack of long-range spatial order in real liquids may be responsible for the difference between the experimental and theoretical values of the exponents. Indeed, Bernal (1964) has argued that one of the characteristic features of the liquid state is its irregularity, a feature that is not utilized in the conventional approaches to the liquid state. While his idea of a statistical geometry has many appealing features, the absence of a suitable mathematical description has made it impossible to say precisely what effect this irregularity will have on the thermodynamic properties.

Indeed, the question of irregularity is not only of relevance to the liquid state. Recently there has been considerable interest in amorphous alloys and their properties, in particular amorphous ferromagnetism. Here also the basic problem is to find out how the irregularity will affect the ferromagnetic properties.

In this paper we will try to gain an insight into this question by applying to irregular networks some of the techniques that have proved so successful for regular lattices. Rather than attempt to evaluate exact thermodynamic properties, we will limit our considerations to what Domb (1970) calls the self-avoiding walk approximation. The *raison d'être* for this approximation is based on evidence obtained from the exact numerical investigations on regular lattices. These show that in the initial stages of each expansion of a thermodynamic function the largest contribution comes from one particular type of basic graph. For example, in the specific heat expansion this graph is a polygon, while for the pair-correlation function and the susceptibility it is in the chain. Although other graphs eventually do make a significant contribution to the expansion coefficients, the critical exponents will reflect, to some extent, the properties of the self-avoiding walks. Consequently, if the spatial irregularity of the underlying structure does, in fact, change the critical behaviour we would expect these effects to become apparent in the properties of the self-avoiding walks.

The properties of the walks themselves can also have direct physical significance. For example, light scattering in dilute polymer solutions can be related to the mean-square end-to-end distance of the individual molecules. Much of the information for this quantity has come from analysing walks on regular lattices. However, the use of a regular network has often been criticized because it imposes an artificial constraint on the end points of the polymer. We will show that this criticism is not valid.

From the data obtained on the regular lattices, it has been conjectured that for large n

$$C_n \simeq \mu^n n^g; \qquad U_n \simeq \mu^n n^h \qquad \text{and} \qquad \langle R_n^2 \rangle \simeq A n^\theta \tag{1}$$

where C_n is the exact number of self-avoiding walks of n steps, $\langle R_n^2 \rangle$ their mean-square end-to-end distance, and U_n is the number of n-sided self-avoiding polygons (see Domb 1970). The connective constant μ has the same value for walks and polygons. Furthermore the numerical evidence also suggests that g, h and θ are simple fractions that depend only on the dimensionality and not on the details of the individual structures. The specific purpose of this paper is to see whether this situation is altered when the underlying network is irregular.

2. The networks

We have obtained data for the walks from two basically different irregular networks, the random packing (RP) network and the mutilated face-centred cubic (MFCC) network. The former is generated from the sphere-centre coordinate data obtained by packing together about 8000 equal radii steel ball-bearings at a maximum density of 0·637 (Finney 1970). A network with an average coordination number of 6·259 is constructed by joining the centres of touching spheres. This network combines a varying connectivity with a random spatial distribution of nodes.

An MFCC network is obtained from a computer-simulated regular face-centred cubic lattice by eliminating bonds chosen at random. The mean coordination number $\bar{q}$ is, of course, determined by the number of bonds eliminated. In this network the nodes occupy the same spatial positions as they did in the original regular FCC lattice but the connectivity varies randomly from point to point.

In order to see whether the spatial randomization of nodes in the RP network produces any significant differences we have analysed in some detail the data obtained

from an MFCC network with $\bar{q} = 6{\cdot}25$. In figure 1 we compare the neighbour distribution functions for these two networks.

We have also carried out a limited investigation of the properties of walks on MFCC networks with $\bar{q} = 8$, 6 and 5. These data support the results obtained from the 6·25 model and will not be presented here. However, in § 5, we will make use of the end-to-end data obtained from $\bar{q} = 8$.

