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Numerical investigation of closure approximations in the selfavoiding walk problem

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Abstract. The hierarchy of equations relating the successive density functions for self-avoiding walks on a lattice are solved numerically using two closure approximations and the results are compared with the exact enumeration results of Domb.

1. Introduction

The conformational properties of polymers with excluded volume have been extensively studied by numerical and analytical methods. An approach which has been used by many workers is to approximate the properties of the polymer molecule by the properties of a selfavoiding walk on a lattice or in the continuum. Although this represents a considerable simplification of the original problem, the long range correlation is retained and this correlation makes the mathematical treatment extremely complex.

Since the selfconsistent field approach of Edwards (1965) there has been a renewed interest in the problem and a number of related treatments have appeared in the literature (Reiss 1967, Torrens 1968, Yamakawa 1968, Yeh and Isihara 1969, Whittington 1970, Yamakawa 1971 and Freed 1971). For both the lattice and continuum models a sequence of coupled equations can be derived relating the density functions of successive orders (Whittington 1970, Yamakawa 1971 and Freed 1971) and these equations are reminiscent of the Kirkwood–Born–Green hierarchy derived for this problem by Naghizadeh (1968).

The importance of such hierarchies of equations is that they can be combined with a closure approximation which supplies a second relationship between a density function of a certain order and the density functions of lower order. The equations can then be solved to yield approximate information about the low order density functions.

Before attempting to use the hierarchies of equations, coupled with a closure approximation, to investigate a particular model of polymer conformation, it is important to have some quantitative idea of the reliability of the closure approximation. Yamakawa (1971) has examined some closure approximations for the continuum model but chose to solve the resulting equations in the uniform expansion approximation. It is not entirely clear how much of the resulting errors arise from the closure approximation and how much from the mathematical convenience of using the uniform expansion approximation. There are some quite reliable Monte Carlo data (Bruns 1969) on the pearl necklace model of a polymer in the continuum, against which results can be tested.

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However, the enormous quantity of exact enumeration and Monte Carlo data for self-avoiding walks on a variety of lattices suggests that the lattice model is more convenient for evaluating the relative reliabilities of closure approximations.

In this paper we examine two closure approximations in the hierarchies of equations for the square, triangular and cubic lattices. These approximations are discussed physically and the equations are solved numerically (but accurately) for selfavoiding walks up to between 20 and 30 steps. It would be rather easy to push the calculations beyond this stage but this should be sufficient to indicate the adequacy of these closure approximations. Exact values are available up to sixteen and ten steps for the square and cubic lattices and up to nine steps for the triangular lattice (Domb 1963) as well as asymptotic estimates of the dependence of the mean square length on the number of steps in the selfavoiding walk. We compare the values of the mean square lengths, calculated using the closure approximations, with the exact values.

2. The closure approximations

We first briefly restate the equations derived previously for the cubic lattice (Whittington 1970) in a form applicable to any lattice. Let $p(\boldsymbol{r}, n)$ be the probability that the walk reaches point $\boldsymbol{r}$ after n steps and let $p_2(\boldsymbol{r}, n; \boldsymbol{s}, m)$ be the probability that the walk reaches $\boldsymbol{r}$ after n steps and $\boldsymbol{s}$ after m steps. The p and p_2 are related through the equation

$$p(\boldsymbol{r}, n+1) = A\left(\sum_{\boldsymbol{s}} p(\boldsymbol{s}, n)q(\boldsymbol{r}, \boldsymbol{s}) - \sum_{\boldsymbol{s}} \sum_{m=0}^{n-1} p_2(\boldsymbol{s}, n; \boldsymbol{r}, m)q(\boldsymbol{s}, \boldsymbol{r})\right) \tag{1}$$

where $q(\boldsymbol{r}, \boldsymbol{s}) = 1$ if $\boldsymbol{r}$ and $\boldsymbol{s}$ are neighbouring lattice points or zero otherwise, and A is a normalization constant.

