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LETTER TO THE EDITOR

Correction-to-scaling exponents and amplitudes for the correlation length of linear polymers in two dimensions

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Abstract. We consider the scaling behaviour of the radius of gyration for a system of dilute linear polymers. We focus on ρ_N, the mean-square end-to-end distance of an N-step self-avoiding walk for which an additional two terms were recently calculated for the close-packed triangular lattice. Combining several extrapolation methods, we find that a consistent description of the scaling behaviour exists if and only if the correction-to-scaling exponent Δ is roughly half as large as commonly believed. We conclude that all data are consistent with the equation $\rho_N = AN^{2\nu}(1+B/N^{\Delta}+C/N)$ where $\nu = \frac{3}{4}$, $\Delta \cong \frac{2}{3}$, $A \cong 1/\sqrt{2}$, $AB \cong 0.21$ and $C < 10^{-1}$.

The scaling behaviour of polymeric systems has attracted considerable experimental and theoretical attention. For example, the mean-square radius of gyration appears to scale with the polymerisation index N as

$$R_g^2 \sim N^{2\nu}, \tag{1}$$

where the critical exponent ν is thought to depend only on the spatial dimension d. The exponent ν has been measured with an increasing level of accuracy in recent years, and results are in rough accord with the Flory formula (Flory 1953, Fisher 1969)

$$\nu_F(d) = 3/(d+2) \qquad (1 \leqslant d < 4). \tag{2}$$

However, for $d = 3$ there are slight deviations between experimental values and the Flory formula (see e.g. Cotton 1980, de Gennes 1979 and references therein). Hence it is important to understand whether or not these signal a breakdown of the Flory formula.

Very recently Nienhuis (1982) put forth a non-rigorous argument in favour of the exact result

$$\nu(d=2) = \tfrac{3}{4}, \tag{3}$$

for the exponent characterising the mean-square end-to-end distance ρ_N of a self-avoiding walk (SAW), a model of a dilute polymer solution in which repulsion of the chains provides the only steric constraint. Since ρ_N is assumed to scale with N with the same exponent as R_g^2, the Nienhuis result has been interpreted as a dramatic confirmation of the Flory formula (2) in two dimensions. However, the Nienhuis result disagrees with what has been one of the most accurate theoretical methods of calculating ν, namely extrapolation of exact enumerations of ρ_N for finite values of

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N; e.g., for the triangular lattice Grassberger (1982) calculates $\nu(d=2)=0.746\pm0.001$, about 0.5% smaller than the value given by the Flory formula. Other calculations provide a range of estimates of $\nu(d=2)$, ranging from 0.7503 ± 0.0002 (Derrida 1981) to 0.756 ± 0.004 (Redner and Reynolds 1981), 0.753 ± 0.004 (Havlin and Ben-Avraham 1983) and 0.77 (Le Guillou and Zinn-Justin 1980).

It is clearly of importance to resolve this discrepancy for several reasons. Firstly, if $\nu(2)=\frac{3}{4}$, then this is one of the relatively few exact results for critical exponents in polymeric systems. Secondly, if $\nu(2)=\frac{3}{4}$, it is important to understand where the exact enumeration methods have erred, since normally these methods are taken to be the most precise method of estimating critical exponents for systems in which exact results are not known. Thirdly, if $\nu(2)=\frac{3}{4}$, then this opens up an important theoretical question: given that the Flory theory makes certain approximations (des Cloizeaux (1976) and references therein), why should it predict an exact result for the critical exponent ν?

In this letter, we find (figure 1) that estimates of the 'correction-to-scaling' exponent Δ depend quite strongly on the magnitude of the 'scaling' exponent ν where

$$\rho_N = AN^{2\nu}(1+B/N^{\Delta}+C/N+\ldots), \tag{4}$$

and dots are understood to represent higher-order analytic and non-analytic terms.

