Asymptotic behaviour of the mean square length of neighbour-avoiding walks

1977 J. Phys. A: Math. Gen. 10 1345

(http://iopscience.iop.org/0305-4470/10/8/013)

J. Phys. A: Math. Gen., Vol. 10, No. 8, 1977. Printed in Great Britain. © 1977

Asymptotic behaviour of the mean square length of neighbour-avoiding walks

G Torrie and S G Whittington
Lash Miller Chemical Laboratories, University of Toronto, 80 St George St, Toronto, Canada M5S 1A1

Received 28 February 1977

Abstract. Previous exact enumerations of the numbers and mean square lengths of short, first-neighbour-avoiding walks on the face-centred cubic, body-centred cubic and tetrahedral lattices have been extended to 12, 13 and 21 terms, respectively. Examination of the augmented data suggests an asymptotic expression for the mean square length of the form

$$\langle R_n^2\rangle \sim An^{6/5}+Bn^{\alpha}.$$

For the tetrahedral lattice this conjecture is supported by some new Monte Carlo data.

1. Introduction

The configurational properties of polymer chains in dilute solution are very often modelled by self-avoiding walks on lattices. Since such primitive models evidently represent a very great simplification of the physics of a real polymer, it is important to determine whether their properties are sensitive to minor changes in the Hamiltonian. For example, both exact enumeration (Domb 1963, Martin *et al* 1967, Watts 1974) and Monte Carlo (Wall and Erpenbeck 1959, Gans 1965) studies suggest that the asymptotic behaviour of the mean square end-to-end length of self-avoiding walks is given by

$$\langle R_n^2\rangle_0 \sim n^{\gamma_0} \tag{1}$$

where the exponent $\gamma_0 = 6/5$ for all three-dimensional lattices. This result is also confirmed by analytic approaches to the problem, such as the self-consistent field theory of Edwards (1965) and, more recently, the renormalisation group method as applied to the polymer problem by de Gennes (1972). The situation is less clear, however, for neighbour-avoiding walks in which the excluded-volume constraint is extended to forbid nearest-neighbour contacts as well. Monte Carlo calculations of $\langle R_n^2\rangle$ have tended to suggest that γ, the corresponding exponent for neighbour-avoiding walks, has a value greater than 6/5 which may depend on the lattice in question as well. Thus McCrackin *et al* (1973) propose $\gamma = 1{\cdot}22$ for the simple cubic lattice and Mark and Windwer (1967) suggest $\gamma = 1{\cdot}255$ for the tetrahedral (TET) lattice. Kumbar and Windwer (1971) carried out exact enumerations of neighbour-avoiding walks on the TET and four-choice cubic lattices and concluded that γ was about 1·25. By extending the enumerations on the TET lattice we were able to show (Torrie and Whittington 1975, to be referred to as I) that this estimate was much too high, but conventional extrapolation procedures nevertheless suggested a value of γ greater than 1·20.

On the other hand, there are strong theoretical arguments for expecting that the mean square length exponent will not depend on the details of the excluded-volume constraint. We have already commented in I on a proof by Watson (1970) of a correspondence between self-avoiding walks on a lattice and neighbour-avoiding walks on the covering lattice; in the same paper Watson refers to some unpublished exact enumerations by Hioe of neighbour-avoiding walks on the simple cubic and face-centred cubic (FCC) lattices as indicating $\gamma = 6/5$. More generally, the close analogies between the statistical mechanics of polymers and of magnetic spin systems suggest that the renormalisation group methods so successful in describing the critical behaviour of the latter ought to apply as well to the polymer problem. In particular, the exponents such as γ, characterising the critical (i.e. infinite length) behaviour of polymers ought to depend only on such general features as dimensionality, and not on the lattice or the detailed nature of the interactions (McKenzie 1976). However, as Domb (1974) has pointed out, for any particular problem the numerical data, necessarily restricted to finite n, may not clearly exhibit the anticipated asymptotic behaviour. Recently, Rapaport (1976) has obtained some exact enumeration data on the FCC lattice which suggest such convergence problems do in fact exist for neighbour-avoiding walks. In varying the excluded-volume condition smoothly from the self-avoiding to the neighbour-avoiding case he observed increasing curvature in conventional ratio estimate plots of γ_n against n^{-1}, and concluded the extrapolations did not converge well enough to rule out the possibility $\gamma = 1{\cdot}20$. This is a particularly significant result since convergence might be expected to be rapid on this close-packed lattice (Sykes *et al* 1972).

