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A generic model for long self-avoiding chain molecules

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Abstract. A generic model, which applies rigorously to finite chains in the absence of inter-segmental interactions, and to subchains of infinite chains with practically arbitrary interactions, furnishes a simple recurrence relation. Self-avoiding walks on the diamond lattice (SAW-D) form the paradigmatic example for polymer science. The generic model as a whole is solved (in terms of parameters) for configurational statistics, asymptotically (large number n of segments) and on stated plausible conjectures, by classical methods, i.e. without postulating a singularity of power law form. The appropriate generalisation of the power law form of scaling theory emerges very simply, e.g. in terms of Kummer's hypergeometric function.

Extensive computations on the SAW-D model lead to two correction terms to the crude scaling form. In this way, some arguments in the literature on asymptotic theories can be settled. Several examples illustrate the danger of mistaking non-asymptotic experimental results for those desired in the asymptotic range. Thus, contrary to his own conclusions and those of Fleming, Bruns's data for freely hinged hard-sphere chains are here reconciled with the 'universal' exponent γ of Le Guillou and Zinn-Justin. For the SAW-D model, subject always to further refinements (which will never produce a final answer), the present experimental estimate for γ is also shown to be about 1.2, in line with conjectural estimates from many forms of modern theory. This conclusion follows, even though we remove some bias which is usually inherent in relevant data analyses. In a number of ways, the successful cancellation by scaling theories of errors in non-asymptotic ranges due to finite-chain effects, etc, is quantitatively demonstrated. The non-singular generic model is briefly compared with the singular 'universal' blob model. A deeper methodological discussion of 'asymptopia' is reserved for a later publication.

1. Introduction

A reformulation of the excluded-volume problem for isolated polymer chains, which is generally regarded as a dominant ingredient of polymer theories, is presented here in the form of a *generic model* for such chains which includes many of the variants usually treated. One can show that a unique solution of the model exists on minimal assumptions, specifically without assuming the existence of a series expansion (see Cowell *et al* 1986). By accepting the cost of such an assumption, we obtain below a convergent asymptotic solution which appropriately generalises that obtained by scaling theory. Ours emerges in the hypergeometric series form, which is highly characteristic for the methodology of uniform expansions in the physics of critical phenomena. In this and other respects, our results allow us to establish clear lines of continuity with

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developments in 19th and 20th century mathematics (see Cowell *et al* 1986), even though the problem is attacked mathematically from an angle which differs from most of the voluminous—and often exciting—physical literature on critical phenomena (for reviews see, e.g., renormalisation group methods: Barber (1977); scaling: de Gennes (1979); simulation: Baumgärtner (1984)).

Much of the novelty and purpose of this work depends on interchanging, relative to standard practice, the following factors:

(i) the order in which two underlying limits, the thermodynamic limit and the configurational one, are generally taken (cf § 2), except implicitly in the 'blob' model (see § 9);

(ii) the roles played by a point and an interval in statistical tests for discriminating between classical and 'modern' theories of criticality by the fit of data. In traditional tests a single point corresponds to the classical exponent value, and an interval to modern values (see equation (12) and Cowell *et al* 1986);

(iii) the relative levels of generality of mathematical formulations of classical and modern models (see § 9 and Cowell *et al* (1982, 1986)).

The three interchanges will be discussed in Cowell *et al* (1986) as part of a deeper discussion, while this paper focuses on the description, solution and data analysis of the generic model proposed. The motivation is outlined below.

1.1. The objective of rehabilitating non-singular classical models

Our aim is to rehabilitate the use of *non-singular* or '*classical*' models which, unlike 'modern' scaling and renormalisation group models, are characterised by not starting from the *postulate* of a singularity in the free energy at a critical point (though a singularity may be obtained *a posteriori* in individual cases). The same aim has been pursued using critical phenomena other than chain configurations under excluded-volume constraints, e.g. phase equilibria of polymer solutions (Gordon and Torkington 1980) and elastic properties of gels (Gordon and Torkington 1981, Gordon 1984). The claims frequently voiced, e.g. by Fisher (1965) and de Gennes (1979), that physical or computer experiments can prove classical models to be qualitatively wrong are here again controverted. These claims have arisen from the vagaries of 'asymptopia', a hybrid of asymptotics and utopia, which continue to surprise both experimentalists and theoreticians (see § 9, concerning equations (39) and (40), and Cowell *et al* (1986)). The simplest examples merely rest on mistaking non-asymptotic results for asymptotic ones (see §§ 6 and 9), or on large differences in the span of asymptotic domains of different statistical parameters of a model (see § 5). The mathematical snare of slow crossover domains is generally expected to simulate, by almost linear plots, attainment of the asymptotic region, because this very snare is implicit (Gordon and Irvine 1980, Gordon and Torkington 1981, Cowell *et al* 1986) in the indispensable methodologies of refining (cf § 5) or perturbing models. Classical models, and the refinement procedures based on uniform convergence which are appropriate for them, score at present in this respect and in other ways, especially in their ease of handling system-specific features (cf Gordon and Torkington 1981, Gordon 1984).

Accordingly, our objectives lie in the application of models to physical or computational experiments. Where we point out weaknesses of present-day scaling and renormalisation group theory, our purpose is not, therefore, to detract from their achievements, especially in advancing computational techniques and in generating asymptotic statistics of *abstract models* in numerical form. Such numerical results, whether integral,

rational or irrational, are obtained by non-rigorous methods which are frequently of great elegance. However, unlike these asymptotic theories, non-singular methods typically develop their refinements by proceeding inwards towards a critical point, and therefore by a series of corrections in free energy of decreasing magnitude (Gordon and Torkington 1980, 1981). Accordingly, such model theories can never be considered qualitatively wrong since their inward-moving process of uniformly convergent model refinement has not been, and could not be, blocked by more refined experiments, nor need it involve an excessive number of adjustable parameters. By contrast, the refinement outwards from the asymptotic region towards 'crossovers' (cf § 9) by modern theories go in increasing changes of free energy.

2. Description of the generic model

The generic model here proposed is defined by a simple stationarity condition:

$$\langle s_i \cdot s_j \rangle = \langle s_{i+k} \cdot s_{j+k} \rangle. \tag{1}$$

In this notation the phase-average scalar product $\langle s_1 \cdot s_n \rangle$ of the initial and final segment vectors s_1 and s_n of the subchain is the familiar correlation function. Equation (1) is valid for all i, j, k of *infinite chains*, on or off a lattice, belonging to models with any physically relevant type of intramolecular interaction behaviour. It is also valid for *finite chains* which are freely intersecting (i.e. devoid of interactions). For illustration we choose in this paper the statistical ensemble of configurations of doubly infinite walks on the diamond lattice, with self-intersections allowed only if the loops formed thereby contain more than r links. This parameter r, the *non-intersection range*, must be sent to infinity to generate the familiar self-avoiding random walk case. For finite r, the ensemble of walks represents those of a finite-order Markov process (Domb and Hioe 1970). The theory is developed below for the configurational statistics of the *finite subchains* in this ensemble and their asymptotic behaviour. If the configurational asymptotics were found not to agree with those of the self-avoiding free chains usually treated (see § 4), the subchain behaviour is the physically relevant one, because we can scatter only from finite objects!

3. Solution of the model

In terms of the difference operator

$$\nabla f(n) = f(n) - f(n-1) \tag{2}$$

the following two equalities are easily derived from equation (1) for chains comprising n segments:

$$\nabla^4[(n+1)^2 R_n^2] = \nabla^2 L_n^2 = 2\langle s_1 \cdot s_n \rangle \tag{3}$$

where by definition the length of the end-to-end vector is

$$L_n^2 = \sum_1^n \sum_1^n \langle s_i \cdot s_j \rangle \tag{4}$$

the steps being labelled sequentially. Equation (3) for the mean-square radius R_n^2 follows similarly via its expression in terms of $\langle s_i \cdot s_j \rangle$.