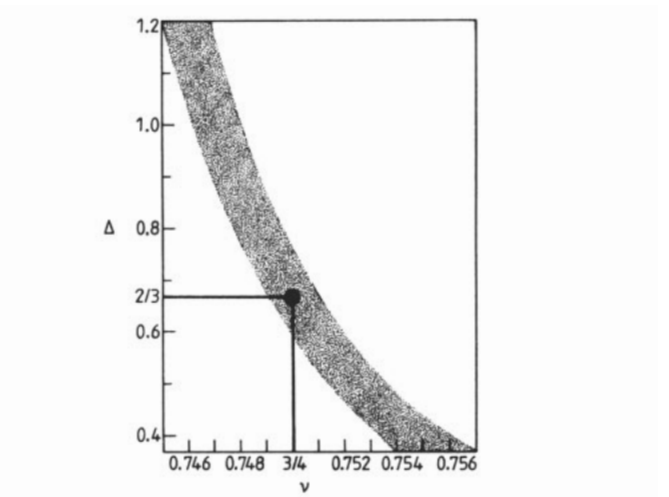

Figure 1. Dependence of the correction-to-scaling exponent Δ on ν_t, the 'trial' value of ν, showing that even a very small change in ν leads to a very large change in Δ. The shaded region indicates the combination of several independent methods of estimating this dependence.

To this end, we have focused attention on the close-packed triangular lattice. Two new terms, ρ_{17} and ρ_{18}, were recently added (Majid *et al* 1983). Here we analyse the extended series by *several* independent methods. We conclude that there is no substantial evidence for excluding the Nienhuis value $\nu=\frac{3}{4}$. More importantly, we find that the reason for the low series value of ν arises from the assumption that $\Delta>1$, when in fact we shall see that the evidence by all methods strongly suggests that $\Delta<1$.

The key problem is to extrapolate the exact results for the first 18 values of ρ_N to obtain estimates for the critical exponents ν and Δ. What we shall call 'Method I' was used by Grassberger (1982) to obtain the estimate $\nu = 0.746 \pm 0.001$ for the leading scaling exponent on the triangular lattice. One defines a sequence of 'effective' exponents $\nu^{\mathrm{I}}_{\mathrm{eff}}(N)$

$$\nu^{\mathrm{I}}_{\mathrm{eff}}(N) = \tfrac{1}{2}N(\rho_{N+1}/\rho_N - 1) = \nu - \Delta B/2N^{\Delta} - C/2N + \nu(2\nu - 1)/2N + \ldots . \tag{5}$$

The second equality follows directly from (4).

The function $\nu^{\mathrm{I}}_{\mathrm{eff}}(N)$ is plotted against $1/N$ as the top curve in figure 2(a). Since $\nu^{\mathrm{I}}_{\mathrm{eff}}(N)$ decreases with N, it is clear why Grassberger concluded that $\nu < 0.75$. However, *if* it should be the case that $\Delta < 1$, then from (5) the limiting slope is $-\infty$, and hence the curve *must* have a minimum. This minimum makes extrapolation of the data of figure 2(a) extremely difficult. The intercepts of successive pairs of points of figure 2(a) are plotted against $1/N$ in figure 2(b). From this plot we conclude there is substantial upward curvature in figure 2(a), and hence $\Delta < 1$.

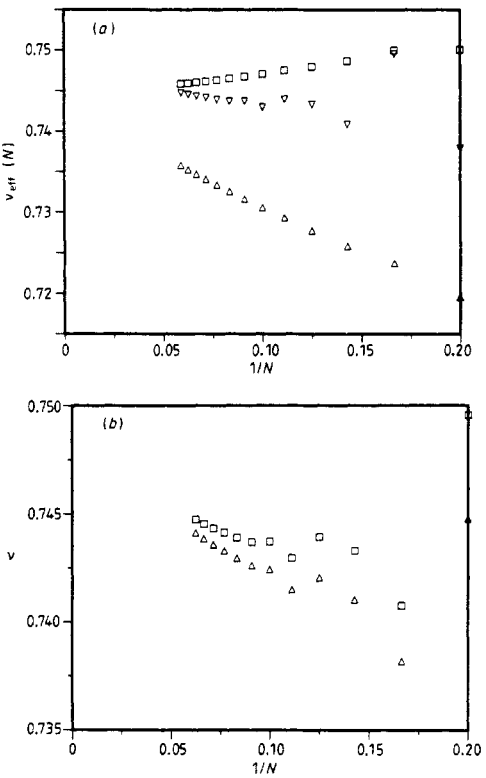

Figure 2. (a) shows the dependence on $1/N$ of the three sequences of successive approximations $\nu_{\mathrm{eff}}(N)$ to the correlation length exponent ν for the triangular lattice SAW problem. □, equation (5); △, equation (6); ▽, equation (7). (b) shows the sequence of intercepts obtained by placing a straight line segment through successive pairs of points in part (a).