Two closure approximations, which attempt to relate p to p_2, have appeared in the literature. The first of these is an independence assumption

$$p_2(\boldsymbol{r}, n; \boldsymbol{s}, m) = p(\boldsymbol{r}, n)p(\boldsymbol{s}, m)$$

and the second is a Markov assumption

$$p_2(\boldsymbol{r}, n; \boldsymbol{s}, m) = p(\boldsymbol{s}, m)p(\boldsymbol{r}-\boldsymbol{s}, n-m) \qquad n > m.$$

The primary purpose of this paper is to explore the adequacy of these approximations in the treatment of selfavoiding walks. It is helpful to consider briefly what these approximations imply physically about the process and to notice that we should not expect either of them to lead to an exact treatment of the problem.

The first approximation implies that reaching $\boldsymbol{r}$ after n steps and $\boldsymbol{s}$ after m steps are independent events and, to this extent, the connectivity of the polymer is being ignored. Reiss (1967) has suggested that use of this closure approximation will completely remove the excluded volume effect and we shall show that, although this is not true, it does indeed underestimate the importance of the excluded volume effects.

The second approximation implies that the behaviour of the first m steps of the walk is independent of the behaviour of the next $(n-m)$ steps. For an unrestricted random walk this closure is exact. However, for a selfavoiding walk we must take account of interactions between these two segments of the walk and, in general

$$p_2(\boldsymbol{r}, n; \boldsymbol{s}, m) < p(\boldsymbol{s}, m)p(\boldsymbol{r}-\boldsymbol{s}, n-m)$$

so that this approximation overestimates the excluded volume effect by making the correction term involving p_2 too large. This conclusion is supported by the numerical results.

3. Numerical solution of the equations

Using the independence approximation, equation (1) reduces to

$$p(\boldsymbol{r}, n+1) = A\left(1 - \sum_{m=0}^{n-1} p(\boldsymbol{r}, m)\right) \sum_{\boldsymbol{s}} p(\boldsymbol{s}, n) q(\boldsymbol{s}, \boldsymbol{r})$$

with the boundary condition $p(\boldsymbol{r}, 0) = \delta(\boldsymbol{r})$. This equation can be conveniently solved using a marching technique.

With the Markov assumption, equation (1) becomes

$$p(\boldsymbol{r}, n+1) = A \sum_{\boldsymbol{s}} p(\boldsymbol{s}, n) q(\boldsymbol{r}, \boldsymbol{s}) - \sum_{m=0}^{n-1} p(\boldsymbol{r}, m) \sum_{\boldsymbol{u}} p(\boldsymbol{u}, n-m) q(\boldsymbol{u}, \boldsymbol{O}). \tag{2}$$

The solution of this equation using a marching technique requires a large quantity of computer store and it is more convenient to use a generating function technique. We give below the details for the cubic lattice, the argument for any other lattice being similar to this. Define

$$G_n(\alpha, \beta, \gamma) = \sum_{x,y,z} p(x, y, z, n) \alpha^x \beta^y \gamma^z.$$

It then follows from equation (2) that:

$$G_{n+1} = A\left(g G_n - 6 \sum_{m=0}^{n-1} G_m p(1, 0, 0, n-m)\right)$$

where $g = \alpha + \alpha^{-1} + \beta + \beta^{-1} + \gamma + \gamma^{-1}$. We can express G_n as a power series in g

$$G_n = \sum_{m=0}^{n} a_{nm} g^m$$

and it is straightforward to show that, for n odd

$$p(1, 0, 0, n) = \sum_{m=0}^{n} a_{nm} \sum_{i,j,k} \frac{n!}{i!(i+1)!(j!)^2(k!)^2}$$

where $2(i+j+k) = n-1$ and $i, j, k \geqslant 0$. For n even, $p(1, 0, 0, n) = 0$.

This gives a simple computational scheme for calculating the generating functions in this approximation. Of course, all the information contained in $p(x, y, z, n)$ is also contained in $G_n(\alpha, \beta, \gamma)$ and, in particular, we can calculate the mean square end-to-end length of the n step walk as

$$\langle r_n^2 \rangle = 3 \frac{\partial}{\partial \alpha}\left(\alpha \frac{\partial G_n}{\partial \alpha}\right)\Bigg|_{\alpha=\beta=\gamma=1}.$$

4. Results and discussion

We have calculated the mean square end-to-end lengths of selfavoiding walks for small n on the square, triangular and cubic lattices using the two closure approximations discussed above. The calculated values are compared with Domb's exact enumeration results in table 1. It is clear that the independence assumption underestimates and the Markov assumption overestimates the excluded volume effect.