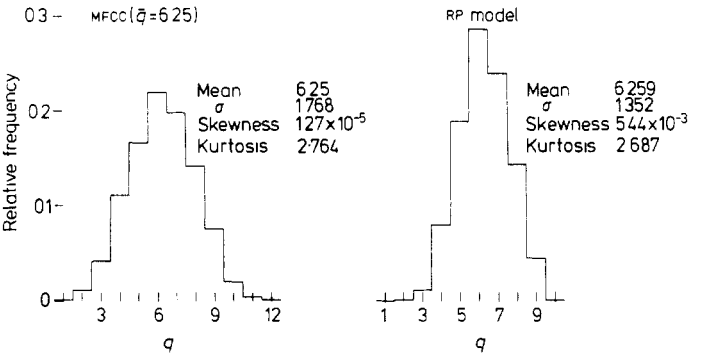

Figure 1. Coordination distribution functions for the MFCC ($\bar{q} = 6{\cdot}25$) and the RP model.

3. Method of analysing results

The asymptotic forms (1) indicate that successive walk ratios should lead to a linear plot against $1/n$, at least for large n because

$$\frac{C_n}{C_{n-1}} \simeq \frac{\mu^n n^g}{\mu^{n-1}(n-1)^g} \sim \mu\left(1+\frac{g}{n}\right)+\mathrm{O}\left(\frac{1}{n^2}\right) \tag{2}$$

$$\frac{U_n}{U_{n-1}} \sim \mu\left(1+\frac{h}{n}\right)+\mathrm{O}\left(\frac{1}{n^2}\right) \tag{3}$$

and

$$\frac{\langle R_{n+1}^2\rangle}{\langle R_n^2\rangle} \sim 1+\frac{\theta}{n}+\mathrm{O}\left(\frac{1}{n^2}\right). \tag{4}$$

For regular lattices these ratios quickly settle onto a straight line and it is found that even for values of $n \leqslant 10$ the ratios can be extrapolated to their limiting behaviour for large n with some degree of confidence. Indeed, the extensive numerical data now available for the regular structures show that once a straight line behaviour appears, ratios for higher n confirm the initial trends and allow a more accurate determination of g, h, θ and μ.

In the case of the irregular networks, each and every centre has a different environment so that the number of walks will depend on the starting point and therefore we obtain a set of exact values $C_n(i)$, $U_n(i)$ and $\langle R_n^2(i)\rangle$ for each centre i. If we plot $C_n(i)/C_{n-1}(i)$ or $U_n(i)/U_{n-1}(i)$ against $1/n$ we find no regular behaviour. The fluctuations are large and very little can be learnt from the individual walks. On the other hand the ratios $\langle R_{n+1}^2(i)\rangle/\langle R_n^2(i)\rangle$ are much smoother and extrapolation of the individual ratio plots is feasible.

Since we are primarily interested in the average properties of the networks it would seem appropriate to look at the behaviour of the walks when they are *averaged* over a number of different origins. We could choose either the arithmetic mean formed by

$$N^{-1}\sum_{i=1}^{N} C_n(i) = C_n(\mathrm{A})$$

or we can consider the geometric mean

$$C_n(\mathrm{G}) = \left(\prod_{i=1}^{N} C_n(i)\right)^{1/N}.$$

Here, N is the total number of different centres used as the origin for each set of walks.

When the ratios of these means, i.e., either $C_n(\mathrm{A})/C_{n-1}(\mathrm{A})$ or $C_n(\mathrm{G})/C_{n-1}(\mathrm{G})$ are plotted against $1/n$ the fluctuations are considerably reduced and linear plots appear for both sets of averages. Indeed, although it is well known that for any distribution the geometric mean is always less than the corresponding arithmetic mean, we find that within our confidence limits it is not possible to distinguish between the results obtained from the two methods of averaging. Therefore in this paper we will only report the results obtained by using the arithmetic mean.