These considerations have prompted us to re-examine the numerical data on three lattices to see if the behaviour of the mean square length might be described by

$$\langle R_n^2 \rangle \sim An^{6/5} + Bn^{\alpha}, \qquad \alpha < 6/5 \tag{2}$$

in which the dominant singularity does in fact have an exponent corresponding to $\gamma = 6/5$, though this might not be readily apparent for finite n because of the slowly decaying effect of a confluent singularity. The analysis of the exact enumeration data is described in the following section where we also report some new enumerations extending the earlier results. The asymptotic formula for $\langle R_n^2 \rangle$ deduced in § 2 is then compared in § 3 with Monte Carlo data for longer walks on the TET lattice and in § 4 we summarise our conclusions regarding the asymptotic behaviour of the mean square length based on consideration of both types of numerical results.

2. Exact enumerations and analysis

We have carried our earlier enumerations (I) of the numbers, C_n, and mean square lengths, $\langle R_n^2 \rangle$, of neighbour-avoiding walks on the body-centred cubic (BCC) and TET lattices a further one ($n = 13$) and two ($n = 20, 21$) terms, respectively. Also, we have extended Rapaport's data on the FCC lattice an additional three terms to $n = 12$ for the completely neighbour-avoiding case only. The computer program used is a slightly improved version of that described in I to which we refer the reader for computational details. The new terms are

$$\text{BCC} \qquad C_{13}^2 = 6\,612\,947\,048 \qquad \langle R_{13}^2 \rangle = 103{\cdot}19441$$

TET	$C_{20} = 1\,379\,279\,724$	$\langle R_{20}^2\rangle = 177{\cdot}41870$
	$C_{21} = 3\,807\,507\,996$	$\langle R_{21}^2\rangle = 189{\cdot}07815$
FCC	$C_{10} = 315\,466\,884$	$\langle R_{10}^2\rangle = 54{\cdot}99869$
	$C_{11} = 2\,068\,604\,028$	$\langle R_{11}^2\rangle = 62{\cdot}28771$
	$C_{12} = 13\,549\,151\,244$	$\langle R_{12}^2\rangle = 69{\cdot}73303.$

(We have used a metric in which $R_1^2 = 3$ for the BCC and TET cases and $R_1^2 = 2$ for the FCC lattice.)

If the divergence of $\langle R_n^2\rangle$ can be described by a single exponent

$$\langle R_n^2\rangle \sim A'n^{\gamma} \tag{3}$$

then we can form successive estimates of γ by the usual ratio methods:

$$\gamma_n = n\left(\frac{\langle R_{n+1}^2\rangle}{\langle R_n^2\rangle} - 1\right). \tag{4}$$

For the loose-packed lattices, much of the odd–even alternation in estimates such as (4) can be removed by taking the mean of successive pairs of γ_n's:

$$\gamma_n^* = \tfrac{1}{2}(\gamma_n + \gamma_{n+1}) \tag{5}$$

and the limiting value of γ is then estimated by successive linear extrapolants of pairs of γ_n^*'s:

$$\gamma_n^{(1)} = (n+1)\gamma_{n+1}^* - n\gamma_n^*. \tag{6a}$$

For the close-packed FCC case we would not expect odd–even alternation to be a problem so that we may form instead the extrapolants

