Polymer chain statistics and universality. I

1978 J. Phys. A: Math. Gen. 11 361

(http://iopscience.iop.org/0305-4470/11/2/013)

J. Phys. A: Math. Gen., Vol. 11, No. 2, 1978. Printed in Great Britain. © 1978

Polymer chain statistics and universality I

M Lax†, A J Barrett‡ and C Domb§‖

† Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel
‡ Department of Mathematics, Royal Military College of Canada, Kingston, Ontario, Canada
§ Department of Physics, Bar-Ilan University, Ramat Gan, Israel

Reived 11 August 1977

Abstract. A brief summary is given of the concept of universality in the theory of critical phenomena. The concept is applied to random walks and self-avoiding walks on lattices corresponding to the $n=-2$ and $n=0$ universality classes. The Domb–Joyce model of a random walk on a lattice with a δ function interaction of strength w is identified with crossover behaviour, w serving as a crossover parameter. Exact enumerations are undertaken of the mean-square end-to-end length $\langle R_N^2\rangle$ for the Domb–Joyce model for a number of three-dimensional lattices. Using the smoothness postulate of Griffiths, estimates are obtained of the asymptotic behaviour of the expansion factor $\alpha^2=\langle R_N^2\rangle/N$ in the range $0{\cdot}5<w<1$. By combining these with exact virial coefficients for small w the range is extended to $w=0$. The two-parameter approximation which assumes that α^2 is a function of $wN^{1/2}$ is satisfied with maximum errors of 2 or 3%. The two-parameter function which has been the subject of much discussion by polymer theorists is estimated and an empirical formula is proposed.

1. Introduction

There are a number of statistical averages associated with a polymer chain whose behaviour as a function of temperature and intramolecular forces help to characterise the size and shape of the chain. Well known examples are the mean-square end-to-end distance $\langle R_N^2\rangle$, higher moments of the end-to-end distance $\langle R_N^{2p}\rangle$, the mean-square radius of gyration $\langle S_N^2\rangle$, the correlation between two points of the chain, and various associated moments. These averages can be calculated with relative ease for a random chain, but when intramolecular forces are introduced there is an enormous increase in complexity.

It has been usual in polymer theory to approximate the intramolecular forces by means of a pseudopotential, i.e. a δ-function interaction of appropriate strength (see e.g. Yamakawa 1971). If $V(\boldsymbol{r})$ represents the intramolecular potential, the forces are replaced by $-\nu\delta(\boldsymbol{R}_{ij})$, where $\boldsymbol{R}_{ij}$ is the distance between the ith and jth steps of the walk and

$$\nu=\int [1-\exp(-\beta V(\boldsymbol{r}))]\,\mathrm{d}\boldsymbol{r} \qquad (\beta=1/kT). \tag{1}$$

Little systematic work has been attempted to assess how good an approximation this

‖ Royal Society Visiting Professor on leave of absence from Physics Department, King's College, Strand, London WC2R 2LS, UK.

is, and we shall not pursue the point further here (recent publications raising this matter are Smith and Fleming 1975, Barrett 1976). We shall accept the pseudopotential approximation, so that all the above averages are functions of the two variables N and ν, and it will be our aim to find reliable methods of estimating these functions.

In conventional polymer theory two approaches have been followed. The first is to derive closed-form approximations of self-consistent field type. The best known of these is the Flory formula for the expansion factor $\alpha^2(=\langle R_N^2\rangle/N)$ of a chain,

$$\alpha^5-\alpha^3=\frac{3\sqrt{3}}{2}z \qquad \left(z=\left(\frac{3}{2\pi}\right)^{3/2}\nu N^{1/2}\right). \tag{2}$$

However, there are at least a dozen closed formulae each claiming to be a valid approximation, and all differing from one another very significantly (see e.g. Domb and Barrett 1976).

The second approach derives virial expansions in powers of the parameter z in (2) which are strictly valid only in the limit of N large and ν small (the two-parameter approximation). Only a few terms of the expansion are available, and since we are interested in large N their region of usefulness is very limited. In fact, it has been demonstrated recently that the expansions are not convergent but divergent (Edwards 1975, Oono 1975).

To make progress in this confusing situation we shall draw on the experience of second-order phase transitions and critical phenomena where problems of a similar kind have been tackled effectively in recent years. Such transitions occur in lattice and continuum models with a variety of different types of interaction. One of the most important ideas to have emerged is that of 'universality'—that certain important features of the behaviour are lattice independent in a given dimension, and others even model independent for a wide range of interactions. If such features can be identified calculations can be made for lattice models whose results will be valid for continuum models. Numerical methods can be pursued much more effectively for lattice models, and calculations for a number of lattices can be undertaken to check on the universality property.

We shall suggest that a similar characterisation can be made of lattice and continuum models of polymer chains, and that many of the statistical averages mentioned above can be related to universal quantities. We shall then make use of lattice enumerations to provide new estimates of these statistical averages in the pseudopotential approximation.