For freely intersecting random flight chains we have $r = 1$, equations (3) are valid and can be solved to yield classical results such as Flory's (1969) equations (20) and (22).

The following recursion defines the function $f(n, r)$:

$$\langle s_1 \cdot s_n \rangle = x \langle s_1 \cdot s_{n-1} \rangle \exp f(n, r) \qquad (r > 0, n > 1) \tag{5}$$

as a measure of the excluded volume, in whose absence $f(n, r) = 0$. Here x is the neighbour correlation in chains with range 2:

$$x = \langle s_1 \cdot s_2 \rangle \qquad (r = 2) \tag{6}$$

e.g. in free trimers with excluded volume. We restrict our model to $x > 0$, i.e. mean bond angles $> 90°$. (The function $f(n, r)$ is not defined for the highly artificial case of infinite self-avoiding walks restricted to right-angled steps on a square lattice.)

The following two conjectures are not needed subsequently, but introduced merely to show that $f(n, r)$ is almost certainly well behaved. Formal proofs of (7) and (8) for specific classes of submodels do not seem out of reach.

Conjecture 1.

$$\langle s_1 \cdot s_n \rangle \geqslant x \langle s_1 \cdot s_{n-1} \rangle. \tag{7}$$

Conjecture 2.

$$\langle s_1 \cdot s_{n-1} \rangle \geqslant \langle s_1 \cdot s_n \rangle. \tag{8}$$

Equation (7) assumes that the correlation between the end links of a subchain are not increased by freeing one end link from some overlap restrictions. Equation (8) assumes that the correlations do not increase with the length n of the subchain. Equations (7) and (8) are respectively equivalent to (9) and (10) which *bound* $f(n, r)$:

$$1/x \geqslant \exp f(n, r) \tag{9}$$

$$\exp f(n, r) \geqslant 1 \tag{10}$$

for all n, r specified in equation (5). In the same spirit we occasionally adopt the following for specific arguments.

Conjecture 3.

$$f(n, r+1) \geqslant f(n, r) \qquad (\text{for all } r, n) \tag{11}$$

i.e. increasing the range of overlap restrictions does not decrease the correlation between the end links. Finally we adopt

Conjecture 4.

$$\lim_{r \to \infty} f(n, r) = g(n) \qquad \text{and} \qquad \lim_{n \to \infty} g(n) \text{ exists.} \tag{12}$$

This formalises an assumption generally implied. All previous model theories for the asymptotics of the excluded-volume effect would need refinement if (12) were not true. Scaling theories require the limit $g(n) \to -(\ln x)$. We now introduce one important new assumption 1, for convenience first in a strong form 1*a*, to be greatly weakened later to form 1*b* in a later paper (Cowell *et al* 1986).

Assumption 1 (1a, strong form). For all r, the functions $f(n, r)$ can be uniquely expanded in a convergent series of the form

$$f(n, r) = a_0(r) + a_1(r)/n + a_2(r)/n^2 + \ldots \tag{13}$$

(for $r = 1$, all the coefficients a_i vanish).

This assumption suffices to obtain from simpler premises, and very easily (see next paragraph), an asymptotic solution that contains the usual scaling form as a very special case. The *existence* of series (13) for $f(n, r)$ is, of course, unproblematical if n is finite, but the problem is its uniqueness. With increasing n and increasing truncation point at order $n-1$, the coefficients $a_i(r)$ may or may not converge. In Cowell *et al* (1986) we give the minimal restriction on our function space that ensures uniqueness for $a_0(r)$, $r = 2, 3, \ldots$, by its convergence when $n \to \infty$.

Substituting equation (13) iteratively in equation (5) and summing yields

$$\langle s_1 \cdot s_n \rangle \simeq A'(x \exp a_0)^n \exp(a_1 \ln n + a_2/n + \ldots) \tag{14}$$

$$\simeq A'' \exp(-\varepsilon n)/n^{2-\gamma}. \tag{15}$$

The dependence on r of the a_i and of derived parameters:

$$-\varepsilon \equiv a_0 + \ln x \tag{16}$$

$$\gamma \equiv 2 - a_1 \tag{17}$$

has been suppressed, but should be borne in mind. The crudely truncated form of the solution shown in equation (15) is substituted into equation (3) to calculate L_n^2 and R_n^2 by approximating respectively the two or four necessary summations by termwise integrations after expansion of the exponential in series. This leads to solutions given in terms of *Kummer's hypergeometric function*:

$$M(a, b, z) = 1 + az/b + [a(a+1)/b(b+1)]z^2/2! + \ldots + [(a)_n/(b)_n]z^n/n! + \ldots \tag{18a}$$

where b must not be a negative integer, and

$$(a)_n \equiv a(a+1)\ldots(a+n-1). \tag{18b}$$

The solutions are

$$L_n^2 \simeq A_L n + B_L n^\gamma M(\gamma - 1, \gamma + 1, -\varepsilon n)/\gamma(\gamma - 1) \tag{19}$$

$$R_n^2 \simeq A_R n/6 + B_R n^\gamma M(\gamma - 1, \gamma + 3, -\varepsilon n)/\gamma(\gamma - 1)(\gamma + 1)(\gamma + 2). \tag{20}$$

The A are new integration constants and the B are related to A'' in equation (15). The A and B can be compared with experimental data.

We recall the asymptotic form (Abramowitz and Stegun 1970) of the Kummer function:

$$M(a, b, z) \simeq (\Gamma(b)/\Gamma(b-a))(\ -z)^{-a}(1 + O(z^{-1})) \qquad 0 \geqslant \mathrm{Re}(z). \tag{21}$$

Accordingly, from equations (19) and (20), the familiar expansion ratios

$$\alpha_L^2 \equiv L_n^2/n \tag{22}$$

$$\alpha_R^2 \equiv R_n^2/6n \tag{23}$$

both tend, for large n at constant r, to

$$\alpha^2 \simeq \Gamma(\gamma + 1)/(\varepsilon^{\gamma - 1}) \tag{24}$$

i.e. to a finite constant—as in 'classical' model theories—but here with the exception of the case $\varepsilon = 0$.

4. Comparison of finite chains with subchains of infinite chains

Consider a subchain of n_s steps in an infinite freely intersecting ($r = 1$) chain, and increase the excluded-volume interaction range stepwise by raising r in unit steps. It is plausible that when r reaches $r = n_s$, the subchain would have larger dimensions than a free non-intersecting chain of length n_s. This is because, while any conformation available to the subchain is also available to the free chain, some rather compact conformations of the free chain are *not* accessible to the subchain of an infinite chain, namely those that trap the chain ends in positions where continuation of the chain to infinity is impossible. Pursuing the comparison between a free chain and a subchain of an infinite chain of the same length n_s, let $r_{\min}(n_s)$ be the lowest value of $r(n_s)$ for which the dimensions of the subchain exceed those of the free chain. Here the dimensions may be expressed by L_n^2 or R_n^2, which might yield slightly different $r_{\min}$. In either case

$$n_s \geqslant r_{\min}(n_s) \tag{25}$$

and we adopt the following conjecture.

Conjecture 5.

$$r_{\min}(n_s) = \mathrm{O}(n_s). \tag{26}$$

Indeed, the only alternative, ($r_{\min}(n_s) = \mathrm{o}(n_s)$), is quite implausible. It would imply that, for sufficiently large length n_s, the free non-intersecting chain would be less expanded than the subchain (in an infinite chain) of the same length n_s whose Markovian (loop-avoidance) range r was an indefinitely small fraction of its length n_s. Use of conjecture 5 allows the asymptotic laws (19) and (20) to be applied to non-intersecting free finite chains, as distinct from finite subchains of infinite chains with self-intersections restricted to range greater than r. Note that for free non-intersecting chains $r = n$, and the suppressed r dependence of ε and of γ becomes a suppressed n dependence. Only the proportionality constants would change, not necessarily by exactly the same factor for L_n^2 and R_n^2, owing to the rescaling involving $r_{\min}$. Equation (19) becomes

$$L_n^2 \simeq An + Bn^{\gamma} M(\gamma - 1, \gamma + 1, -\varepsilon n) \tag{27}$$

and similarly for R_n^2 (equation (20)).