$$\gamma_n^{(1)} = (n+1)\gamma_{n+1} - n\gamma_n. \tag{6b}$$

The values of γ_n^* (γ_n for the FCC case) and $\gamma_n^{(1)}$ for the three lattices are shown in table 1. In all three cases the estimates of γ converge much more slowly than for the self-avoiding walk case; the odd–even alternation in $\gamma_n^{(1)}$ for the FCC lattice is quite uncharacteristic of similar estimates for self-avoiding walks on the same lattice. The new data presented here and the slightly different extrapolations used do not alter the conclusions reached in I: the data show some curvature and, although a value of γ as low as 6/5 cannot be convincingly demonstrated, the earlier estimate of Kumbar and Windwer (1971) of $\gamma = 1{\cdot}255$ for the TET lattice based on a shorter series can be safely ruled out. This latter point is important because it is this value of γ which appears to give the best fit to Monte Carlo data for much longer walks (see § 3, also Mark and Windwer 1967). This suggests that, for the range of n covered by the Monte Carlo and exact enumeration studies, the simple form (3) for $\langle R_n^2\rangle$ is inadequate and we are led, therefore, to the inclusion of a subdominant singularity as in (2). We have investigated this possibility for each lattice by assuming a series of values for the second exponent α and calculating for each the estimates of B/A for successive values of n according to

$$D_n \equiv (B/A)_n = (R_n^* - 1)/[(n+j)^{\alpha-6/5} - R_n^* n^{\alpha-6/5}] \tag{7}$$

where

$$R_n^* = \frac{\langle R_{n+j}^2\rangle n^{6/5}}{\langle R_n^2\rangle (n+j)^{6/5}}$$

Table 1. Estimates γ_n^*, γ_n and $\gamma_n^{(l)}$ (equations (5), (6)) of γ assuming no confluent singularity.

	Tetrahedral lattice		BCC lattice		FCC lattice	
n	γ_n^*	$\gamma_n^{(l)}$	γ_n^*	$\gamma_n^{(l)}$	γ_n	$\gamma_n^{(l)}$
4	1·50074	1·30168	1·48106	1·33701	1·47377	1·23242
5	1·46093	1·36846	1·45225	1·32973	1·42550	1·25072
6	1·44552	1·10502	1·43183	1·21658	1·39637	1·21934
7	1·39687	1·27610	1·40108	1·24340	1·37108	1·22716
8	1·38178	1·26315	1·38137	1·23602	1·35309	1·21179
9	1·36860	1·27781	1·36522	1·23822	1·33739	1·21659
10	1·35952	1·25573	1·35252	1·21469	1·32531	1·21016
11	1·35008	1·26791	1·33999		1·31484	
12	1·34323	1·23652				
13	1·33503	1·25427				
14	1·32926	1·22015				
15	1·32198	1·24798				
16	1·31736	1·22167				
17	1·31173	1·24412				
18	1·30797	1·21777				
19	1·30324					

with $j = 1$ for the FCC lattice and $j = 2$ for the BCC and TET lattices. The resulting values of D_n are plotted against n for a series of possible exponents α for the TET lattice in figure 1 and, on an expanded scale, for the BCC and FCC lattices in figures 2 and 3, respectively. In all cases as n increases $-D_n$ appears to approach a stable value from below for $\alpha = 0{\cdot}4$–$0{\cdot}6$. The situation is clearest for the TET lattice where data have been obtained for longer walks and strongly suggest the presence of a subdominant singularity with exponent $\alpha = 3/5$. For the BCC and FCC lattices the existence of such a singularity also seems very likely, though the precise value of the exponent is difficult to estimate from the more limited data. A universal value of 3/5 for α does not appear likely since, for this assumed exponent, $-D_n$ for both lattices rises to a maximum and

