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LETTER TO THE EDITOR

Self-avoiding walks and real polymer chains

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Abstract. The model of Domb and Joyce enables a continuous transition to be effected between a random and self-avoiding walk on a lattice. By combining a virial expansion with exact enumerations for this model, it has been possible to derive numerical estimates of the expansion factor $\alpha^2 = \langle R_N^2 \rangle / N$ for different values of N and w (the excluded volume parameter) for different three-dimensional lattices. The results have been used to test the two-parameter approximation, and the closed form expressions of Flory, Flory and Fisk, and Alexandrowicz and Kurata.

The model of a self-avoiding walk (SAW) on a lattice has been widely used as a convenient representation of a polymer molecule in which the excluded volume is taken into account in a realistic manner. Using methods analogous to those which have been successful for the Ising model, a number of important statistical and geometrical properties of SAW's have been conjectured; these include the total number of walks of N steps, the number of ring closures, the mean square end-to-end length, the mean square radius of gyration, the probability distribution of end-to-end length, and the correlation between pairs of points on the walk. (For a general review see Domb 1969.) Recently the new renormalization group technique has been applied by de Gennes (1972) to SAW's and the results obtained for the exponents fit in very well with the above conjectures. Following the general expansion scheme of Wilson (1972) for a ferromagnetic model in spin dimension n , de Gennes describes a SAW as a ferromagnetic model in zero dimensions.

However, although the above calculations have been useful in a general way for determining the exponents which characterize the various properties, they have not been able to provide numerical estimates for real polymer chains which are not constrained to a lattice, and in which the magnitude of the excluded volume can vary from a large value down to zero. A more acceptable model is the gaussian chain of N segments joining $(N+1)$ identical beads with complete flexibility at each bead. The beads interact by means of an intermolecular potential which is incorporated into a pseudopotential $\gamma\delta(\mathbf{R}_{ij})$. Here $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$, \mathbf{R}_i and \mathbf{R}_j being the positions in space of the $(i+1)$ th and $(j+1)$ th beads; $\delta(\mathbf{R})$ is the three-dimensional Dirac δ function; and γ is a variable which characterizes the excluded volume.

For this model following the development initiated by Zimm in 1946 a number of terms of a 'virial expansion' have been calculated exactly for the expansion factor due to the excluded volume:

$$\alpha^2 = \frac{\langle R_N^2 \rangle}{\langle R_N^2 \rangle_0} = 1 + A_1 z + A_2 z^2 + A_3 z^3 + \dots \quad (1)$$

where

$$z = -(3/2\pi b^2)^{3/2} \gamma N^{1/2} \quad (2)$$

and b^2 is the mean square length of each segment of the chain (for values of A_1, A_2, A_3 see Yamakawa 1971). This expansion is exact only in the limit $N \rightarrow \infty, \gamma \rightarrow 0, \gamma N^{1/2}$ finite, which we shall refer to as the 'two-parameter function'. Also, with only 3 terms of the series available, its practical range of application is very limited. An alternative approach to this model was provided by Flory in 1949 who obtained a closed form expression for α ,

$$\alpha^5 - \alpha^3 = \frac{3\sqrt{3}}{2} z. \quad (3)$$

Flory's formula does not give the correct expansion (1) for small z and therefore there have been a number of subsequent attempts to modify the formula so as to remedy this defect (see eg Alexandrowicz and Accad 1973). Also Flory's argument is 'mean field' in character (Fisher 1969); surprisingly it yields the correct exponent whereas the same type of approach in the Ising problem yields incorrect exponents (Burley 1972). However, it would be useful if formulae such as (3) could be tested in the same way as the Ising closed-form solutions.

For this purpose we suggest that the generalized model introduced by Domb and Joyce (1972) can be used, since it applies equally to lattice and continuum models. For a lattice walk of N steps an interaction $w\delta_{ij}$ is introduced between every pair of points of any configuration of the walk, i and j being the lattice sites occupied by the i th and j th points of the walk. Thus $w = 0$ corresponds to a random walk, $w = -1$ to a SAW; w plays a similar role to γ in (2). A perturbation series can be developed for finite N of the form

$$\alpha^2(w) = 1 + k_1 w + k_2 w^2 + k_3 w^3 + \dots \quad (4)$$

but the k_r are functions of N whose leading term is of order $N^{r/2}$ (it is not certain whether or not there are $\ln N$ factors for $r > 3$ and this point is currently under investigation; in the present work we shall use only the first three terms). Thus if we take only the leading term of k_r into account we obtain a two-parameter function for this model. Domb and Joyce showed how to calculate the k_r in terms of the Green function for returns to the origin in a random walk on the lattice,

$$R(x) = e(x) + f(x)(1-x)^{1/2} \quad (5)$$

where

$$\begin{aligned} e(x) &= e_0 + e_1(1-x) + e_2(1-x)^2 + \dots \\ f(x) &= f_0 + f_1(1-x) + f_2(1-x)^2 + \dots \end{aligned} \quad (6)$$