The maximum value of n that can be investigated is limited by two factors: (a) the size of the network available, and (b) the number of centres that must be averaged over in order to reduce sufficiently the fluctuations in the ratio plot. Unfortunately, the size of the RP model is limited by the 8000 ball-bearings used in setting up the network and we found that we could only use $n \leqslant 7$ for the walks and $n \leqslant 10$ for the polygons. This gave a sample of 49 centres which could act as origins for the walks.

The MFCC network is limited only by computing time considerations. However, we found that for the purposes of this paper adequate results could be obtained with $n \leqslant 8$ for walks and $n \leqslant 10$ for polygons using a sample of 40 different initial points.

4. Results for self-avoiding walks and polygons

In figure 2 we present a $1/n$ plot of the ratios $\mu_n = C_n(\mathrm{A})/C_{n-1}(\mathrm{A})$ and $\nu_n = U_n(\mathrm{A})/U_{n-1}(\mathrm{A})$ obtained from the MFCC network with $\bar{q} = 6{\cdot}25$, while in figure 3 we present the corresponding ratios for the RP network. These graphs are very similar to the corresponding ones obtained from the regular FCC lattice (see Domb 1969). The data which we will analyse in detail below is again consistent with the conjecture $\lim_{n\to\infty} \mu_n = \lim_{n\to\infty} \nu_n = \mu$. This result has been shown to be rigorously true for a simple cubic network by Hammersley (1961). Although cubic symmetry has been used to construct this proof, it is probably not essential and our results confirm this fact.

In order to find the critical constants we will follow the methods used by Hiley and Sykes (1961), and Martin *et al* (1967) for the regular lattices. The quantity μ is first estimated for the RP network by forming the linear extrapolants $B_n = n\mu_n - (n-1)\mu_{n-1}$. In the case of the MFCC network we use $B_n^* = n\mu_n - (n-2)\mu_{n-2}$ to take account of the small odd–even effect that appears in the data. These results are presented in tables 1 and 2. Since we only have a limited amount of data we have found it necessary to compare our results with the corresponding results obtained for the regular FCC lattice. These are presented in table 3. The steady increase in the B_n for the regular lattice has been fully exploited by the methods used in Martin *et al* (1967). Unfortunately, our

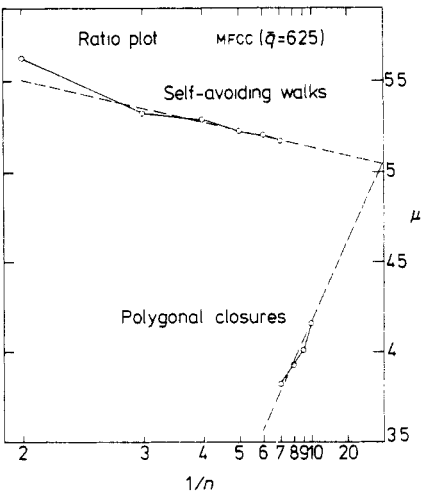

Figure 2. Ratio plot for MFCC ($\bar{q} = 6{\cdot}25$). Self-avoiding walks $\mu_n = C_n(\mathrm{A})/C_{n-1}(\mathrm{A})$ and polygonal closures $\nu_n = U_n(\mathrm{A})/U_{n-1}(\mathrm{A})$ against $1/n$.

