On the Domb–Joyce Model for Self-Avoiding Walks in the Continuum

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The Domb–Joyce model is reviewed in the light of new results of Muthukumar and Nickel, and of DesCloizeaux. The importance of correction terms is emphasized and it is suggested that the summation of the two-parameter series for the expansion factor α^2 of a polymer chain provides only part of the description of α^2 for large values of the excluded volume variable z. An appropriate definition of z for continuum walks is suggested and bounds for the binary cluster integral for the freely-jointed chain are calculated.

1. INTRODUCTION

It has been understood since Kuhn's 1934 paper[1] that a polymer is a *statistical* object; the modern notion of a polymer as a *critical* object seems to have clearly emerged in the early 1950s. This is immediately apparent from early articles by Temperley[2] and Fisher and Sykes,[3] for instance, on the relationship between the polymer excluded-volulme problem and the Ising model. Much of the relationship between these two problems had become clear by the late 1960s,[4] before the powerful techniques of field theory and the renormalization group were applied and before DeGennes[5] has clarified the analogy between an excluded-volume

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polymer and a magnetic syustem in 1972. DeGennes' very important article is often cited as the beginning of the understanding of polymers as critical systems. This view is somewhat unjust, since it ignores the considerable and valuable body of work on critical properties of self-avoiding walks, much of it at King's College, London, prior to the development of the renormalization group and the insights it brought.

In the present article, I am primarily concerned with one important development of what might be termed the "King's College school," namely the Domb–Joyce "universal" model of an excluded-volume polymer. This model has had considerable success in describing the configurational properties of real polymers[6,7] and has received wide acceptance from polymer scientists. However, recent developments seem to indicate that the Domb–Joyce model may not be applicable to self-avoiding walks in the continuum. If so, then this is a matter for concern. The model was developed within the framework of random and self-avoiding walks on lattices, and it very precisely describes the dimensions of such walks.[8] But if our understanding of a polymer as a critical object is at all correct, then predictions of the model cannot depend on the presence or absence of lattice structure, provided that the chains are sufficiently long.

To say that the predictions of the model do not depend on the details of the fine structure does not mean that the fine structure can be entirely ignored. What it means, rather, is that variables must be defined, or units chosen, so that all details of fine structure are contained within these variables or units. The universal character of any model depends on an appropriate definition of the variables.

The most important predictions of the Domb–Joyce model, as with other models, are expressed in terms of the familiar *two-parameter* variable z, where z has the form

$$z = \text{const} \times N^{1/2}v$$

Here N is the number of bonds (steps) in the chain and v is a measure of the strength of the excluded-volume condition. The precise definition of the constant requires some care, since it is this constant which incorporates all the lattice or model dependence. I shall show that the apparent difficulties with the Domb–Joyce model may be explained in terms of corrections to the two-parameter approximation.

2. THE TWO-PARAMETER MODEL

The expansion factor of a self-avoiding walk is defined to be

$$\alpha^2 = \langle R_N^2 \rangle / N$$

where $\langle R_N^2 \rangle$ is the mean square end-to-end length of the walk. It is by now very well known[9] that for sufficiently long walks and a sufficiently weak excluded-volume interaction, α^2 may be expressed as a perturbation series in z, that is,

$$\alpha^2 = 1 + \tfrac{4}{3}z + \cdots$$

On the basis of the series and a famous formula due to Flory,[10] it has long been postulated that for sufficiently long chains, α^2 is a function of z only, even for large z. This is the *two-parameter* hypothesis. The hypothesis received strong support from the work of Domb,[11] who showed that for self-avoiding walks on a variety of lattices, the mean square end-to-end length behaves as

$$\alpha^2 \sim A z^{2\nu - 1}, \qquad z \to \infty$$

with $2\nu \approx 1.2$ and $A \approx 1.64$. All lattice dependence is included in the variable z. This asymptotic behavior has been confirmed by more recent work based on the renormalization group and field-theoretic techniques. A number of these calculations have provided the most precise estimate available of the exponent, although the exact value of the prefactor remains a matter for discussion.