5. Asymptotics of the finite-chain correction: resolution of historical problems

The truncation in (14) renders (15) approximate, but it becomes exact if ε is allowed to become a function of n. It is generally thought that for self-avoiding walks (SAW) on the diamond lattice, $\gamma > 1$, as is indeed likely, which is here equivalent to $\varepsilon \to 0$ as $n \to \infty$. Monte Carlo studies cannot discriminate between zero and non-zero ε, but at best lead to conjectured bounds, and the same applies to attempts to discriminate

between unity and other values for γ. For purposes of illustration, consider the plausible asymptotic form for ε:

$$\varepsilon \simeq \varepsilon_0 n^{\rho-1} \qquad (0 \leqslant \rho \leqslant 1). \tag{28}$$

Outside this range, ρ does not affect the exponent γ: for $\rho < 0$, $M(a, b, z) \to 1$; for $\rho > 1$, correlations would decay faster than the exponential rate of the self-intersecting chain, which is unlikely. We find, after rearranging terms,

$$\alpha_L^2 \simeq n^{(1-\rho)(\gamma-1)} \tag{29}$$

with the aid of (21). Such an asymptotic contribution by ρ to the exponent would inject a crossover behaviour or very slow continuous variations into the apparent exponent in physical or computation experiments, if they can be extended far enough to enter the range of validity of equation (28).

Two examples of difficulties encountered in previous theories, which are removed in the light of our Kummer function solution, now follow.

The Monte Carlo data (below) suggest that $\varepsilon(n)n$ is a slowly varying function, so that the Kummer function M in equation (27) remains nearly constant over the range $100 > n > 20$. Assuming B and γ to be in their asymptotic ranges, the following behaviour is thereby *simulated* by data:

$$L_n^2 \simeq An + Bn^{\gamma}. \tag{30}$$

The divergence of views between Domb (1963) and Flory and Fisk (1966) may thus be reconciled. Domb obtained reasonable results for γ using n values up to as little as 15, while Flory and Fisk contended that $n \simeq 10^6$ is required in practice for approach to the asymptotic limit. (Here Domb omitted the term An in (30), but included the constant term—arising as an integration constant—which we dropped here for the asymptotic range.) The latter authors were right in that $\varepsilon \to 0$ is required so that the *correlation* decay for the mid-chain be dominated by the power law rather than the exponential form, thus reflecting the long range nature of the excluded-volume effect. But Domb was right in that, as our computer results now show, εn turns out to be nearly constant ($\simeq 3$, as seen in table 5 for ε) for $20 \leqslant r \leqslant 100$, and probably even for a larger range. Thus the usual plot will show a practically constant γ; this may be the correct asymptotic value for γ, e.g. for equation (28), provided $\rho = 0$, but not otherwise. Thus our analysis provides conditions for which two ranges of n lead to consistent exponent values, namely Domb's low range and Flory and Fisk's much higher range, at which the orientational correlations have adequately decayed. However, experiments can render exact values of $\rho > 0$ plausible, but never prove them.

Next, to compare the asymptotics of R_n^2 with those of L_n^2, assume that for both cases $Bn^{\gamma-1} \gg |A|$ in equations (19) and (20). By putting $\varepsilon n \simeq k$, a constant, and approximating $\gamma \simeq 1.2$, so that $[(\gamma+1)(\gamma+2)]^{-1} \simeq 0.142$, these equations yield the result

$$R_n^2 / L_n^2 = 0.142 M(\gamma-1, \gamma+3, -k) / M(\gamma-1, \gamma+1, -k). \tag{31}$$

Previous theories omitted the correction term for finite systems provided by the ratio of Kummer function values in (31), so that the ratio R_n^2 / L_n^2 was predicted to be 0.142. McKenzie (1976), noting that computer experiments gave a value of about 0.157, remarked 'the reason for this disprepancy is not clear'. Again, since we find $\varepsilon n = k \simeq 3$ (table 5), we immediately obtain, via equation (31), $R_n^2 / L_n^2 = 0.154$. Thus our model theory has eliminated the problem, locating it in the second approximation to the finite-system correction, which arises mathematically from the delicate manner in which the asymptotic limit is approached.

6. Application to Brun's Monte Carlo modelling of the excluded volume

Bruns (1977) generated chains by a computer dimerisation technique, with hard-sphere potentials, centred at hinge and endpoints, of diameter λ ($=0.1$, 0.3, 0.5, 1.0) times the link length. For $\lambda = 2$, the model could also be suitably reinterpreted. He fitted his data for L_n^2 and R_n^2 to the power laws an^γ and $a'n^{\gamma'}$ respectively (table 1). His concern was to test the *universality hypothesis*, i.e. that a universal exponent depends only on the dimensionality of space. Since table 1 shows a dependence of the fitted slopes (figure 1) on the strength λ of the excluded-volume effect, Bruns rejected the hypothesis, and Fleming (1979) reached a similar conclusion from different data. The immediate acceptance of the slopes as representing asymptotic exponents of an assumed

Table 1. Bruns's (1977) test for universality using his Monte Carlo data (see text).

λ	a	γ	a'	γ'
0.0	1.000	1.000	0.1667	1.000
0.1	1.089 ± 0.022	1.013 ± 0.004	0.1904 ± 0.0025	1.005 ± 0.003
0.3	0.865 ± 0.003	1.113 ± 0.007	0.1442 ± 0.0032	1.111 ± 0.004
0.5	0.966 ± 0.018	1.174 ± 0.004	0.1586 ± 0.0017	1.169 ± 0.002
1.0	1.603 ± 0.050	1.194 ± 0.006	0.2460 ± 0.0045	1.198 ± 0.003
2.0	4.87 ± 0.16	1.159 ± 0.006	0.6410 ± 0.012	1.189 ± 0.004

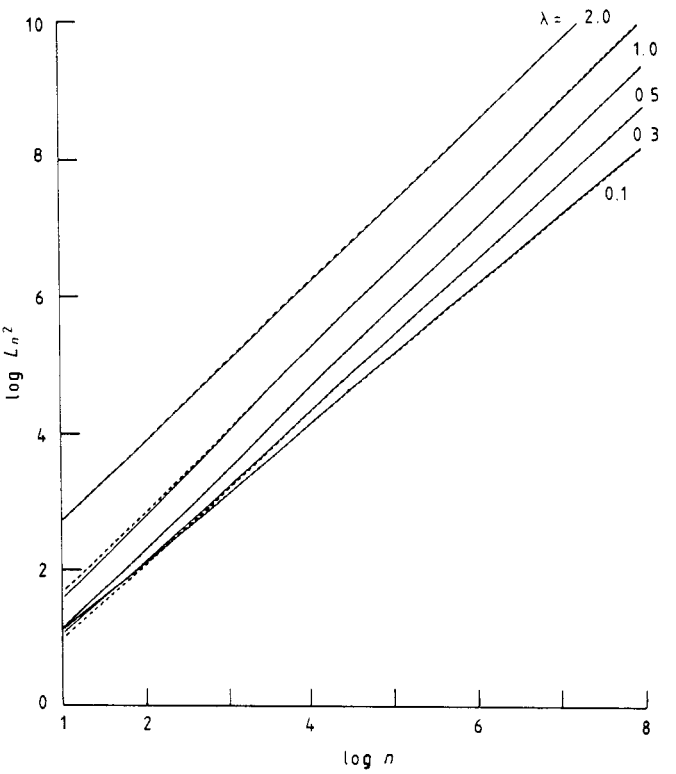

Figure 1. Bruns's (1977) test for universal exponent using his Monte Carlo data (see text).

power law is *always* statistically questionable (Gordon and Torkington 1980, 1981, Gordon 1984), as we again illustrate now. Bruns's model requires at least the more searching asymptotic laws (cf equation (30)):

$$L_n^2 \sim an + bn^{\gamma} \tag{32}$$

$$R_n^2 \sim a'n + b'n^{\gamma'}. \tag{33}$$

Figure 1 shows that fits of equation (32) with fixed $\gamma = 1.176$, the value suggested by scaling theory (Le Guillou and Zinn-Justin 1977), to Bruns's data are virtually indistinguishable from his own fits with variable γ but fixed $a = 0$. Table 2 lists our parameters for equations (32) and (33), optimised using Bruns's data; the values of a and a' are reasonable, as can be made plausible by simple arguments.