2. Universality in critical phenomena

One of the most difficult problems in classical statistical mechanics is the condensation of a gas of molecules with intermolecular forces consisting of a hard-core repulsion and a short-range attraction. Particular interest centres on the critical point of the gas–liquid system and the detailed behaviour in its neighbourhood. Despite great formal progress in developing the virial series expansion, it was not possible to calculate enough terms to provide any reliable information on critical behaviour.

In the 1950's therefore interest turned to 'lattice-gas' models in which the molecules are constrained to occupy the sites of an arbitrary lattice. This model is mathematically identical with the Ising model of ferromagnetism, for which exact calculations are available of a number of properties in two dimensions. For lattice

models the discrete nature of the problem and the symmetry introduce great simplification, and enable virial expansions to be taken very much further than for continuum models. Using the known exact solutions as a check on numerical accuracy, it was then possible to assess the critical behaviour of a given lattice model with considerable confidence.

Information on critical behaviour was at first assembled empirically; it was then noted that the data fitted into a simple pattern which could be described in terms of a scaling hypothesis. During the past five years a theoretical justification for this pattern has emerged. We shall summarise briefly the main conclusions; further details are available for example in Domb and Green (1974).

The behaviour of thermodynamic functions near a critical or Curie point T_c is described by certain characteristic *critical exponents*. For example the specific heat, C_H, and initial susceptibility, χ_0, are given by

$$\begin{aligned} C_H &\sim A(T-T_c)^{-\alpha}, \\ \chi_0 &\sim C(T-T_c)^{-\gamma}, \end{aligned} \qquad (T>T_c) \tag{3}$$

and α and γ are termed the high temperature exponents. It was first noted that these exponents depend on the dimension d of the model but not on the lattice structure in a given dimension. Further, an alternative magnetic interaction to the Ising model, the Heisenberg model, considered interacting classical vector spins in three dimensions, and this could readily be generalised to interacting vector spins in n dimensions. The next conjecture was that critical exponents depend only on the symmetry of the ordered state, which can be characterised by the integer n. Finally it became clear from exact solutions for long-range forces that even in a given dimension an exponent will depend on the range of intermolecular forces, and a third parameter σ should be used to characterise this range. In our present discussion we will be concerned only with short-range forces; we can then say that any critical exponent depends only on d and n. In a terminology introduced by Kadanoff (1971) we say that a particular pair of values of d and n defines a *universality class*.

If scaling constants are introduced for each lattice *universal functions* can also be defined which characterise critical behaviour. For example, the magnetic equation of state in the critical region can be put in the form

$$M = \phi(t_0 T, h_0 H) \tag{4}$$

where t_0 and h_0 vary from lattice to lattice but ϕ is universal. Thus although the amplitudes A and C in (3) vary from lattice to lattice, they can be expressed in terms of t_0, h_0 and ϕ; hence if ϕ is known they can be calculated for any lattice for which t_0 and h_0 are known.

Next the transition from one universality class to another was considered. If a simple cubic lattice has interactions J in the x and y directions and J' in the z direction, then as long as $J'>0$ the critical exponents and functions correspond to $d=3$. But when $J'=0$ the system becomes two dimensional and there is a transition to $d=2$ critical behaviour. The value $J'=0$ is thus of particular significance; for small J' a scaling constant j_0 can be introduced for a particular lattice, and the equation of state near $J'=0$ covering the transition region can be put in the form

$$M = F(j_0 J', t_0 T, h_0 H). \tag{5}$$

F is then called the *crossover function* from $d=2$ to $d=3$, and is also universal.

None of the above results has been established rigorously in the mathematical sense. But a mass of numerical data has been assembled to support them, as do theoretical arguments based on the concept of the renormalisation group (see e.g. Fisher 1974).

3. Universality in random and self-avoiding walks

The properties of a random walk on a lattice or in a continuum are well known, and we shall now reformulate them in terms of the universality concept. The mean-square end-to-end length is given by

$$\langle R_N^2 \rangle = N, \tag{6}$$

so that the exponent of N is the same for all lattices (and all dimensions) and is therefore universal. The mean-square radius of gyration is given by

$$\langle S_N^2 \rangle \sim \tfrac{1}{6} N \tag{7}$$

for all lattices and dimensions; hence the factor $\frac{1}{6}$ for $\langle S_N^2 \rangle / \langle R_N^2 \rangle$ is also universal.