$R(x)$ varies from one lattice to another, and can also be chosen appropriately to apply to the gaussian continuum model.

The aim of the present letter is to describe two recent developments which taken together have enabled the closed formulae to be tested. The first (CD and AJB) is the calculation of the coefficients k_1, k_2 and k_3 in (4) as functions of N for a variety of three-dimensional lattices; for each lattice these calculations provide reliable estimates of $\alpha^2(w)$ near $w = 0$. The second (CD and ML) is a series of exact enumerations of $\alpha^2(w)$ for small values of N following the pattern of SAW enumerations. It was found that for $w = -0.5$ to $w = -1.0$ asymptotic estimates could be made for $\alpha^2(w)$ in the same way as for SAW's ($w = -1.0$). One small but important modification to the

extrapolation formulae used by Domb (1963) is the assumption of a Darboux form:

$$\alpha^2(w) = N^{1/5}(A(w) + B(w)/N). \tag{7}$$

Refined analysis has shown that this form provides a good fit to Ising coefficients and SAW's (see eg Domb 1970, Sykes *et al* 1972). The assumption that there is no change in analytic form on passing through $w = -1$ is in accord with the Griffiths (1970) 'smoothness postulate'. Detailed descriptions of the above developments will be given in separate publications.

Having good estimates for a given lattice of $\alpha^2(w)$ near $w = 0$ and from $w = -0.5$ to -1.0 it is an easy matter to interpolate and cover the whole range from $w = 0$ to $w = -1.0$. Typical results for the simple cubic lattice are shown in figure 1. From

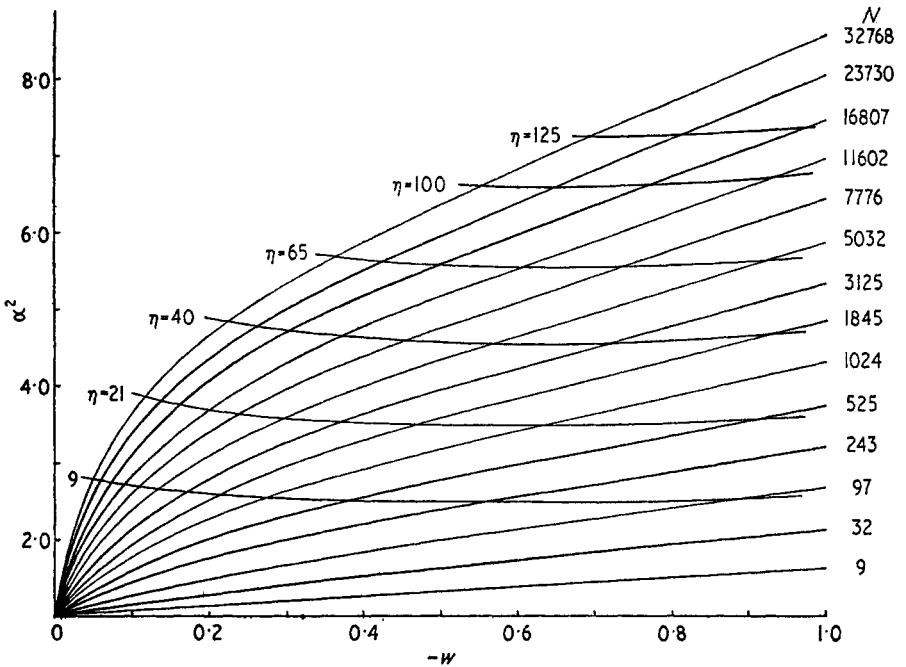


Figure 1. Expansion factor α^2 for a chain on the sc lattice. Lines of constant $\eta (= -wN^{1/2})$ would be horizontal in the two-parameter approximation.

these curves it is possible to assess the validity for this lattice of the approximation which replaces the true α^2 by the two-parameter function. If the approximation were correct the lines of constant $\eta (= -wN^{1/2})$ would be horizontal. In fact it will be seen that the deviations from horizontal are relatively small.