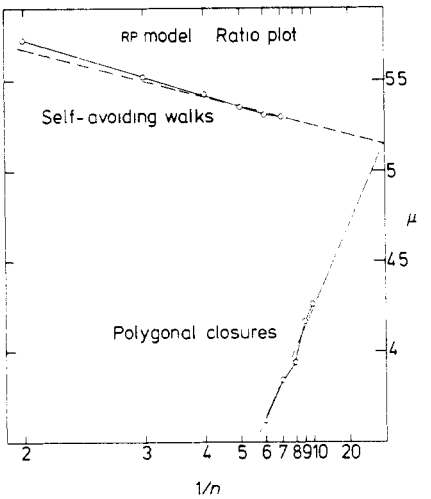

Figure 3. Ratio plot of RP model. Self-avoiding walks $\mu_n = C_n(\mathrm{A})/C_{n-1}(\mathrm{A})$ and polygonal closures $\nu_n = U_n(\mathrm{A})/U_{n-1}(\mathrm{A})$ against $1/n$.

data from both irregular networks show remanent fluctuations and we must modify their procedure. As a first approximation to μ we will take the mean of the last three readings of B_n. For the regular FCC lattice this gives $\mu_{\mathrm{FCC}} = 10{\cdot}020$ whereas the best estimate is 10·035, a difference of only 0·15%. For the irregular networks we estimate $\mu_{\mathrm{RP}} = 5{\cdot}151$ and $\mu_{\mathrm{MFCC}} = 5{\cdot}048$.

These approximate values of μ can now be used to estimate g and h. We do this by first forming the sequences

$$g_n = (n\mu_n/\mu) - n \tag{5}$$

$$h_n = (n\nu_n/\mu) - n. \tag{6}$$

Table 1. Analysis of $C_n(A)$ and $U_n(A)$ for RP network.

n	μ_n	B_n	g_n	n	ν_n	$-h_n$
2	5·7177			5	3·2313	1·863
3	5·5181	5·119	0·214	6	3·6159	1·788
4	5·4173	5·115	0·207	7	3·8356	1·787
5	5·3503	5·082	0·193	8	3·9422	1·877
6	5·3144	5·135	0·190	9	4·1726	1·709
7	5·3030	5·235	0·207	10	4·2560	1·737
		Mean of last three terms $\mu = 5·151$				

Table 2. Analysis of $C_n(A)$ and $U_n(A)$ for MFCC ($\bar{q} = 6·25$) network.

n	μ_n	B_n^*	g_n	n	ν_n	$-h_n$
2	5·6284			5	3·2669	1·764
3	5·3307		0·230	6	3·3770	1·986
4	5·2909	4·953	0·192	7	3·8256	1·695
5	5·2255	5·068	0·176	8	3·9309	1·770
6	5·2041	5·030	0·185	9	4·0548	1·771
7	5·1746	5·047	0·175	10	4·1669	1·745
		Mean of last three terms $\mu = 5·048$				

Table 3. Analysis of C_n and U_n for regular FCC lattice.

n	μ_n	B_n	g_n	n	ν_n	$-h_n$
2	11·0000			5	6·3636	1·825
3	10·6364	9·909	0·184	6	6·9286	1·851
4	10·4701	9·971	0·180	7	7·4186	1·817
5	10·3763	10·001	0·178	8	7·7949	1·776
6	10·3173	10·022	0·178	9	8·0593	1·761
7	10·2764	10·031	0·179	10	8·2637	1·753
		Mean of last three terms $\mu = 10·020$ Best estimate $\mu = 10·035$	$g \to 0·167$			$h \to -1·75$

For the regular FCC lattice we find the expected steady decrease in g_n except for the last value which actually increases. This rise is due to our underestimating μ and does not occur if we use $\mu = 10·035$. Martin *et al* (1967) have shown that with larger values of n the sequence g_n appears to be approaching the conjectured limit $g = \frac{1}{6}$.

The MFCC network shows an overall decrease in g_n towards the same value although it is somewhat masked by small fluctuations. The RP network also shows a steady decrease although the actual values are rather higher and there is a rise in the value of g,

similar to the one found in our limited analysis of the regular FCC lattice. This, again, is probably due to a small underestimation of the value μ_{RP}.

The data for polygonal closures on both irregular networks seem to show the same general trends that are found for the regular FCC lattice and it appears to be consistent with the conjectured value $h = -\frac{7}{4}$. We have tried more refined ways of analysing our data by using, for example, the Padé approximant method but these do not lead to a more accurate assessment of the critical parameters.