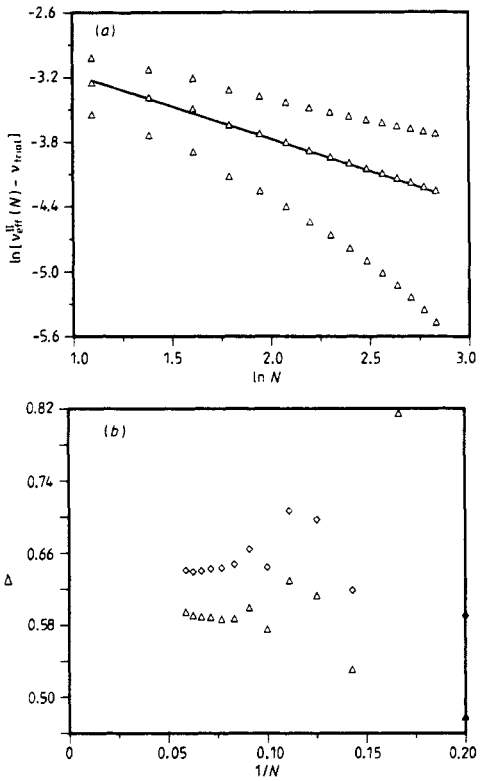

Figure 3. Dependence on ln N of $\ln[\nu^{\mathrm{II}}_{\mathrm{eff}}(N) - \nu_{\mathrm{trial}}]$ using 'method II' (equation (6)), for the choices $\nu_{\mathrm{trial}} = 0.74$, 0.75 and 0.76 (top curve). Since the limiting slope is $-\Delta$, we show in (b) the sequence of slopes obtained by placing a straight line segment through successive pairs of points in (a). Also shown in (b) (◇) are estimates of $\Delta(N)$ obtained by 'method IV' (equation (8)); these should approach correction-to-scaling exponent Δ.

Grassberger assumes that the field theory prediction $\Delta \cong 1.15$ (Le Guillou and Zinn-Justin 1980) was of sufficient accuracy to exclude the possibility $\Delta < 1$. Although no estimate of the error bars or confidence limits has ever been given for the field theory value, it *is* clear from table V of Le Guillou and Zinn-Justin (1980) that for $d = 2$ their 'four-loop' calculation leads to substantial errors in even the leading scaling exponents (for example, $\nu = 0.77$ for the SAW, while $\nu = 1.03$ for the Ising model). Hence it would not be too surprising if the field theory method *also* makes substantial errors in predicting the correction-to-scaling exponents. There is only one independent confirmation of their estimate $\Delta = 1.15$, based on Monte Carlo simulations of SAWS (Havlin and Ben-Avraham 1983) which also predict $\nu = 0.753 \pm 0.004$. Figure 1 shows that if the estimate of ν is in error, then the estimate of Δ is affected strongly.

Method II involves defining a different sequence of effective exponents

$$\nu_{\text{eff}}^{\text{II}}(N) = \tfrac{1}{2}\ln(\rho_N/\rho_{N-1})/\ln[N/(N-1)] = \nu - \Delta B/2N^{\Delta} - C/2N + \ldots, \tag{6}$$

where the second equality follows from (4) and the dots have the same meaning. Note that the positive term $\nu(2\nu-1)/2N$ (which dominates the $N = 10$–20 behaviour) in (5) is not present in (6); hence *no minimum in* $\nu_{\text{eff}}^{\text{II}}(N)$ is expected if B, C have the same sign. Moreover, (6) itself is a 'local' definition, in that it is the 'numerical derivative' of the conventional log–log plot used for calculating critical exponents; in this sense, (6) is analogous to the local fractal dimensionality (Havlin and Ben-Avraham 1982).