The Domb–Joyce model[12-15] is based upon weighted overlap walks on lattices. A statistical weight $1 - w$ is assigned to each intersection of a random lattice walk with itself; the appropriate definition of z for the model is

$$z = (3/2\pi)^{3/2} N^{1/2} \beta w$$

The passage from a random to a self-avoiding walk is achieved by varying w from 0 to 1. Here β represents the volume per lattice site, and this is *fixed*, regardless of the value of w.

It is now possible to perform a rigorous, convergent, expansion of α^2 in powers of w, for any finite N:

$$\alpha^2(w) = 1 + k_1 w + k_2 w^2 + \cdots$$

where

$$k_r = a_0 N^{r/2} + a_1 N^{(r-1)/2} + a_2 N^{(r-2)/2} + \cdots$$

If N is sufficiently large, then only the leading term in each coefficient is retained, and we recover the usual two-parameter series. This series is asymptotic.[16]

Alternatively, we may write α^2 as a series in $N^{1/2}$ whose coefficients are functions of w:

$$\alpha^2(N) = 1 + l_1 N^{1/2} + l_2 N + \cdots$$

where

$$l_r = b_0 w^r + b_1 w^{r+1} + b_2 w^{r+2} + \cdots$$

If w is sufficiently small, then only the leading term in each coefficient is retained, and again we recover the usual two-parameter series. But for a fully self-avoiding walk, that is, for $w = 1$, it is clear that the expansion factor is not defined by the two-parameter series; there are important correction terms which must be taken into account.

The region of large excluded volume is studied by analysis of numerical results for weighted overlap lattice walks[15] for $0.5 \leqslant w \leqslant 1$. The results have been summarized as

$$\alpha^2(z) \sim 1.64 z^{0.2}, \qquad w > 0.5, \qquad N \text{ large} \tag{1}$$

This relationship should be regarded as a good approximation, rather than rigorous. Nonetheless, it appears that a two-parameter principle applies for weighted-overlap walks on lattices.

Correction terms are important in the large excluded-volume regime as well. If c_N represents the number of N-step self-avoiding walks, then it is possible to define a generating function

$$P(x) = \sum_{N=0}^{\infty} c_N x^N$$

which is known to have the dominant singular behavior

$$P(x) \sim (1 - \mu x)^{-g-1} \tag{2}$$

The coefficient of x^N in (2) is proportional to

$$\frac{N^g}{\Gamma(g+1)} \left[1 + \frac{A}{N} + \frac{B}{N^2} + \cdots \right]$$

The terms in $[\cdots]$ are Darboux corrections,[17] and must be accounted for if numerical data are to be correctly analyzed. In addition, there are corrections due to subdominant singularities, and it is now generally agreed that the most important of these is proportional to $N^{-\Delta}$, where Δ is close to $1/2$.

The Domb–Joyce model thus extends the two-parameter series to lattices and provides for the inclusion of large-excluded-volume behavior as exemplified by self-avoiding walks. It also provides for the computation of corrections to the two-parameter predictions. The "universal" hypothesis is that, for sufficiently long chains, the expansion factor may be described by a single function of z which provides for "crossover" from the random to the self-avoiding walk. The two-parameter components of the Domb–Joyce construction are summarized in the Domb–Barrett interpolation formula,[13] which is designed to have the correct small-z expansion as well as the appropriate large-z behavior:

$$\alpha^2 = (1 + 6.67z + 12.57z^2)^{0.2} \tag{3}$$

This equation is not complete unless a recipe for the calculation of z is given. For lattice walks, this is a trivial task; β is the volume per lattice site. For self-avoiding walks in the continuum it is a more subtle problem.[18] First of all, we must define what we mean by such a walk. For the purposes of this article, we take a self-avoiding walk in the continuum to be the bond set of a freely-jointed chain. We expect that the characteristics of these walks will depend on the bead diameter. If, for any bead diameter, we imagine a *random network* such that a self-avoiding walk on the network is indistinguishable from a walk in space, then we may equate the excluded volume of the latter with the volume per site of the former.