The total number of random walks on a lattice of coordination number q is

$$c_N = q^N, \tag{8}$$

which is not universal since q is lattice dependent. The total number at the origin after N steps is

$$u_N \sim B q^N N^{-d/2}. \tag{9}$$

This again is not universal although the exponent of N is universal. However, c_N and u_N cannot really be defined for a continuum walk, and if we wish to define a quantity which can have significance both for a lattice and a continuum it is better to use

$$u_N / c_N \sim A N^{-d/2}. \tag{10}$$

If we consider the shape of the walk $f(\boldsymbol{u})$ after N steps ($\boldsymbol{u} = \boldsymbol{R}/\langle R_N \rangle$) we obtain a universal function (Domb 1971)

$$f(\boldsymbol{u}) \sim (d/2\pi)^{d/2} \exp(-\tfrac{1}{2} d u^2). \tag{11}$$

A self-avoiding walk is a random walk on a lattice which is not allowed to visit any point more than once. The self-avoidance condition is extremely difficult to deal with mathematically and there are few rigorous results. However, exact calculations can be undertaken for a considerable range of N, and Monte Carlo enumerations can be set up without too much difficulty. As a result the asymptotic behaviour of self-avoiding walks can be conjectured with considerable confidence (see e.g. Domb 1969).

The exponents for self-avoiding walks are completely different from their counterparts for random walks; hence we can describe them as belonging to a different universality class. Instead of (6) we now have

$$\langle R_N^2 \rangle \sim D N^{\gamma} \tag{12}$$

where γ is universal, and approximately equals $\frac{3}{2}$ in two dimensions, and $\frac{6}{5}$ in three dimensions. Instead of (7) we have

$$\langle S_N^2 \rangle / \langle R_N^2 \rangle \sim \theta \tag{13}$$

where θ is no longer $\frac{1}{6}$. Numerical estimates suggest that $\theta \sim 0{\cdot}140$ in two dimensions and $0{\cdot}155$ in three dimensions. Domb and Hioe (1969) suggest that θ might also be universal; the same suggestion in relation to three-dimensional lattices has been made previously by Windwer (1965); we shall see later how this fits in with the general universality pattern which we shall propose.

Instead of (8) we now have

$$c_N \sim E\mu^N N^g \tag{14}$$

where g is universal and approximately equal to $\frac{1}{3}$ in two dimensions, and $\frac{1}{6}$ in three dimensions; μ is known as the *connective constant* and is lattice dependent and not universal. Instead of (9) we have

$$u_N \sim F\mu^N N^{-h} \tag{15}$$

where h is universal and approximately equal to $\frac{3}{2}$ in two dimensions and $\frac{7}{4}$ in three dimensions. We cannot define a self-avoiding walk for a continuum, but a useful lattice-independent quantity which might have a continuum interpretation is

$$u_N/c_N \sim GN^{-h-g}. \tag{16}$$

The shape of a self-avoiding walk gives rise to a universal function; instead of (11) we have

$$f(u) \sim Hu^{\phi} \exp(-Ku^{\delta}) \tag{17}$$

where $\delta \simeq 4$ in two dimensions and $\frac{5}{2}$ in three dimensions (the value of ϕ is not very well established).

The exponents introduced in this section are related to N whilst those of the previous section (equation (3)) are related to $T - T_c$. But in fact every $(T - T_c)$-exponent for an interacting model is uniquely related to an N-exponent by means of a partition function as follows. For any function of N, $f(N)$, we define $\phi(T)$ as

$$\phi(T) = \sum_{N=1}^{\infty} F(N) \exp(-\beta NJ) = \sum_{N=1}^{\infty} f(N) y^N \qquad (\beta = 1/kT,\ y = \exp(-\beta J)). \tag{18}$$

For example for c_N in (14),

$$\phi(T) \sim \sum_{N=1}^{\infty} E\mu^N N^g \sim L(1-\mu y)^{-g-1} \sim M[1-(T_c/T)]^{-g-1}. \tag{19}$$

Using this relationship we can define an 'interaction' model corresponding to self-avoiding and random walks, and they can be fitted into the d, n classification of the previous section. De Gennes (1972) showed that self-avoiding walks correspond to $n = 0$; Balian and Toulouse (1973) and Fisher (1973) showed that random walks correspond to $n = -2$.

4. The Domb–Joyce model

A lattice model which parallels the pseudopotential continuum model was investigated by Domb and Joyce (1972). The delta function $\delta(r_{ij})$ is replaced by a discrete Kronecker function δ_{ij} where i and j are the lattice sites occupied by two points of the

walk; any configuration of the walk is then weighted by the factor

$$\prod_{\text{pairs } i,j} (1 - w\delta_{ij}), \tag{20}$$

where w plays a role analogous to ν in equation (1).

Domb and Joyce developed a virial expansion for this model as a power series in w which is clearly analytic for finite N. The formalism applies equally well to a continuum model, the change to a different lattice or to a continuum being achieved by changing a generating function.

One particularly important feature of the model is the behaviour when $w = 1$; all configurations in which a site is occupied more than once then have zero weighting, from equation (20), and hence the result is a self-avoiding walk on the lattice. Thus, the model serves as a transition between random and self-avoiding walks, i.e. between the $n = -2$ and $n = 0$ universality classes. Domb and Joyce argued that the value of the parameter w at which the change in universality class takes place is $w = 0$. Thus for any value of $w > 0$ critical exponents and functions should be those of a self-avoiding walk.