5. Results for the mean-square end-to-end distance

The ratios $\langle R^2_{n+1}(i)\rangle/\langle R^2_n(i)\rangle$ for individual centres on both irregular networks give remarkably good straight lines when plotted against $1/n$. This line becomes even smoother when we average over a number of initial centres. The usual way of estimating the value of θ is to use equation (4) to form the sequence

$$\theta_n = n[(\langle R^2_{n+1}(\mathrm{A})\rangle/\langle R^2_n(\mathrm{A})\rangle) - 1]. \tag{7}$$

We have calculated these sequences for the RP network and for two MFCC networks, one with $\bar{q} = 8$ and the other with $\bar{q} = 6{\cdot}25$. The results are presented in figure 4. The corresponding values for the regular FCC lattice are also included. This graph shows that the RP values are steadily approaching the conjectured limit $\theta = 1{\cdot}2$ whereas the MFCC values with $\bar{q} = 6{\cdot}25$ appear to be moving very slightly away from this limit. On the other hand the values for the MFCC network with $\bar{q} = 8$ appear to be approaching $1{\cdot}2$ again after an initial decrease. Even though it is not possible to extrapolate these results with any degree of confidence, it should be noted that the values of θ_n are already well within $\pm 2\%$ of the conjectured limit.

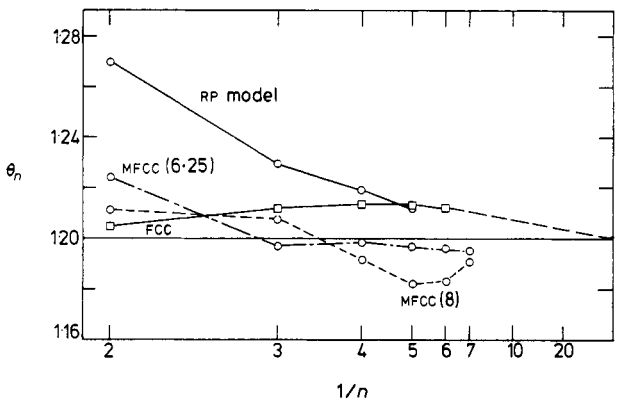

Figure 4. θ_n as a function of $1/n$.

6. Conclusions

Apart from small fluctuations in the averaged data, the overall behaviour of the averaged walks on the irregular network is remarkably similar to the corresponding behaviour for the walks on the regular FCC lattice and we can find no evidence to suggest that the irregularity of the network will affect the critical exponents that arise in the

self-avoiding walk problem. Our results for the mean-square end-to-end distances are of particular interest. Here we might have expected to find some detectable change when the end points of the walks are randomly distributed in space rather than being confined to the regular lattice points. Although the earlier terms do show some differences these are smaller than the differences found between the regular lattices (see Domb 1970, Martin and Watts 1971).

The effects of irregularity on the critical exponents of the thermodynamic properties of an Ising-like model are a little more difficult to assess. The higher coefficients of the series have significant contributions from graphs other than chains and polygons. Although we have not analysed these contributions in detail it is difficult to see how they could be significantly affected by the irregularity of the underlying network particularly in view of the results that have been obtained from the various three-dimensional regular lattices. Indeed in the critical region the correlation functions decay very slowly with distance so one would not expect the finer details of the lattice structure to matter (see Kadanoff *et al* 1967). These considerations seem to suggest that the difference between the critical exponents for the liquid–gas transitions and those predicted by the lattice gas model are unlikely to be entirely accounted for by the spatial irregularity that is present in real liquids although Gaunt and Domb (1975) have reported the presence of some structural effects in the density expansion of a lattice gas. We are at present unable to say anything meaningful about the effects of irregularity on the thermodynamic properties away from the critical region.

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