Table 2. Optimised parameters fitting (see figure 1) equations (32) and (33) to the data of Bruns (1977).

λ	a	b	a'	b'
0.1	1.064 ± 0.024	0.039 ± 0.009	0.188 ± 0.001	0.003 ± 0.0004
0.3	0.577 ± 0.021	0.392 ± 0.008	0.100 ± 0.005	0.063 ± 0.002
0.5	-0.009 ± 0.063	0.959 ± 0.023	0.007 ± 0.007	0.150 ± 0.003
1.0	-0.639 ± 0.104	2.010 ± 0.038	-0.111 ± 0.010	0.320 ± 0.004
2.0	0.807 ± 0.349	4.084 ± 0.128	-0.223 ± 0.079	0.766 ± 0.029

7. Application to data on light scattering from polystyrene solutions

By examining five fractions of polystyrene in toluene, Utiyama *et al* (1977) reported a *non-linear* concave-downward plot of (R_m^2/m), the ratio of mean-square radius to molecular weight m, against ln m, contrary to previous theoretical expectations. The exponents γ deduced from the variable slope decreased monotonically from 1.25 to 1.1 for $10^6 < m < 16 \times 10^6$. They concluded that the true asymptotic exponent was probably unity. Ross-Murphy (1980) noted that 'this unexpected result, if sustained, has consequences for much of the current work'. The experimental requirements, e.g. corrections for multiple scattering, etc, do make such investigations extremely demanding. The more recent reinvestigation by Miyaki *et al* (1978) of polystyrene fractions up to $m = 57 \times 10^6$ in benzene has reassured scaling theorists. The linear fit of α^2 against $M_w^{0.2}$ (i.e. $\gamma = 1.2$) is much better, though some decline in the exponent at very high molecular weight is also visible in their figure 10 and in two similar plots for other polymer/solvent systems (their figure 11). This merely confirms that some crossover effect at high molecular weights is to be expected, depending not only on multiple scattering effects, but also on solvent quality and hence sensitively on solvent purity, etc, and hence also progressively less reproducible as the molecular weight is raised. These findings support our strategy of cautiously extending the refinement of the non-singular classical model towards the critical point, which we now exemplify using the data of Utiyama *et al* (1977) as an example.

Our model suggests an attempt to fit these data to the asymptotic form

$$\alpha^2 = Bm^{\gamma-1} M(\gamma - 1, \gamma + 3, -\varepsilon m) \tag{34}$$

Table 3. Optimised fit to equation (34) of data by Utiyama *et al* (1977). $B = 2.33$, $\gamma = 1.274$, $\varepsilon = 3.11 \times 10^{-7}$.

$m/10^6$	Experiment	Theoretical
1.29	1.56	1.561
2.58	1.69	1.697
6.12	1.86	1.857
11.1	1.95	1.947
15.9	1.99	1.995

namely equation (20) with $A = 0$ and n rescaled to the molecular weight m, and consequent rescaling of B and ε. Table 3 indicates that the three-parameter fit is clearly within experimental error. Of the three parameters, γ is optimised at 1.274, not very far from estimates produced by singular theories which *assume* an asymptotic power law to exist and to apply in the experimental range. The 'amplitude' B is freely adjusted by optimisation, as is usual. Finally the Kummer function becomes a correction factor multiplying the usual scaling form $Bm^{\gamma-1}$, if $\varepsilon \neq 0$. The optimum value $\varepsilon = 3.11 \times 10^{-7}$ surely makes a minute contribution to the Hamiltonian and reflects effects which are of doubtful reproducibility at present. Its reproducibility could be tested by repeating the experiments of Utiyama *et al* (1977). If ε is proved to be irreproducible, neither scaling nor classical theories can be rejected by light-scattering experiments. If ε proves to be reproducible, its physical meaning in terms of its definition (16) encourages attempts at its theoretical interpretation. Such theories would depend on system-specific parameters (especially through the contribution $\log x$, which is easily calculated from molecular models).

If we optimised the fit of (34) to the data of Miyaki *et al* on different polystyrene samples and a different solvent, ε would be even closer to zero, and its reproducibility accordingly poorer. Since the scattering units are finite chains, a finite ε is expected theoretically, and no appeal to universality considerations can logically invalidate this classical strategy of model refinement.

We now illustrate the same immunity towards invalidation of the proposed strategy by Monte Carlo experiments.

8. Computations

8.1. 1000-step self-avoiding walks using Lawler's (1980) loop deletion method

Five sets of Monte Carlo data were generated for 1000-step four-choice walks on a diamond lattice, subject to non-intersection ranges $r = 20$, 40, 60, 80 and 100. Thus any loop of less than r steps ocurring during the generation of the random walk was deleted, and the walk continued from that point. To this end the point coordinates reached after each step, relative to the origin at the start of the walk, were stored in the virtual memory of the computer, which allowed simple but time consuming checks on loop formation.

It is known that the weighting of all distinct SAW is biased by the loop deletion process. Thus if SAW of fixed length n are collected as they arise from truly random walks of fixed length $n + m$, say, but with each loop being deleted as it occurs (with

overall shortening of the walk from $n+m$ to n), different rotomers among the SAW may be formed with different frequencies instead of being equiprobable. For example, for the square lattice, with $n=3$, $m=5$, the most compact trimer, shaped like the Greek letter pi, is generated in 12 ways, while the most extended (straight line) trimer is generated in 13 ways. However, our procedure, instead of using fixed m, in effect averaged all weights over $0 < m < y$, with $y \gg 1$, which intuitively should reduce this bias.

On completion of the loop-free walk, the orientation vectors of each of its steps were found. Correlations between pairs of these vectors (cf equation (1)) were readily evaluated and scaled to integer values ± 1, ± 3, (the only possible values for a diamond lattice up to a normalisation). The total storage for each average correlation thus required only three integers: (i) the number of correlations added, (ii) their sum and (iii) the normaliser ($=3$). Counters (i) and (ii) directly accumulated results for successive walks which were generated. This integer representation was important in eliminating rounding errors which otherwise attend manipulation of such large amounts of real variable data. Each run of approximately 1 h CPU generated data from between 1100 and 1700 walks, depending on the non-intersection range r, which were stored in a data file. Approximately 60 files (see table 4) were generated for each r value, and then condensed to a single file for each r.

Table 4. Totals for numbers of files and loop-deleted walks generated and upper cut-off values of n employed in optimising data to equations (35)-(37).

Range r	Number of files	Number of walks	Cut-off (35), (36)	(37)
20	59	100 300	39	24
40	58	87 000	64	41
60	61	79 300	89	54
80	57	62 965	90	66
100	60	64 954	90	75

The total number of Monte Carlo walks in our data sample is probably among the largest ever created for examining the excluded-volume problem. Each 1000-step walk may be considered as equivalent to $1000/r$ SAW of r steps. Hence our database is equivalent to between 660 000 100-step and 5×10^6 20-step walks.

Data on the means and standard deviations of the correlations $\langle s_i \cdot s_{k-i} \rangle$ as functions of the subchain length $j = k - i$ were collected, using subchains *with ends i and k falling in the central 800 steps* of each 1000-step walk only, in order to minimise end effects.