When N becomes large and w small, $N^{1/2}w$ remaining finite, the two-parameter function is approached, and the virial series is no longer convergent but asymptotic. Domb *et al* (1973) noted that in this limit (with the exception of a scaling constant h_0 for each lattice) the first three virial coefficients are identical for all lattices and for a continuum. They suggested that the same property would hold for virial coefficients to any order. One would then have for the expansion factor of a chain,

$$\alpha^2 = \langle R_N^2 \rangle / N \sim \psi(z), \qquad (z = h_0 N^{1/2} w) \tag{21}$$

and $\psi(z)$ is the universal crossover function from $n = -2$ to $n = 0$. This suggestion was tested numerically for standard three-dimensional lattices and particular values of z (Domb 1974, Domb and Barrett 1976) and the results were in satisfactory agreement with (21).

We should expect the behaviour of $\langle S_N^2 \rangle$ to be similar to that of $\langle R_N^2 \rangle$, and hence by analogy with (21)

$$\alpha_s^2 = 6\langle S_N^2 \rangle / N \sim \psi_s(z). \tag{22}$$

The Domb–Joyce model enables us to check on the accuracy of the two-parameter function as an approximation for finite N and w, and to estimate two-parameter functions like $\psi(z)$ in (21). Our method is to enumerate $\langle R_N^2 \rangle$ exactly from different lattices for finite N and a variety of w between 0 and 1. The hypothesis of universality enables us to conjecture an asymptotic form in the neighbourhood of $w = 1$ (say $w = 0{\cdot}5$ to 1), and near $w = 0$ we use a power series expansion in w for finite N. We test how well the (N, w) data can be represented by a single function of $N^{1/2}w$, and since the different lattices have different values of h_0 in (21), we can examine different regions of z.

In principle we can calculate the two-parameter function for any statistical average for which self-avoiding walk data and asymptotic conjectures are available. Domb and Hioe (1969) calculated a number of other moments analogous to $\langle S_N^2 \rangle$ for self-avoiding walks, for example $\langle Q_n^2 \rangle$ the mean-square distance of an element of the chain from the end-part of the chain. They used these moments to construct an estimate of the pair correlation function for pairs of points along the chain. The same enumerations have been undertaken by one of us (ML) for the Domb–Joyce model,

but we shall defer a detailed study and analysis to a subsequent paper. In the present paper we shall concentrate on the function α^2 which has been the subject of much discussion by polymer theorists.

The numerical calculations are as follows. We first enumerate c_{Nk}, the number of walks with k contacts, by the program described in the appendix. Typical results for the simple (SC) lattice with $N = 10$ are shown in table 1. We then define a partition function for the Domb–Joyce model by

$$c_N(w) = \sum_k c_{Nk} v^k \qquad (v = 1 - w). \tag{23}$$

Table 1. Typical enumerations for the Domb–Joyce model (SC lattice, $N = 10$).

k	$\Sigma r^2 c_{Nk}(\boldsymbol{r})$	u_{Nk}	$c_{Nk}(\boldsymbol{r})$
0	24692980	48240	8809878
1	32907824	142560	15775476
2	22659900	228360	14419194
3	9397560	191520	7903212
4	6587668	195150	6061614
5	2253008	143040	2918988
6	1032576	66900	1327548
7	723608	74040	1089816
8	250684	32550	447546
9	157752	24720	276636
10	56304	8880	124452
11	19800	7200	49764
12	23720	6090	55476
13	9040	2400	22680
14	3312	600	8280
15	0	0	0
16	1104	300	2760
17	96	0	240
18	0	0	0
19	0	0	0
20	24	6	60

The value $v = 0$ ($w = 1$) corresponds to a self-avoiding walk, and $v = 1$ ($w = 0$) to a random walk.

For other properties of interest, we define corresponding functions. For polygonal closure we define

$$u_N(w) = \sum_k u_{Nk} v^k \tag{24}$$

and consider the asymptotic behaviour of

$$u_N(w)/c_N(w) \tag{25}$$

which must vary between the value $AN^{-d/2}$, given by (10) when $w = 0$, and GN^{-h-g} given by (16) when $w = 1$.

To investigate the mean-square end-to-end distance we enumerate $c_{Nk}(\boldsymbol{r})$ as the number of walks with contacts which terminate at $\boldsymbol{r}$ and define the second moment

$$c_N^{(2)}(w) = \sum_k v^k \sum_{\boldsymbol{r}} \boldsymbol{r}^2 c_{Nk}(\boldsymbol{r}). \tag{26}$$

$\langle R_N^2(w)\rangle$ is then given for the model by

$$\langle R_N^2(w)\rangle = c_N^{(2)}(w)/c_N(w), \tag{27}$$

and the expansion factor $\alpha^2(w)$ by

$$\alpha^2(w) = \langle R_N^2(w)\rangle/N. \tag{28}$$

The asymptotic value varies from 1 when $w = 0$ (equation (6)) to $DN^{\gamma-1}$ (equation (12)) when $w = 1$.