Table 1. Mean square lengths calculated using the closure approximations

n	Independence	Markov	Exact
Triangular			
3	3·7925	4·2174	4·2174
4	5·2884	6·4401	6·3495
5	6·8555	9·0290	8·7407
10	15·818	26·307	—
20	38·241	77·367	—
Square			
3	3·9767	4·5556	4·5556
4	5·7034	7·0400	7·0400
5	7·2364	9·8576	9·5634
10	16·858	28·876	26·243
20	40·753	84·997	—
Cubic			
3	3·5263	3·8800	3·8800
4	4·8130	5·5538	5·5538
5	5·9958	7·2897	7·2343
10	12·394	17·434	16·817
20	25·790	42·078	—

If we assume that, for large n, $\langle r_n^2 \rangle \simeq n^\gamma$. We can estimate γ by the linear extrapolants

$$\gamma_n = n\left(\frac{\langle r_{n+1}^2 \rangle}{\langle r_n^2 \rangle} - 1\right)$$

or by $\gamma_n^* = \frac{1}{2}(\gamma_n + \gamma_{n+1})$ to compensate for the odd–even alternation. Values of γ_n or γ_n^* are given in table 2. Except for the cubic lattice with the Markov assumption, the sets of γ_n or γ_n^* values are monotonic in n and we can attempt to estimate the limiting values for large n by extrapolating against $1/n$. For the cubic lattice with the Markov assumption such an extrapolation is not possible and we can only notice that the last few values lie between 1·282 and 1·287. It appears that the limiting value might lie in the range $1{\cdot}284 \pm 0{\cdot}003$. Our final estimates for these extrapolated values are given in table 2. These results are not remarkably close to the extrapolated exact values (1·5 in two dimensions and 1·2 in three dimensions) but they are obtained with computing

times of a few seconds (on an IBM 360/50) instead of many hours as would be required for exact enumeration results. It appears that the Markov assumption is rather better than the independence assumption.

Table 2. Values of γ_n or γ_n^* for each closure approximation

	Triangular, γ_n		Square, γ_n^*		Cubic, γ_n^*	
n	independence	Markov	independence	Markov	independence	Markov
18	1·3093	1·5854	1·3110	1·5878	1·0664	1·2849
19	1·3136	1·5848	1·3139	1·5868	1·0668	1·2834
20	1·3178	1·5841	1·3198	1·5861	1·0687	1·2824
21	1·3216	1·5835	1·3225	1·5852	1·0689	1·2852
22	1·3254	1·5827	1·3276	1·5845		1·2847
23	1·3289	1·5821	1·3303	1·5837		1·2827
24	1·3322	1·5816	1·3348	1·5830		1·2863
25	1·3353	1·5810	1·3373	1·5822		1·2851
26	1·3385	1·5804	1·3412	1·5816		
27	1·3414	1·5800	1·3436	1·5810		
∞	1·425	1·567	1·41	1·566	1·09	1·284
	±0·005	±0·002	±0·01	±0·002	±0·01	±0·003

We have already commented (Whittington 1970) on the relationship between the Markov closure approximation and a generating function technique used by Wall and Whittington (1969). The present results allow us to remark in more detail on this connection. From table 1 we can see that this closure approximation breaks down at the fifth step for the square and cubic lattices and at the fourth step for the triangular lattice. This is the stage at which theta graphs of the type $(n, 1, 1)_\theta$, $n > 1$, first enter on these lattices so that the Markov closure may not take correct account of graphs of this type. If we conjecture that the Markov approximation breaks down on first encountering graphs of this type, then we would expect it to give exact values up to and including three steps on close packed lattices (triangular, face centred cubic, etc) and up to and including six steps on the hexagonal and tetrahedral lattices.

It is interesting to notice that, in general, γ_n and γ_n^* increase with n with the independence approximation and decrease with n with the Markov approximation. This has the effect that the resulting estimates of γ are rather better than one might expect by looking at the first few values of $\langle r_n^2 \rangle$. It is also interesting that the extrapolated values of γ for each approximation are almost the same for the triangular and square lattices so that these approximations, although giving different values of γ at least give values of γ which are almost independent of the lattice and depend only on dimensionality.

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