8.2. Data analysis

The Monte Carlo data were fitted to each of the forms (cf equation (15)):

$$\langle s_1 \cdot s_n \rangle = A \exp(-\varepsilon n)/n^{2-\gamma} \tag{35}$$

$$\ln(\langle s_1 \cdot s_n \rangle) = \ln(A) - \varepsilon n - (2-\gamma)\ln(n) \tag{36}$$

$$[(\langle s_1 \cdot s_n \rangle / \langle s_1 \cdot s_{n-1} \rangle) + (\langle s_1 \cdot s_{n+1} \rangle / \langle s_1 \cdot s_n \rangle)]/2 = \exp(-\varepsilon)[1-(2-\gamma)/n]. \tag{37}$$

While (35) and (36) contain three parameters, (37) represents an attempt at fitting the data with two. Equation (35) required a Newton-Raphson procedure, whilst linear least-square analyses sufficed for equations (36) and (37), the parameters being found by minimising the sum of squares of residuals. Sums of both weighted and unweighted residuals were formed. The weights were taken as the reciprocal standard deviations of the data over the appropriate sets of approximately 60 files for each r. The range of n values used for the optimisation varied with r as follows: the lower limit of $n = 10$ was chosen as a compromise between including the most accurate data (the standard deviations increased more than linearly with n), and the aim of restricting the use of equations (35)–(37) to their *unknown* range of asymptotic (large n) validity. Domb and Hioe (1969) and Edwards (1965) proposed that SAW of as few as 10 steps are close to exhibiting the asymptotic exponent behaviour, so that our choice was probably reasonable. The upper value was taken as the first data point, on increasing n from 10, at which *either* the standard deviation became greater than or equal to the data point $\langle s_1 \cdot s_n \rangle$ itself, *or* $n = 90$; this was found to ensure that $\langle s_1 \cdot s_n \rangle$ was positive (and its logarithms real for equation (36)). The set of upper n values is shown in table 4, column 4.

The upper limit for n was modified when using equations (37) (or (38) below) by choosing the first data point (on increasing n) for which the error estimate was greater than 0.05. Here some cut-off, inevitably selected arbitrarily, was needed to satisfy the competing demands of a sufficiency of data for optimisation and reasonable accuracy.

Figure 2 shows plots for each of the five r values of the mean correlation against j. The plots are smooth and support conjectures 1 and 2. Figures 2 and 3 show the

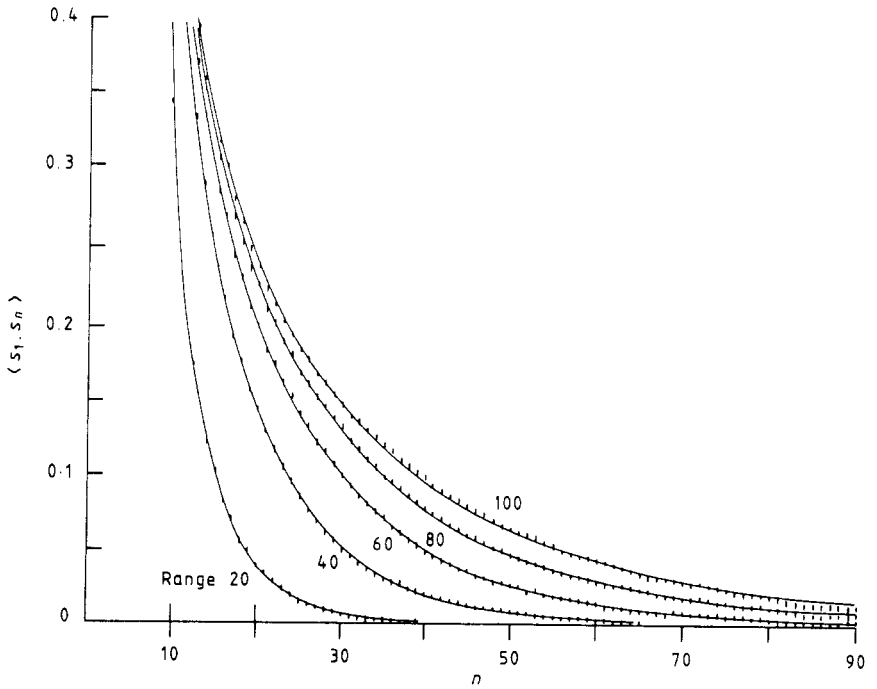

Figure 2. Decay of correlations $\langle s_1 \cdot s_n \rangle$ with length n of walks for five different non-intersection ranges r. Data are represented by error bars and the curves are optimised fits to equation (35).

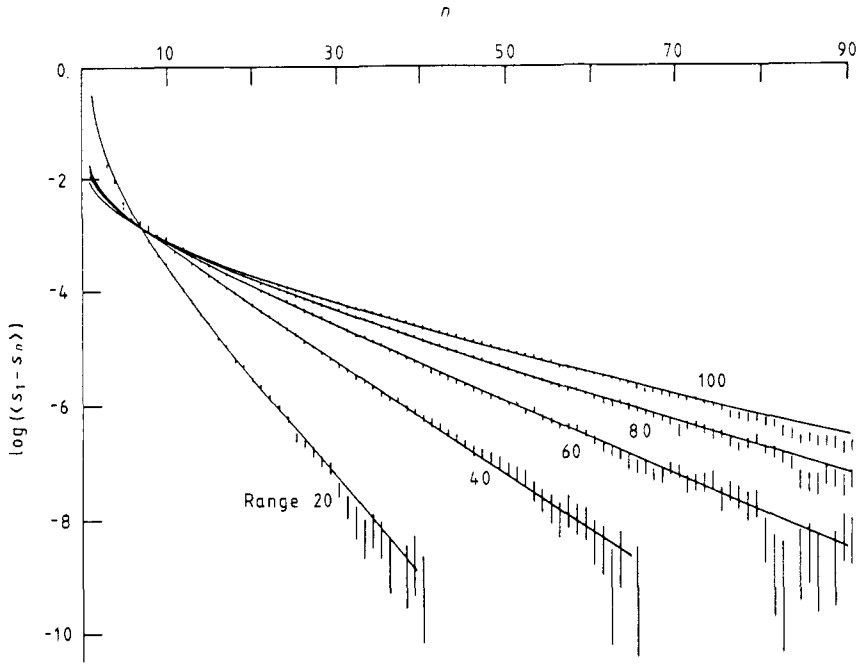

Figure 3. Fitting of logarithmic form of correlation decay (equation (36)) to the data (cf figure 2).

Table 5. Weighted and unweighted fits to equation (35) for the correlation $\langle s_1 \cdot s_n \rangle$, using 1000-step random walks generated with deletion of loops of size less than r steps and subchains of length $n \leqslant$ the cut-off values in table 4.

Weighted fits to function form					
r	20	40	60	80	100
A	0.547 ± 0.131	0.134 ± 0.008	0.136 ± 0.005	0.159 ± 0.004	0.175 ± 0.006
ε	0.156 ± 0.009	0.098 ± 0.002	0.061 ± 0.001	0.041 ± 0.001	0.031 ± 0.001
$2-\gamma$	0.607 ± 0.142	0.091 ± 0.032	0.233 ± 0.020	0.377 ± 0.014	0.458 ± 0.016
εr	3.11 ± 0.18	3.96 ± 0.08	3.65 ± 0.06	3.28 ± 0.08	3.07 ± 0.10
Unweighted fits					
r	20	40	60	80	100
A	0.534 ± 0.128	0.136 ± 0.008	0.133 ± 0.005	0.157 ± 0.004	0.171 ± 0.006
ε	0.156 ± 0.009	0.098 ± 0.002	0.061 ± 0.001	0.041 ± 0.001	0.031 ± 0.001
$2-\gamma$	0.593 ± 0.142	0.099 ± 0.032	0.225 ± 0.019	0.372 ± 0.135	0.448 ± 0.016
εr	3.13 ± 0.19	3.91 ± 0.07	3.68 ± 0.05	3.29 ± 0.05	3.10 ± 0.06

data and optimised weighted fits to equations (35) and (36) respectively. The error bars show small systematic (periodic) deviations. They suggest that fine-scale properties of SAW would be missed by the smoother statistics of chain dimensions, e.g. L_n^2. Tables 5 and 6 reveal that, as r increases, the parameters obtained from the *weighted* fits of equations (35) and (36) appear to converge, whilst the *unweighted* fits show no such convergence. This suggests that the weighted fits offer a better representation. Certainly they are the only fits useful for extrapolation purposes, and we restrict ourselves to the weighted optimisations from now on.