A convenient way of expressing the factor β for any walk (which might or might not be on a lattice) is as

$$\beta = KV_0$$

where V_0 represents the volume of a bead of the chain. For a lattice walk to nearest neighbors, the bead diameter is always equal to the lattice spacing. Thus, for a simple cubic lattice, K represents the ratio of the volume of a unit cube to that of a sphere of diameter 1, that is, $K = 6/\pi = 1.91$. The value of K for a continuum walk is less easily computed; however, it is a simple matter to establish bounds for the special case of a bead whose diameter is equal to the bond length. The binary cluster integral for a dilute hard sphere gas in $8V_0$. This represents the volume of a sphere with radius equal to the bead diameter, which is excluded to the center of any other bead. If the probability of this excluding volume being shared with another bead is vanishingly small, it may all be associated with a simple bead. However, if the diameter of the bead is equal to the bond length (see Fig. 1), then there must be a minimum of two adjacent beads to share the excluding volume. As only (approximately) half of each of these beads is contained within the volume, the excluded volume
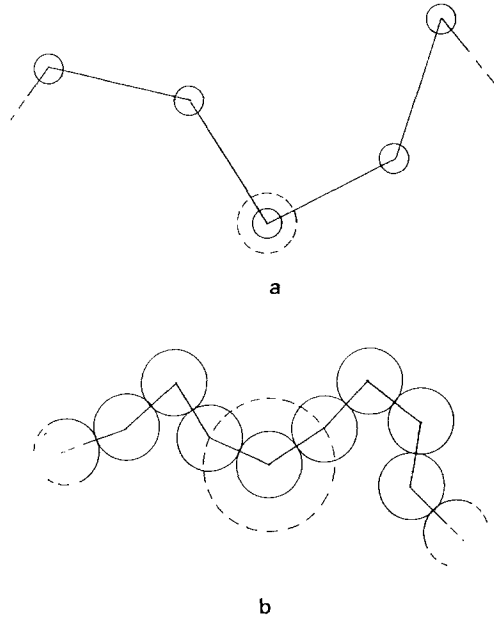
Fig. 1. (a) Binary cluster integral for a freely-joined chain with small excluded volume. (b) Approximate binary cluster integral for a freely-jointed chain with large excluded volume.

which may be associated with the bead under consideration cannot be greater than

$$\frac{8V_0}{1 + 2 \times 0.406} = 4.414 V_0$$

In order to compute a lower bound for K, assume that the random network is as dense as possible and that the vertices represent the sphere centers of a random, close-packed, hard-sphere fluid. The density of such a fluid is known[19] to be 0.637. Since K is the reciprocal of this value, we have

$$1.57 < K < 4.414$$

The two-parameter perturbation series has recently been extended to six terms by Muthukumar and Nickel,[20,21] who have summed the series to obtain an asymptotic expression for the expansion factor. DesCloizeaux et al.[22] have obtained a similar result using a direct renormalization method:

$$\alpha^2 \sim 1.53 z^{0.354} (1 + 0.12 z^{-0.93} + \cdots) \tag{4}$$

The perturbation series may be combined with the large-excluded-volume behavior in an approximate interpolation formula as was done for the Domb–Barrett equation:

$$\alpha^2 = (1 + 7.524z + 11.06z^2)^{0.1772} \tag{5}$$

It is important to remember that these calculations are within the two-parameter framework. The correction term in (4) arises from the subdominant singularity in the summation of the two-parameter series. The other corrections discussed above have not been included.

As with Eq. (3), Eq. (5) requires a definition for z. The correct choice is that commonly used for continuum chains[9]:

$$z = (3/2\pi)^{3/2} N^{1/2} \beta \tag{6}$$

where β is the binary cluster integral. For a freely-jointed chain with small beads, the appropriate value is that of a dilute hard sphere gas, i.e., $8V_0$. One would not, however, expect this value of β to be appropriate for a freely-jointed chain with large excluded volume, since under these circumstances the binary cluster integral should be reduced due to sharing as discussed in the previous section.

The Muthukumar–Nickel result, which is undoubtedly a correct summation of the two-parameter series, predicts

$$\alpha^2 \sim 1 - .53z^{0.354} \tag{7}$$

which is distinctly not in agreement with the Domb–Barrett prediction (1); any attempt to improve the value of the exponent in (1) will tend to exacerbate the disagreement in the prefactors. It is nonetheless important to refine the Domb–Barrett equation in the light of the most recent information. This project, which is underway and will be reported more fully elsewhere, involves a careful analysis of the available data on self-avoiding and weighted-overlap walks using the now precisely known value of the exponent, as well as the new information about corrections. However, a preliminary and crude assessment suggests that (1) should be replaced by

$$\alpha^2 \sim 1.75z^{0.354} \tag{8}$$

It is emphasized that the value of 1.75 is *approximate*, but it is clear that there is a major disagreement between (7) and (8). I suggest that the disgreement is due to the correction terms which are not included in the Muthukumar–Nickel calculation.