Method III (Watts 1974, Zinn-Justin 1979, 1981) eliminates the $1/N$ 'analytic' correction that is present in both (5) and (6),

$$\nu_{\text{eff}}^{\text{III}}(N) = (\rho_{N+1} - \rho_N)(\rho_N - \rho_{N-1})/(\rho_N^2 - \rho_{N+1}\rho_{N-1}) = \nu + O(N^{-\Delta}). \tag{7}$$

Thus, to determine ν, it is absolutely necessary to determine the *sign* of $\Delta - 1$. To this end, we note from (6) that a double logarithmic plot of $[\nu_{\text{eff}}(N) - \nu_{\text{trial}}]$ against N should, for the proper choice of ν_{trial}, become linear with slope given by $-\Delta$. We find that such plots (figure 3) display the greatest degree of linearity with the choice $\nu_{\text{trial}} = 0.750 \pm 0.003$. Moreover, the resulting slopes give *clear* evidence that $\Delta < 1$. To obtain an additional prediction for Δ, we adapted the method of Adler and collaborators (see Adler *et al* (1983) and references therein) to the SAW problem; for a range of reasonable choices of ν_{trial} we again find $\Delta < 1$, provided $B > 0$.

From the above analysis, it is very tempting to assume that the Nienhuis prediction $\nu = \frac{3}{4}$ is correct. Our own estimate is $\nu = 0.7500 \pm 0.0025$. We now use this prediction to calculate 'biased' estimates of the correction-to-scaling exponent Δ. We find that *all* three analysis methods used consistently support the result

$$\Delta = 0.66 \pm 0.07. \tag{8}$$

As an example, to obtain a prediction for Δ based on Method II, we plot against $1/N$ in the lower curve of figure 3(*b*) the successive slopes of the numbers in figure 3(*a*). It is clear that this method predicts Δ quite accurately.

We have found that one of the most reliable methods of estimating Δ is similar to that introduced by Zinn-Justin (1981) and Margolina *et al* (1983). In 'Method IV' for a sequence of trial values ν_t, we form the function

$$F(N, \nu_t) = [(N+1)^{-2\nu_t}\rho_{N+1} - N^{-2\nu_t}\rho_N]/[N^{-2\nu_t}\rho_N - (N-1)^{-2\nu_t}\rho_{N-1}]. \tag{8a}$$

After substituting in (4) with $C \cong 0$, we find the asymptotic behaviour

$$F(N, \nu_t) = [(N+1)^{-\Delta(N)} - N^{-\Delta(N)}]/[N^{-\Delta(N)} - (N-1)^{-\Delta(N)}]. \tag{8b}$$

We calculate $\Delta(N)$ by equating (8*a*) and (8*b*). The top curve of figure 3(*b*) shows $\Delta(N)$ against $1/N$ for the choice $\nu_t = \frac{3}{4}$.

Finally, we return to the general form (4) and attempt to fit the amplitude factors, using the *biased* exponent estimates $\nu = \frac{3}{4}$ and $\Delta = \frac{2}{3}$. We find that

$$A \cong 0.708 \cong 1/\sqrt{2}, \qquad AB \cong 0.21, \qquad C < 10^{-1}, \tag{9}$$

fits all data over the entire range, $N = 10$–18, and also serves to extrapolate our predicted asymptotic behaviour; e.g. we find a minimum in $\nu^{I}_{\text{eff}}(N)$ at $N = 25$, consistent with the curvature apparent in figure 2(*a*).

In summary, we have addressed the problem of estimating the correction-to-scaling exponent Δ as well as the leading scaling exponent ν for the SAW model of a dilute polymer solution. For the $d = 2$ triangular lattice, we find evidence that $\nu = \frac{3}{4}$ (in support of the Nienhuis argument) and that $\Delta = \frac{2}{3}$ (a factor of two smaller than the field theory prediction).

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Note added in proof. After this work was submitted we learned of three other very recent estimates of Δ. (i) Privman (1983) analysed the Grassberger (1982) series for ρ_N on the triangular lattice through order $N = 16$ by a completely new method; he found $\Delta = 0.65 \pm 0.08$ and $A = 0.707 \pm 0.06$, which are consistent with our own estimates in (8) and (9). (ii) Adler (1983) used the chain generating function series for the honeycomb lattice and found $\Delta = 0.95$, but did not analyse the ρ_N series. (iii) Guttmann (1983) added two more terms, c_{17} and c_{18}, to the chain generating function series for the triangular lattice—which, incidentally, agree with our own new results thereby providing an independent check. He found no consistent evidence for $\Delta < 1$. He did not analyse the ρ_N series (and did not calculate the new terms ρ_{17} and ρ_{18}, so that we cannot check our new results for the ρ_N series).

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