Figure 4 (cf table 7) presents data and fits of the form of equation (37), which again show systematic fluctuations. The fluctuations become stronger for the simplified form:

$$\langle s_1 \cdot s_n\rangle/\langle s_1 \cdot s_{n-1}\rangle = \exp(-\varepsilon)[1-(2-\gamma)/n]. \tag{38}$$

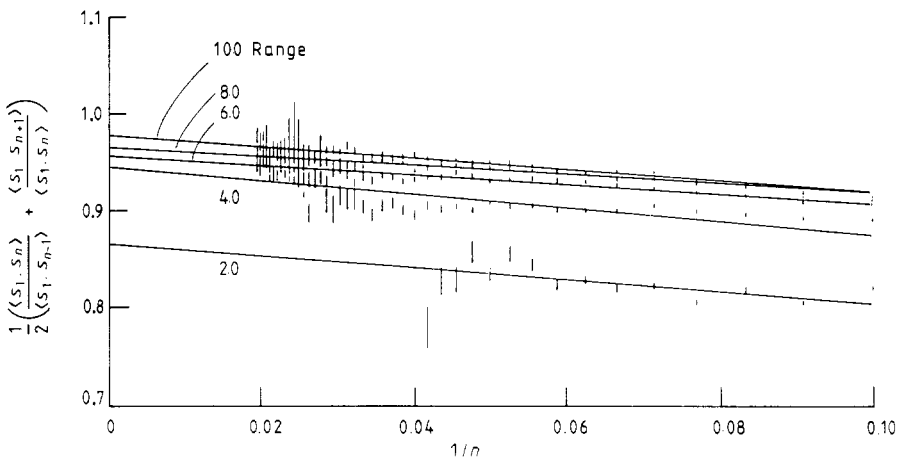

Figure 4. Fitting of ratio form of correlation decay (equation (37)) to the data (cf figure 2); some points are omitted for clarity at large n.

Table 6. Fits similar to those in table 5, but using equation (36).

Weighted fits					
r	20	40	60	80	100
A	0.696 ± 0.342	0.155 ± 0.069	0.133 ± 0.045	0.158 ± 0.033	0.173 ± 0.038
ε	0.146 ± 0.012	0.095 ± 0.002	0.061 ± 0.001	0.041 ± 0.001	0.031 ± 0.001
$2-\gamma$	0.749 ± 0.194	0.160 ± 0.036	0.227 ± 0.022	0.375 ± 0.015	0.456 ± 0.018
εr	2.93 ± 0.24	3.80 ± 0.07	3.66 ± 0.06	3.27 ± 0.05	3.05 ± 0.07
Unweighted fits					
r	20	40	60	80	100
A	0.303 ± 1.068	0.056 ± 0.371	0.063 ± 0.379	0.081 ± 0.179	0.077 ± 0.145
ε	0.181 ± 0.022	0.111 ± 0.005	0.073 ± 0.004	0.050 ± 0.002	0.042 ± 0.001
$2-\gamma$	0.242 ± 0.508	0.299 ± 0.154	0.111 ± 0.151	0.087 ± 0.068	0.106 ± 0.055
εr	3.62 ± 0.44	4.46 ± 0.19	4.37 ± 0.22	4.02 ± 0.13	4.16 ± 0.13

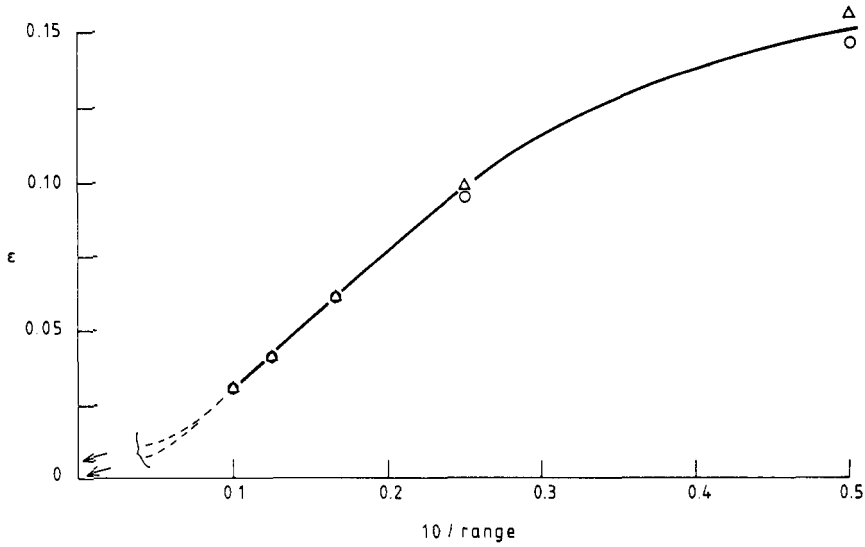

Figure 5. Exponential decay parameter ε deduced from weighted fits to equation (35) (triangles) and equation (36) (circles), plotted against an inverse non-intersection range scale. Lengths of walks = 1000. Interpolation curve drawn by hand; note the uncertain extrapolation to 1/range = 0: lower arrow ($\varepsilon = 0$), scaling theory; upper arrow: ($\varepsilon > 0$): classical theories.

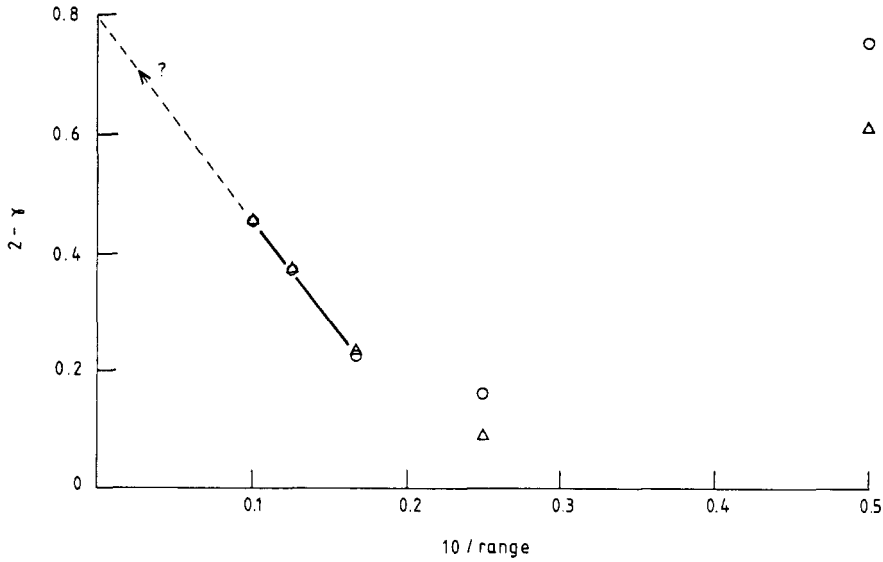

Figure 6. Plot of $2-\gamma$ against 1/non-intersection range r. Equation (35) (triangles) and equation (36) (circles) were used to deduce values of γ. Note that γ goes through a maximum ($2-\gamma$ through a minimum) between $r = 30$ and 50. Long extrapolation agrees with approximate scaling theories and early Flory theory. Markovian theory: $2-\gamma \to 1.0$.

Domb (1963) employed a similar smoothing device when analysing his exact enumeration data for short chains to remove even-odd effects, as did earlier authors cited by him. For much longer chains, our data suggest the existence of additional systematic variations of periods greater than 2.

Figure 5 plots the optimised ε values for equations (35) and (36) against $10/r$. The finiteness of correlations must enforce $\varepsilon(\infty) \geqslant 0$. Therefore, the roughly linear form ($\varepsilon r \simeq$ constant), seem to govern the range $20 < r < 100$, and which probably extends to higher r values, must eventually yield to a concave-upward course for sufficiently large r.