5. Expansion factor

The expansion factor α^2 defined in (21) can be developed as a power series in w for finite N,

$$\alpha^2(w, N) = 1 + k_1 w + k_2 w^2 + k_3 w^3 + \ldots \tag{29}$$

where the coefficients k_r are evaluated in terms of the number of returns to the origin, r_N, in a random walk. The formula applies equally to lattice and continuum walks. Calculations of the first three coefficients have been undertaken for $N \leqslant 50$ and asymptotic formulae have been derived (Domb and Joyce 1972, Barrett 1975). In general

$$k_r \sim A_r^{(0)} N^{r/2} + A_r^{(1)} N^{(r-1)/2} + A_r^{(2)} N^{(r-2)/2} + \ldots \tag{30}$$

and if the A_r^0 term only is retained, the two-parameter approximation results, the series in $N^{1/2}w$ being asymptotic.

When $w = 1$ lattice models give rise to a self-avoiding walk whose properties have been investigated with considerable precision (Domb 1969). It is found that the numerical data can be well fitted by the formula

$$\alpha^2(1, N) \sim N^{1/5}(C_0 + D_0/N). \tag{31}$$

The smoothness postulate (Griffiths 1970) then suggests that in the neighbourhood of $w = 1$, one might expect the data to be fitted by the formula

$$\alpha^2(w, N) \sim N^{1/5}(C(w) + D(w)/N). \tag{32}$$

We have found that formula (32) provides a reasonable fit to the numerical data for values of w between 0·5 and 1·0, and the estimates of $C(w)$ and $D(w)$ for the FCC, BCC, SC and diamond lattices are reproduced in table 2. We think that the estimates of $C(w)$ are reliable (i.e. errors not more than a few per cent) even down to $w = 0{\cdot}5$, but that the estimates of $D(w)$ become more speculative in this region; however, the general pattern of behaviour represented by the $D(w)$ is reasonably parallel to the true pattern. For values of w less than 0·5, additional terms are necessary in (32), and it is more convenient to cover this region by interpolation. We fit the first two coefficients k_1 and k_2 in (30) at $w = 0$, and the values of α^2 from 0·5 to 1·0 and interpolate so as to join smoothly at $\alpha = 0{\cdot}5$.

The results for the lattice are presented in figure 1(a) where curves of α^2 as a function of w are plotted for various values of N. Lines of $z =$ constant are also plotted, and if the two-parameter approximations were exactly satisfied these lines would be horizontal. We find that the deviations from horizontal are small amounting

Table 2. Estimates of $C(w)$ and $D(w)$ ($\alpha^2 \sim N^{1/5}[C(w)+(D(w)/N)]$.

Lattice	w	1·0	0·9	0·8	0·7	0·6	0·5
FCC	$C(w)$	0·920	0·879	0·836	0·791	0·747	0·203
	$D(w)$	0·037	0·123	0·236	0·362	0·498	0·630
BCC	$C(w)$	0·961	0·915	0·868	0·822	0·777	0·231
	$C(w)$	0·019	0·114	0·216	0·326	0·438	0·559
SC	$C(w)$	1·068	1·013	0·959	0·904	0·852	0·800
	$D(w)$	−0·074	0·0	0·085	0·190	0·296	0·409
Diamond	$C(w)$	1·30	1·22	1·14	1·07	0·996	0·927
	$D(w)$	−0·294	−0·207	−0·139	−0·056	0·055	0·203

only to one or two per cent and hence the two-parameter approximation is well satisfied in the whole region.

Similar results are obtained for the FCC lattice (figure 1(*b*)), the BCC lattice (figure 1(*c*)) and the diamond lattice (figure 1(*d*)). In all cases the two-parameter function provides a good fit, and the scaling from one lattice to another involves an error too small to be represented in graphical plotting on the scale chosen. We can therefore regard these data as a numerical confirmation of the applicability of the universality hypothesis.

Some examples of the difference between different three-dimensional lattices, and their convergence to the two-parameter function for large N and small w have been given in previous publications (Domb 1974, Domb and Barrett 1976).