We may observe that the simple formula (7) is no longer valid near $w = 0$ and enumerations for far higher values of N would be needed in this region to obtain a valid asymptotic estimate. Perhaps this partially resolves the difference between one of the present authors (CD) and P J Flory on the value of N required to achieve asymptotic behaviour (see *Faraday Society Discussion* No 49 1970, p 76).

To make use of the data in figure 1 as a check on formulae like (3) we quote the result (CD and AJB) that in the expansion (4) only a single variable $f_0 w N^{1/2}$ enters in

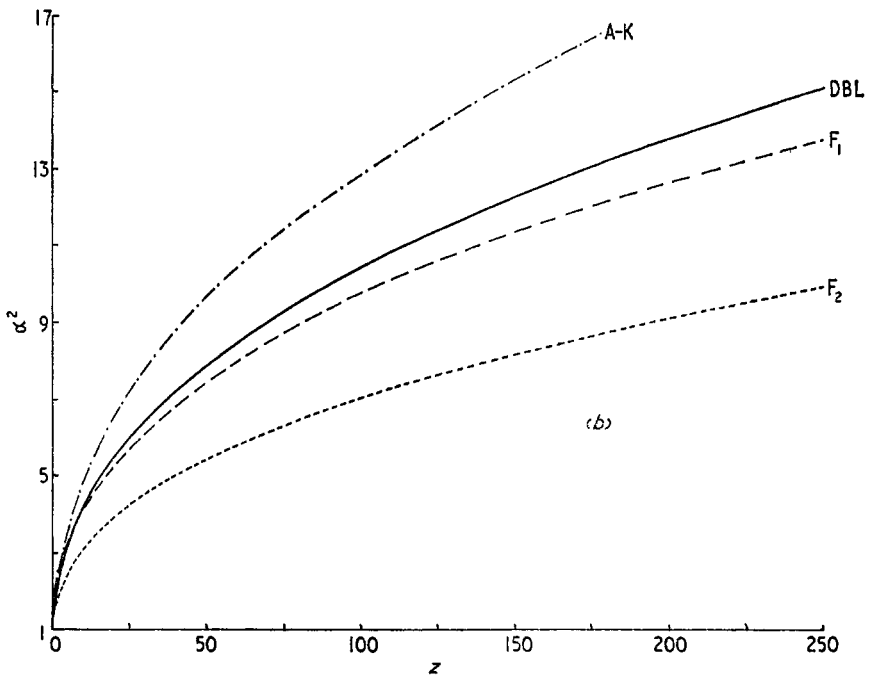
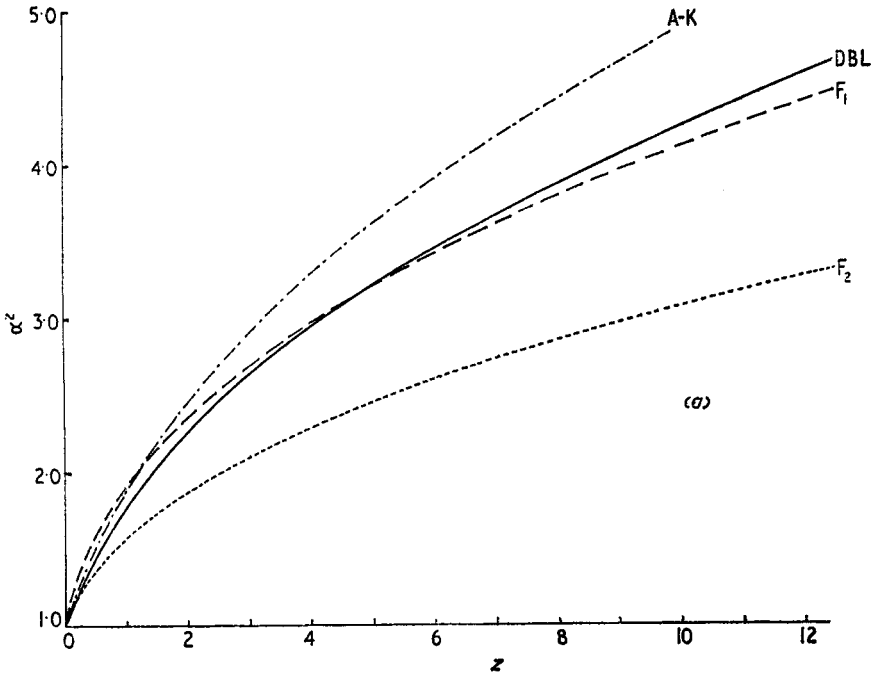