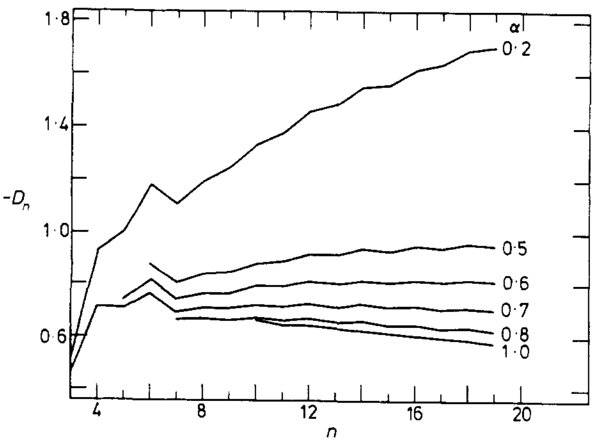

Figure 1. Estimates, D_n, of the relative amplitude of the subdominant singularity for the tetrahedral lattice.

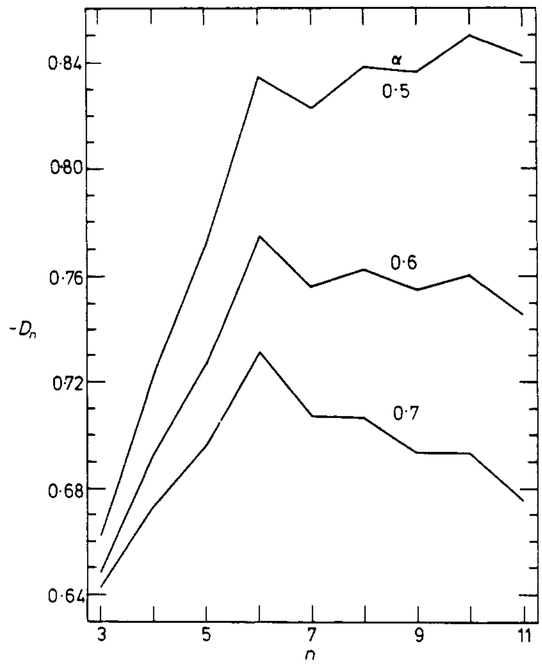

Figure 2. As figure 1 but for the body-centred cubic lattice.

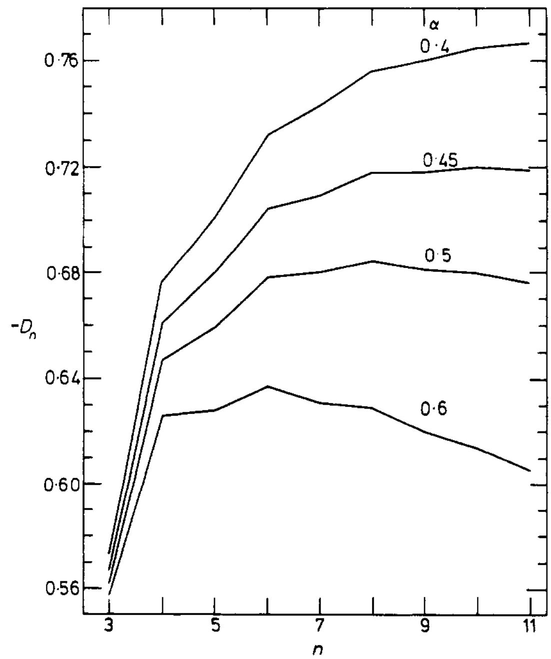

Figure 3. As figure 1 but for the face-centred cubic lattice.