6. Scaling hypothesis and scaling function

In the two-parameter approximation, the virial series for the expansion factor $\psi(z)$ in (21) is

$$\psi(z) = 1 + b_1 z + b_2 z^2 + b_3 z^3 + \ldots \tag{33}$$

with the following numerical values of the coefficients (Barrett 1975):

$$b_1 = \tfrac{4}{3}, \qquad b_2 = \tfrac{28}{27}\pi - \tfrac{16}{3} = -2{\cdot}075385, \qquad b_3 = 6{\cdot}29688. \tag{34}$$

These values have been calculated by a new method; the first two coefficients are in the agreement with previous calculations for a continuum model (Yamakawa 1971) whilst the third differs by a few per cent. Details of the calculations have been given in Barrett (1975), and will be published shortly. As noted previously (equation (21))

$$z = h_0 N^{1/2} w \tag{35}$$

the value of h_0 being given by

$$h_0 = \left(\frac{3}{2\pi}\right)^{3/2} \frac{g}{a^3} \tag{36}$$

where g is the volume per site of the lattice and a the length of a step of the walk. For the SC, BCC and FCC lattices g/a^3 has the values 1, $4/3^{3/2}$, $2^{-1/2}$ respectively; for the diamond lattice with two sites per unit cell the corresponding g/a^3 is $8/3^{3/2}$. For the

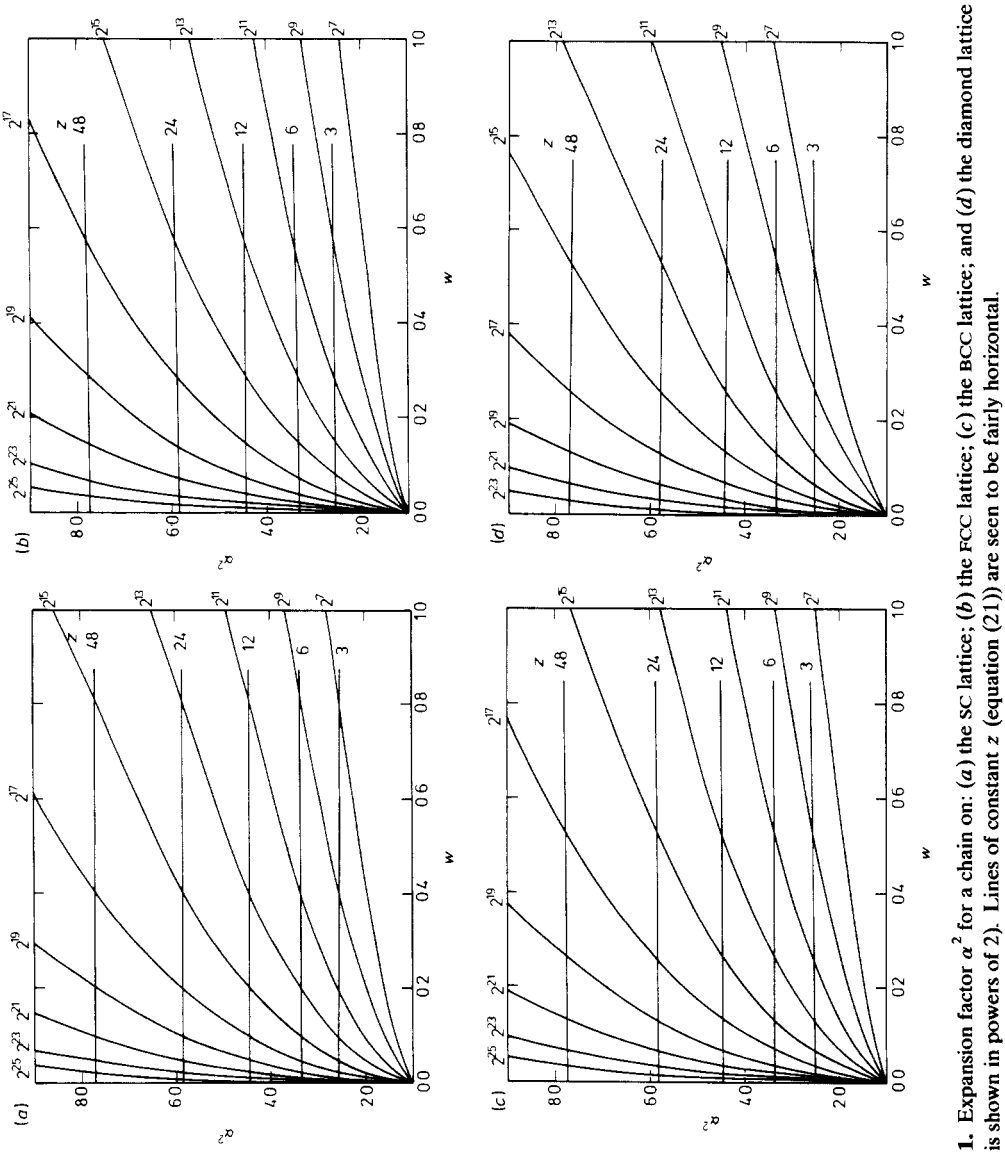

Figure 1. Expansion factor α^2 for a chain on: (*a*) the SC lattice; (*b*) the FCC lattice; (*c*) the BCC lattice; and (*d*) the diamond lattice (chain size N is shown in powers of 2). Lines of constant z (equation (21)) are seen to be fairly horizontal.