The very fact that the amplitude determined for self-avoiding walks on lattices (1) differs significantly from that obtained by summing the two-

parameter series indicates strongly that correction terms become very important in the large-excluded-volume regime, at least for lattice walks. It may be that, to some extent, the reduction in z is offset by the corrections to the two-parameter expression which become important as we move from the small-excluded-volume regime to the large-excluded-volume regime.

We note that the distinction between (3) and an amended equation is not likely to be significant for the molecular weights used presently in experiment.

3. CONCLUSIONS

The recent extension of the two-parameter series and the summation of that series is a wonderful achievement, which must be seen as a significant advance in the understanding of polymer excluded volume. It was initially somewhat distressing to see that the result is in clear disagreement with the well-established universal formula based on the Domb–Joyce model. The inevitable conclusion is that the Muthukumar–Nickel equation (5) does not work for lattices. Why not? The most likely answer is to be found in consideration of the lattice data on which the asymptotic expression (1) is based. The numerical evidence suggests that a two-parameter principle applies, but the results are mildly lattice dependent and the computed amplitude is different from that predicted by summation of the two-parameter series. I suggest that this difference is due to the presence of important correction terms which are known to exist and which are known to be model dependent. It would be interesting to apply the Borel summation of Muthukumar and Nickel or the direct renormalization of DesCloizeaux to the series formed by the leading corrections to the two-parameter series coefficients, to see their significance for the freely-jointed chain and for some lattices.

The definition of z for continuum walks with appreciable excluded volume must still be addressed. I have suggested in this article how such a definition might be made, but much work remains to done. It would be interesting to consider ways, either analytical or numerical, in which the constant K, defined by $\beta = KV_0$, might be determined as a function of the bead diameter of a freely-jointed chain. To my knowledge, there has been no investigation whatsoever of self-avoiding walks on random networks, and this might prove a fruitful area for investigation.

Preliminary analysis of Monte Carlo data for the freely-jointed chain (M. Mansfield, private communication) indicates that correction terms which should be important for a freely-jointed chain do not appear to be so if z is defined as for a system of isolated hard spheres. This suggests that, for such chains, the effect of corrections is largely offset by the reduction in

z which takes place as the bead diameter increases with respect to the bond length. If we assume on the basis of the Mansfield results that (5) describes the dimensions of freely-jointed chains, then we find $K = 3.8$ for the special case of bead diameter equal to the bond length. This means that a given bead must share its excluding volume with the equivalent of approximately three other beads. This question is under further study, and the results will also be reported in the course.

The question of whether the Domb–Barrett formula is more or less appropriate than the Muthukumar–Nickel formula is a difficult matter because z cannot be directly determined from experiment. In many instances, z is determined by *inverting* a relation such as (3). Under these circumstances, experimental measurement of α^2 as a function of z is a robust procedure to say the least, and unless extreme care is taken, *either* interpolating function will produce satisfactory agreement. A more practical approach is to measure quantities such as the penetration function Ψ as a function of the expansion factor of the radius of gyration α_S^2. Formulas for such ratios, based on the Domb–Joyce model, have been proposed.[23] However, it must be borne in mind that the Domb–Joyce definition of z differs from that used by Muthukumar and Nickel only by a multiplicative factor, which can be expected to cancel in dimensionless ratios such as Ψ for large z. Moreover, both the Domb–Barrett and Muthukumar–Nickel equations yield identical results for small z. It seems probable, therefore, that the choice of equation may remain a philosophical question, or even a matter of personal preference as far as a particular experimenter is concerned. Nevertheless, I would suggest that a formula based on the Domb–Joyce approach incorporates corrections not found in the summation of the two-parameter series, and is therefore better designed to give correct and consistent results over the entire range of z.

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