begins to fall, though the possibility cannot be completely ruled out in the absence of knowledge about possible additional singularities in the generating function of $\langle R_n^2 \rangle$. However , it seems more natural to attempt to estimate the most likely value of α (and the relative amplitude B/A) keeping in mind the behaviour of the TET lattice estimates for the same values of n. On this basis the amplitude of the dominant singularity can then be estimated as the limiting value of

$$A_n = \frac{\langle R_n^2 \rangle}{n^{6/5}[1+(B/A)n^{\alpha-6/5}]}. \tag{8}$$

We suggest the following values for the parameters in (2):

$$\begin{array}{llll} \text{FCC} & \alpha = 2/5, & B/A = -0{\cdot}77, & A = 3{\cdot}95 \\ \text{BCC} & \alpha = 1/2, & B/A = -0{\cdot}85, & A = 5{\cdot}53 \\ \text{TET} & \alpha = 3/5, & B/A = -0{\cdot}81, & A = 5{\cdot}63. \end{array} \tag{9}$$

3. Monte Carlo results

To further test (2) as a description of the asymptotic behaviour of the mean square length requires information for longer walks than can be enumerated exactly. Accordingly, we have used the Monte Carlo technique of inversely restricted sampling due to Rosenbluth and Rosenbluth (1955) to generate a sample of 100 000 neighbour-avoiding walks of up to 200 steps on the tetrahedral lattice. To obtain asymptotically unbiased estimates of configurational averages by this method (McCrackin 1972) the contribution of the kth n-step walk must be included with a weight $w_k(n)$ so that $\epsilon_M(\langle R_n^2 \rangle)$, the estimate of $\langle R_n^2 \rangle$ from a sample of M walks, is given by

$$\epsilon_M(\langle R_n^2 \rangle) = \frac{\sum_{k=1}^{M} w_k(n) R_{n,k}^2}{\sum_{k=1}^{M} w_k(n)}. \tag{10}$$

Because $w_k(n)$ can vary between unity and $(q-1)^n$, where q is the coordination number of the lattice, enormous fluctuations are possible for large n in estimates such as (10) which therefore must not be accepted uncritically. Even with the relatively large sample used here (about 50% of the walks survive to the full 200 steps) we are unable to place any useful confidence limits on $\langle R_n^2 \rangle$ for $n > 150$; these values are reported in parentheses in table 2. For $n \leq 150$ we have indicated standard errors for each $\langle R_n^2 \rangle$, obtained by applying the usual statistical formulae to the ten independent estimates of $\langle R_n^2 \rangle$ that result from evaluating (10) over successive samples of 10 000 walks. Also shown for comparison are the earlier Monte Carlo data of Mark and Windwer (1967), generated using the enrichment technique of Wall and Erpenbeck (1959), on the basis of which they suggested

$$\langle R_n^2 \rangle \sim 4{\cdot}15 n^{1{\cdot}255}. \tag{11}$$

The predictions of this formula as well as those of equation (2) with the parameters deduced in the previous section, namely,

$$\langle R_n^2 \rangle \sim 5{\cdot}63(n^{6/5} - 0{\cdot}81 n^{3/5}) \tag{12}$$

Table 2. Comparison of Monte Carlo data and theoretical predictions for $\langle R_n^2 \rangle$ on the tetrahedral lattice.

n	Monte Carlo: Mark and Windwer (1967)	Monte Carlo: This work	Equation (12)	Equation (11)
16	131·9	132·4 ± 0·4	132·8	134·8
32	328·7	323·4 ± 0·9	323·8	321·8
48	548·7	537·2 ± 2·8	539·6	535·4
64	777·5	761·3 ± 4·5	772·5	768·2
80	1032	1001 ± 7	1019	1017
96	1266	1270 ± 17	1276	1278
112	1503	1550 ± 38	1542	1551
128	1781	1754 ± 39	1818	1834
144	2075	2072 ± 58	2101	2126
160	2434	(2426)	2390	2427
176	2712	(2658)	2685	2735
192	3154	(2876)	2987	3151

are shown in table 2 alongside the Monte Carlo data. Equation (12) appears to give distinctly better agreement with the present Monte Carlo data than does the formula of Mark and Windwer. This is confirmed when we form S_ω, the sum of square deviations of the present Monte Carlo data from the two formulae between $n = 10$ and $n = 150$, each point weighted with the reciprocal of its variance:

$$S_\omega \text{ (equation (12))} = 237$$

$$S_\omega \text{ (equation (11))} = 1923.$$

This difference remains clear, if somewhat smaller, for S_μ, the sum of unweighted square deviations:

$$S_\mu \text{ (equation (12))} = 81\,903$$

$$S_\mu \text{ (equation (11))} = 132\,170.$$

Meaningful comparisons of the two formulae with the earlier Monte Carlo data are difficult in the absence of any information about the sample size or variance. However, attempting to fit either set of Monte Carlo data to equation (3), in which the subdominant singularities are assumed to be unimportant, leads to values of the exponent γ of 1·24 or 1·25. As discussed in the preceding section these values are higher than any that can be reconciled with the exact enumeration data. They *are*, however, precisely what *would* be expected to result from such a procedure if $\langle R_n^2 \rangle$ is given by equation (12), because of the slow decay of the second singularity. The small amount of curvature that should, in principle, be present in a plot of $\ln \langle R_n^2 \rangle$ against $\ln n$, in the range $10 \leq n \leq 200$, would be too gradual to be distinguished from the statistical noise of the Monte Carlo results, particularly for the larger values of n where it might otherwise be more apparent. We are led, therefore, to accept equation (12) and, more generally, equation (2) as the satisfactory explanation of the asymptotic behaviour of $\langle R_n^2 \rangle$ that is consistent with both the exact enumeration and Monte Carlo results.

4. Conclusion

We have extended exact enumeration data for the mean square length of neighbour-avoiding walks on three lattices. When considered together with Monte Carlo data for longer walks these data show that the simple relationship $\langle R_n^2\rangle \sim A'n^\gamma$ is inadequate. In view of the strong theoretical arguments in favour of a universal value of 6/5 for the dominant exponent we have postulated that $\langle R_n^2\rangle \sim An^{6/5}+Bn^\alpha$ and have shown that this form is capable of accounting for the trends in both the Monte Carlo and exact enumeration data. The subdominant exponent α appears to have a mild dependence on the lattice varying between about 2/5 for the FCC lattice and 3/5 for the tetrahedral lattice.

Acknowledgments

We wish to thank A J Guttman and C Domb for helpful discussions. Financial support from the National Research Council is gratefully acknowledged.

References

Domb C 1963 *J. Chem. Phys.* **38** 2957–63
—— 1974 *Polymer* **15** 259–62
Edwards S F 1965 *Proc. Phys. Soc.* **85** 613–24
Gans P J 1965 *J. Chem. Phys.* **42** 4159–63
de Gennes P-G 1972 *Phys. Lett.* **38A** 339–40
Kumbar M and Windwer S 1971 *J. Chem. Phys.* **54** 5051–7
McCrackin F L 1972 *J. Res. Natl Bur. Stand.* B **76** 193–200
McCrackin F L, Mazur J and Guttman C M 1973 *Macromolecules* **6** 859–871
McKenzie D S 1976 *Phys. Rep.* **27** 35–88
Mark P and Windwer S 1967 *J. Chem. Phys.* **47** 708–10
Martin J L, Sykes M F and Hioe F T 1967 *J. Chem. Phys.* **46** 3478–81
Rapaport D C 1976 *J. Phys. A: Math. Gen.* **9** 1521–37
Rosenbluth M N and Rosenbluth A W 1955 *J. Chem. Phys.* **23** 356–9
Sykes M F, Gaunt D S, Roberts P D and Wyles J A 1972 *J. Phys A: Gen. Phys.* **5** 640–52
Torrie G and Whittington S G 1975 *J. Phys. A: Math. Gen.* **8** 1178–84
Wall F T and Erpenbeck J J 1959 *J. Chem. Phys.* **30** 634–7
Watson P G 1970 *J. Phys. C: Solid St. Phys.* **3** L28–30
Watts M G 1974 *J. Phys. A: Math. Nucl. Gen.* **7** 489–94