Gaussian continuum model gw is replaced by the excluded volume ν given by the binary integral (1).

The asymptotic form (32) for $\alpha^2(w, N)$ corresponds to an asymptotic form for $\psi(z)$ of the form

$$\psi(z) \sim B_1 z^{2/5}(1+\theta/z^2). \tag{37}$$

Hence in the region where the scaling hypothesis is valid (i.e. for sufficiently small w) we should have from (35)

$$C(w) \simeq B_1 h_0^{2/5} w^{2/5}, \tag{38}$$

$$D(w)/C(w) \simeq \theta/h_0^2 w^2. \tag{39}$$

It is difficult to say *a priori* how small w must be for these scaling relations to be satisfied. In practice we find that relation (38) fits with deviations of only a few per cent from $w = 0{\cdot}5$ to $w = 1{\cdot}0$, as illustrated in table 3(a). But relation (39), which represents a correction term, can only be used at $w = 0{\cdot}5$, $0{\cdot}6$, and then provides an order of magnitude estimate of θ. Nevertheless, it is interesting and significant that the values of $D(w)$, which are apparently arbitrary at $w = 1{\cdot}0$ for different lattices, move towards the regular pattern of behaviour represented by (39) as w becomes sufficiently small. We have made the following estimates for the universal parameters B_1 and θ:

$$B_1 = 1{\cdot}64 \qquad \theta = 0{\cdot}013. \tag{40}$$

To fit the data given by (33), (34), (37), and (40) we shall follow the method used previously (Domb and Barrett 1976), taking an empirical form

$$\psi^m = \Phi(z). \tag{41}$$

$\Phi(z)$ is a polynomial whose lowest terms are chosen to fit (33) and (34), and whose highest terms together with the exponent m are chosen to fit the asymptotic form given by (37) and (40). We find that

$$\psi^{15} = 1 + 20z + 155{\cdot}54z^2 + 591{\cdot}86z^3 + 325z^4 + 1670z^6. \tag{42}$$

The coefficient of z^5 is exactly zero in view of assumption (32).

Table 3. Tests of scaling.

(a) $C(w)/h_0^{2/5}w^{2/5}$

Lattice \ w	1·0	0·9	0·8	0·7	0·6	0·5
FCC	1·647	1·641	1·636	1·633	1·641	1·659
BCC	1·663	1·652	1·642	1·641	1·649	1·667
SC	1·664	1·647	1·633	1·625	1·628	1·645
Diamond	1·70	1·67	1·64	1·62	1·60	1·59

(b) $D(w)h_0^2w^2/C(w)$

w	0·6	0·5
FCC	0·0131	0·0122
BCC	0·0123	0·0131
SC	0·0136	0·0139

The following estimates were given in a previous publication

$$\psi^5 = 1 + \tfrac{20}{3}z + 4\pi z^2, \tag{43}$$

based on one term of the virial series and one asymptotic coefficient from self-avoiding walks;

$$\psi^{15} = [1 + 10z + (\tfrac{40}{9} + \tfrac{10}{3})z^2 + 8^{3/2}z^3]^2, \tag{44}$$

based on three terms of the virial series and one asymptotic coefficient from self-avoiding walks. The numerical differences between (42), (43) and (44) are quite small, but we feel that (42) makes proper use of all the numerical information available. If more terms of the virial series or the asymptotic series should become available, formula (41) can easily be used to incorporate them. The major fault of formula (42) is that it does not have the correct analytic behaviour at $z = 0$ since it gives rise to a convergent rather than a divergent series in z; but we feel that this is a minor point.

7. Deviations from scaling—correction terms

The scaling formula of the previous section is strictly valid only for large N and small w, and a study of table 2 shows that in the neighbourhood of $w = 1$ the term $D(w)$ shows significant deviations from scaling for the different lattices. It is of interest to examine the nature of these deviations, and if we assume that formula (30) is valid for all r we can write

$$\alpha^2(N, w) = \psi(z) + N^{-1/2}\psi_1(z) + N^{-1}\psi_2(z) + \ldots. \tag{45}$$

The terms other than $\psi(z)$ will now be lattice dependent; they can be evaluated without difficulty for small z from the virial series.

For large z in order to comply with equation (31) (which does not scale exactly from lattice to lattice) it is clear that $\psi_1(z)$ must have a dominant term of order $z^{7/5}$, $\psi_2(z)$ of order $z^{12/5}$ and so on; the contributions of all these dominant terms sum up to give C_0. Current data on asymptotic behaviour of self-avoiding walks can give an order of magnitude estimate of the first correction term $\psi_1(z)$.

Acknowledgments

The authors are grateful to Mr Michael Broida for assisting in programming details and data analyses.