Figure 2. Comparison of the present estimate of the two-parameter function (DBL) with closed-form approximations $F_1 \equiv$ Flory (1949), $F_2 \equiv$ Flory and Fisk (1966), A-K \equiv Alexandrowicz (1968) and Kurata (1968). (a) $z = 0-12$; (b) $z = 0-250$.

the two-parameter function. Thus with the exception of a scale factor f_0 the two-parameter function is the same for all lattices and for the gaussian continuum model. The two-parameter function can thus be regarded as a 'long range' property independent of lattice structure. Not surprisingly f_0 is inversely proportional to the volume of a unit cell of the lattice. By comparing data for different lattices and extracting the term independent of lattice structure it should be possible to obtain a reliable estimate of the two-parameter function. However, even a single lattice is capable of providing a preliminary estimate and the simple-cubic lattice data of figure 1 have been used to furnish the estimate of the two-parameter function labelled DBL in figure 2.

Figure 2(a) covers the range of small z (0-12) and figure 2(b) the range of large z (0-250). F_1 corresponds to the original Flory formula (3), F_2 to the modification of Flory and Fisk (1966) which replaced the right-hand side of the equation by $9\sqrt{3z}/14$ so as to make the first term of the expansion (1) more nearly correct. A-K refers to the formula advanced independently by Alexandrowicz (1968) and Kurata (1968)

$$\frac{\alpha^5}{5} + \frac{\alpha^3}{3} - \frac{8}{15} = \frac{4}{3}z. \quad (8)$$

It will be seen that the *original* Flory formula comes closest to our own estimate. The error for small z is rapidly corrected and in the range $3 < z < 10$ the two curves are very close. However, for larger z deviations become more apparent. By contrast although both F_2 and A-K start correctly they rapidly deviate in opposite directions from our estimate and this deviation increases as z increases.

Finally to obtain an independent assessment of our estimate we have compared our predictions with the Monte Carlo enumerations of Alexandrowicz and Accad (1973). These are shown in figure 3, and we can reasonably claim a modest degree of agreement.

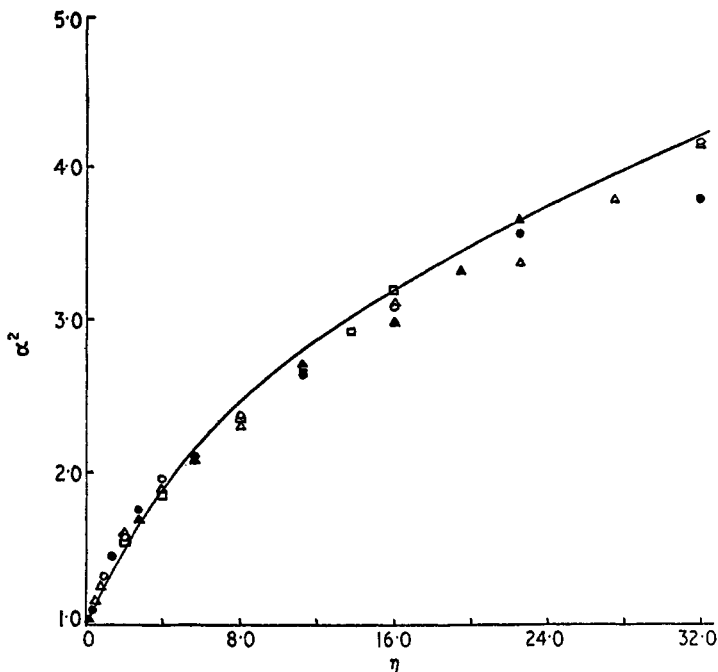


Figure 3. Comparison of the present estimate with Monte Carlo data of Alexandrowicz and Accad (1973). Values of N are: \circ 4096; \bullet 2048; \triangle 1024; \blacktriangle 512; \square 256.

We are grateful to Dr Z Alexandrowicz for making available to us detailed numerical values of his Monte Carlo enumerations. One of us (CD) is indebted to Professor S F Edwards for encouraging and helpful discussion.

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