Figures 6 and 7 plot respectively the apparent exponent γ and the pre-exponential 'constant' A against $10/r$. We see that γ approximately extrapolates to 1.2. This supports the conjectural scaling theory (de Gennes 1979) if and only if $\varepsilon(\infty) = 0$. The interesting fact that γ goes through a maximum with increasing r recalls the maxima in γ against length of free chains in experimental work by Utiyama *et al* (1977) (see

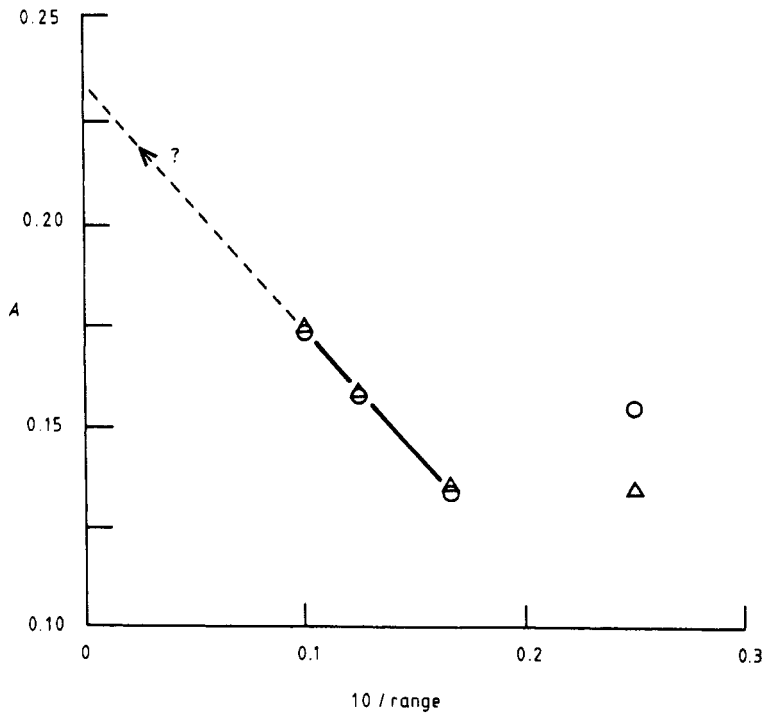

Figure 7. Pre-exponential parameter A from weighted fits of equations (35) (triangles) and (36) (circles). Like $2-\gamma$ (figure 6), A goes through a minimum. Compensations arise because the two parameters are *correlated.* Scaling theory does not predict the extrapolated value.

Table 7. Fits similar to those in tables 5 and 6, but using equation (37).

r	20	40	60	80	100
ε	0.145 ± 0.054	0.057 ± 0.019	0.045 ± 0.009	0.035 ± 0.008	0.023 ± 0.010
$2-\gamma$	0.720 ± 0.088	0.750 ± 0.041	0.530 ± 0.021	0.502 ± 0.019	0.610 ± 0.024
εr	2.90 ± 1.08	2.29 ± 0.78	2.69 ± 0.55	2.79 ± 0.66	2.30 ± 1.03

above) in their theoretical treatment and in other theories (see below). The fact that the pre-exponential 'constant' A goes through a minimum (figure 7) reveals its tendency to compensate the variations of the apparent exponent.

Table 7 presents similar results derived using equation (37). The variations in γ are not now so pronounced, but they fail to give a satisfactory extrapolation. In contrast, ε is well behaved and supports more strongly the suggestion that $\varepsilon r \simeq$ a constant, approximately 2.6.

9. Discussion

The model used in the analysis is the recurrence relation (3), which we extended provisionally by assumption 1*a*, and even by such a crude manoeuvre as guessing an asymptotic form like equation (28). The purpose was to deal, using a minimum number of parameters and in several stages, with what are called crossover phenomena in scaling theory and whose existence is immediately apparent from our data analysis, though it had escaped the notice of several investigators relying on crude scaling because of a 'cancellation of errors' to which we return presently.

These initial crude applications of scaling theories eventually revealed the intrusion of crossovers into experimental ranges also. Several teams recently sought corrections to scaling theory from more extensive Monte Carlo experiments on SAW. Extrapolations from very short walks are presented by Majid *et al* (1983) who generated exactly all SAW on the FCC lattice up to length 12, and Lyklema and Kremer (1985) sampled 6 million two-dimensional SAW (produced with large (99.3%) 'attrition' but without bias) of length 48. They were motivated by the realisation of the 'wide range of (previous) estimates for the correction to scaling exponent' and concluded that previous 'exact enumeration data have been done on series which are too short and consequently cannot give correct results'. Majid *et al* (1984) explored long-chain ensembles of so-called kinetic growth walks generated by Monte Carlo experiments (up to 10 000 walks of length 800 on the cubic lattice). They fitted results to the classical exponent ($\gamma = 1$ in our notation) by assuming a logarithmic correction with an adjustable parameter α, found to be 0.2: $R_n^2 \sim n(\ln n)^\alpha$. Very recently, using an alternative kinetic 'wiggle' method, MacDonald *et al* (1985) could confirm the uncorrected scaling exponent from a log–log plot for chains of lengths in the range 11–251. For a graphical display in their figure 3, they drew a line of slope ($\gamma =$) 1.183, about halfway between their least-square value (1.188, their table 2) and that predicted from series expansion (1.178) by Le Guillou and Zinn-Justin (1977). Even this small reduction of the slope below the least-square value helps to allay the suspicion that the asymptotic regime has not been attained over the range $11 \leqslant n \leqslant 251$, though some curvature towards a lower slope is still suggested at $n \geqslant 200$.

We turn to the *blob theory*, which developed more closely in connection with physical experiments on much longer polymer chains, and abandoned any attempts at the forbidding calculation of the coefficients of the actual scaling series. Instead it invented closed-form correction functions with empirical parameters to the conjectured leading term for the express purpose of coping with the crossovers. Fujita and Norisuye (1981) defined blob theory in terms of two postulates.

The first postulate was exactly equivalent to our equation (1), i.e. to the basic definition of the model we propose here. This means that, implicitly, subchains of infinite chains are used rather than free chains, or one may say that the thermodynamic

limit has been taken before the calculation begins. Weill and des Cloiseaux (1979) make this explicit at the end of their paper: 'It is clear then that the hydrodynamic properties of these subchains are generally sensitive to the same cross-over effects as an isolated chain' (cf § 4).

The second postulate of the blob theory (Fujita and Norisuye 1981, Farnoux *et al* 1978, Weill and des Cloiseaux 1979, François *et al* 1980) (*a*) consists in assuming a power law form for the asymptotic solution, subject to a jump in the value of the exponent γ occurring at some value of n to be determined by data fitting, and (*b*) uses specific empirical equations, with in built discontinuities of the relevant variables.

Domb and Hioe (1969) had used essentially the same approach, but with a smooth empirical power series expansion with adjustable coefficients instead of the specific empirical equations, which thus embody the advance which is found in the blob model. Indeed, Domb and Hioe argued convincingly that the exact form of their expansion was not of interest.