Appendix

The program for the exact enumeration was written in FORTRAN IV and comprised seven routines (the main program and six subroutines) listed below:

1. Main
2. Subroutine LIST
3. Subroutine STEP
4. Subroutine COLLID

5. Subroutine PROPTY
6. Subroutine CHECK
7. Subroutine RESULT

The function of each routine is briefly described below:

1. Main The main program initialises all parameters and calls subroutine LIST.

2. Subroutine LIST This routine defines the step vectors to be used for the enumeration. For the four lattices studied these vectors are as follows.

Diamond lattice
Set 1: $(1, 1, 1)$; $(1, \bar{1}, \bar{1})$; $(\bar{1}, 1, \bar{1})$; $(\bar{1}, \bar{1}, 1)$
Set 2: $(\bar{1}, \bar{1}, \bar{1})$; $(\bar{1}, 1, 1)$; $(1, \bar{1}, 1)$; $(1, 1, \bar{1})$.
The odd steps are chosen from set 1, the even steps from set 2.

Simple cubic lattice
$(1, 0, 0)$; $(\bar{1}, 0, 0)$; $(0, \bar{1}, 0)$; $(0, 1, 0)$; $(0, 0, \bar{1})$; $(0, 0, 1)$

Body-centred cubic lattice
$(1, 1, 1)$; $(1, 1, \bar{1})$; $(1, \bar{1}, 1)$; $(1, \bar{1}, \bar{1})$; $(\bar{1}, 1, 1)$; $(\bar{1}, 1, \bar{1})$; $(\bar{1}, \bar{1}, 1)$; $(\bar{1}, \bar{1}, \bar{1})$

Face-centred cubic lattice
$(0, 1, 1)$; $(0, 1, \bar{1})$; $(0, \bar{1}, \bar{1})$; $(1, 0, 1)$; $(1, 0, \bar{1})$; $(\bar{1}, 0, 1)$; $(\bar{1}, 0, \bar{1})$; $(1, 1, 0)$; $(1, \bar{1}, 0)$; $(\bar{1}, 1, 0)$; $(\bar{1}, \bar{1}, 0)$; $(0, \bar{1}, 1)$

Control returns to the main which calls subroutine STEP.

3. *Subroutine* STEP Adds step vectors, computes present location of walk, calls subroutine COLLID.

4. *Subroutine* COLLID Checks for intersections between newest point and all previous points. If walk has reached desired length calls subroutine PROPTY.

5. *Subroutine* PROPTY Computes configurational properties of individual chains and stores the results for averaging when program finishes. Returns control to colloid which calls subroutine CHECK.

6. *Subroutine* CHECK This routine decides whether or not to continue the enumeration, by checking the number of step vectors used at each step in the walk. It ensures that all permutations are enumerated. If no possibilities are left subroutine RESULT is called, otherwise control is returned to subroutine COLLID, which, if enumeration is complete returns control to MAIN which terminates JOB.

7. *Subroutine* RESULT Computes averages and prints all necessary information.

References

Balian R and Toulouse G 1973 *Phys. Rev. Lett.* **30** 544–6
Barrett A J 1975 *PhD Thesis* University of London
—— 1976 *J. Phys. A: Math. Gen.* **9** L33–7

Domb C 1969 *Adv. Chem. Phys.* **15** 229–59
—— 1971 *Critical Phenomena in Alloys, Magnets and Superconductors* eds R E Mills, E Ascher and R I Jaffee (New York: McGraw-Hill) p 95
—— 1974 *Collective Properties of Physical Systems: Nobel Symposium* vol. 24 (Stockholm: Nobel Foundation, New York: Academic Press) pp 49–53
Domb C and Barrett A J 1976 *Polymer* **17** 179–84
Domb C, Barrett A J and Lax M 1973 *J. Phys. A: Math., Nucl. Gen.* **6** L82–7
Domb C and Green M S (eds) 1974 *Phase Transitions and Critical Phenomena* vol. 3 (London, New York: Academic Press) especially chaps 6 and 7
Domb C and Hioe F T 1969 *J. Chem. Phys.* **51** 1915–28
Domb C and Joyce G J 1972 *J. Phys. C: Solid St. Phys.* **5** 956–75
Edwards S F 1975 *J. Phys. A: Math. Gen.* **8** 1171–7
Fisher M E 1973 *Phys. Rev. Lett.* **30** 679–81
—— 1974 *Rev. Mod. Phys.* **46** 597–616
de Gennes P 1972 *Phys. Lett.* **38A** 339–40
Griffiths R B 1970 *Phys. Rev. Lett.* **24** pp 1479–82
Kadanoff L P 1971 *Critical Phenomena: International School of Physics 'Enrico Fermi'* vol. 51 ed. M S Green (New York: Academic Press) p 103
Oono Y 1975 *J. Phys. Soc. Japan* **39** 25–9
Smith N C and Fleming R J 1975 *J. Phys. A: Math. Gen.* **8** 938–58
Windwer S 1965 *J. Chem. Phys.* **43** 115–8
Yamakawa H 1971 *Modern Theory of Polymer Solutions* (New York: Harper and Row)