These procedures should be compared with our assumption 1*a* and the parameters ε and ρ which it generates. To decide which procedure is statistically best would involve comparative data fittings for detailed analysis of the relative costs in adjustment of empirical parameters. While scaling theory sets out to refine a fixed conjectured asymptotic form, our approach of moving in towards the critical region does not. We thus avoid the need to guess the stage (as n increases here) when physical data have entered the asymptotic range of a sufficiently refined model. (The acceptable entry point depends on the accuracy of the experiments. Ultimately, as experimental accuracy increases indefinitely, the asymptotic range of a *singular* model can never be entered by physical data.) No statistical test can firm up such a guess as long as empirical closed forms or series are involved. Methodologically, we regard our classical procedure of model building as superior on the grounds of simplicity, of economy in parameters, of the smoothness of the 'crossover' implied (in comparison with blob theory) and of the ease of refinement in terms of molecular information. To give up a diamond lattice framework of molecules with tetrahedral bond angles for blobs would need a testable advantage that stands up to analysis.

de Gennes (1979, p 182) has argued that classical theories, e.g. those of Rouse for chain dynamics, or many SCF theories such as Flory's model of chain conformational statistics (de Gennes 1979, p 46), owe their 'unexpected successes' (p 182) to large cancellation of errors. But the cancellation of 'errors' is precisely the mark of a good approximate (e.g. asymptotic) theory, including both classical and scaling types. Indeed, all our models of criticality in physics are inevitably crude simplifications. Whether the errors compensated by approximate theories are estimated to be large or small will depend on the rate of convergence of the solution in the form it emerges from the modelling methodology. *The rate of convergence of physical data towards presumed asymptotic solutions of critical models is generally not known since, even in cases of simple and analytically soluble models, this rate is generally grossly affected by small perturbations of the model.* By a small perturbation we mean a change in the model Hamiltonian amounting to a negligible fraction of kT per particle (per polymer chain here). Possible sources for such minute effects abound, and they can rarely be assigned unambiguously to any single cause. Gordon and Irvine (1980) illustrated this quantitatively by reference to the virial expansion of the Flory–Huggins model, where a small perturbation leads to wild oscillation without necessarily destroying the convergence. The conjectural modern scaling forms often feature series expansions with huge coefficients, often alternating in sign.

Accordingly, the present calculations should be interpreted as indicating that—over the range available to present computer experiments—scaling theory has the *merit* of cancelling the error due to omitting the decay term $\exp(-\varepsilon n)$ when fitting finite chains, for which $r \leqslant n$ and ε is finite. This decay term must clearly be present in experiments on finite chains. Thus our solution, which is marginally less oversimplified by including the exponential decay, leads to the same extrapolated value $\gamma \simeq 1.2$ as is obtained by the tentative scaling procedures. But at the same time the experiments are seen to leave the *true asymptotic* behaviour of our abstract generic model for SAW on the diamond lattice quite open. Indeed, the analysis shows how successive refinements of the theory might lead us to refine or to reject our current conjectures concerning the asymptotics. The extrapolated value of γ is truly the asymptotic value only if $\varepsilon \to 0$, a result which experiments in principle can never prove, and which in practice they leave rather open (see figure 5). We have pursued this asymptotic problem, which preoccupies theoreticians, in two further stages beyond the crude scaling result.

Firstly, by including one extra term ($\exp(-\varepsilon n)$), we succeeded above in exhibiting some of the cancellation of errors by scaling theory through tracing them to variations—over the experimental non-asymptotic range—between the parameters A and γ. This makes γ go through a maximum ($2-\gamma$ through a minimum) with increasing non-intersection range r, while A goes through a minimum. The compensation effect here revealed throws some light on previous puzzles concerning crossovers. Utiyama *et al* (1977) deduced a maximum in γ with increasing chain length from their analysis of scattering data on polystyrene which we suppressed by introducing the small exponential cut-off (table 3). Fujita and Norisuye (1981) point out that the empirical form of the crossover effect introduced by François *et al* (1980) also involved a maximum in γ as a function of n and that this was in contradiction with all previous theories. Our Monte Carlo data suggest that the situation is further complicated because the apparent exponent and pre-exponential parameters pass simultaneously through a maximum and minimum respectively, before entering what may be their asymptotic ranges for large r.

Secondly, to explore this approach, we ascended to yet one further additional term by expanding and truncating a plausible function $\varepsilon = \varepsilon(n)$ (equation (28)), whereby traditional puzzles were resolved, because different statistical parameters are then seen to converge at very different rates.

The lessons drawn apply equally to the familiar ε expansion of renormalisation group theory. It is quite common for investigators to rely confidently on convergence criteria which are far from compelling. Thus a series might be felt to be asymptotic rather than convergent if the $O(\varepsilon^3)$ estimate is worse than the $O(\varepsilon^2)$ estimate in comparison with some rival estimate—a typical example occurs in the review by Barber (1977, p 55). In most instances, even the existence of the series form postulated by renormalisation group theories is not guaranteed by theories at present available.

The reality of this kind of risk can be illustrated from the very field of the study of SAW by reference to a recent debacle with a happy end. Privman (1983) proposed an elegant SAW model with a specific restriction to spiral form of the walks on the square lattice (see also Blöte and Hilhorst 1984, Joyce 1984, Guttmann and Hirschhorn 1984, Guttmann and Wormald 1984). He made the traditional tentative power law assumption that the RMS radius of such walks would go like

$$R_n \sim n^{0.5\gamma} \tag{39}$$

and by comparing enumeration results for $n \leqslant 40$ with series analysis, he deduced that

$0.5\gamma = 0.62 \pm 0.06$, thus apparently placing this kind of SAW in a different 'universality class' from that of unrestricted SAW, whose exponent on the square lattice is estimated to be $0.5\gamma = 0.75$. Soon, however, Whittington (1984) found an exact asymptotic solution to Privman's model and independently so did Blöte and Hilhorst (1984). The latter authors carried the exact asymptotic analysis a stage further to include logarithmic terms, and showed that, instead of (39),

$$R_N \sim N^{1/2} \ln n. \tag{40}$$

The fractional power law conjecture has thus been disproved and the universality hypothesis could not be applied: the 'crossover' would continue at a decreasing pace and never reach the other shore, at which the classical and not a 'universal' exponent γ beckons.

Characteristically, the exact asymptotic solutions for two-dimensional SAW restricted to spirality were found by combinatorial methods (Blöte and Hilhorst 1984, Whittington 1984). Our simple equation (3) summarises the discrete combinatorial situation underlying the asymptotics of subchains occurring in SAW not restricted beyond self-avoidance. For unrestricted SAW exact asymptotic formulae are clearly very hard to attain, but conjectures 1 and 2 might be amenable to proof in suitable cases, and the discrete way forward can at least be discerned.

The present situation concerning the 'universality' approach may accordingly be simply summarised. The widely studied asymptotics of SAW are intermediate between the case of totally unrestricted random walks, which are *proven to satisfy* the requisite power law assumption with $\gamma = 1$, and Privman's SAW with the additional spirality restriction, *proven not to satisfy* the power law assumption. A large literature is based on the assumption that the *intermediate* case of SAW behaves like unrestricted random walks in obeying some power law asymptotics. The present work is not intended to question this judgement, but rather to rescue promising classical model theories from the unfounded accusation that they have been rejected as qualitatively wrong by experimental tests on asymptotic exponents using finite test tubes or finite computers.

We return again to our point that the true merit of scaling theory (or other approximate theories) lies in the cancellation of errors. The meritorious cancellation of finite-chain effects by scaling theory, illustrated repeatedly and in some detail in this paper (e.g. using Bruns's and McKenzie's works), is also supported by the exact analysis of spiral SAW. Thus Blöte and Hilhorst state: 'We found that the coefficients c_N for $1 \leqslant N \leqslant 40$ are fitted better by Privman's formulae, ..., than by our exact asymptotic expression ...'. In this case, however, too many empirical coefficients (c_N) are involved to make the scaling series a useful tool complementary to the known exact asymptotic functions.

Our next paper will include references to representative experiences of theoreticians and experimentalists, especially in the field of magnetic transitions, whose own analyses of the asymptotic behaviour in experiments on various critical points have (or sometimes might have) led them independently to conclusions similar to those drawn here. In the light of the malaise evident in the literature, and the surprise occasionally expressed by experimentalists at their own results, we shall present a deeper discussion of the mathematical situation underlying the two complementary approaches to criticality: outward from a presumed singularity of conjectured form, and inward towards the critical region. This will show that assumption 1*a* can be greatly weakened for our generic model, so that the series expansion (13) for $f(n, r)$ need not be assumed any

more, while the *a priori* assumption of a singular free energy or of the existence of a fractional power-type scaling series continues to be unnecessary.

Acknowledgments

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