Corrections to scaling in two-dimensional polymer statistics

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Writing $\langle R_N^2\rangle = AN^{2\nu}(1+BN^{-\Delta_1}+CN^{-1}+\cdots)$ for the mean square end-to-end length $\langle R_N^2\rangle$ of a self-avoiding polymer chain of N links, we have calculated Δ_1 for the two-dimensional *continuum* case from a *finite* perturbation method based on the ground state of Edwards self-consistent solution which predicts the (exact) $\nu = 3/4$ exponent. This calculation yields $\Delta_1 = 1/2$. A finite-size scaling analysis of data generated for the continuum using a biased sampling Monte Carlo algorithm supports this value, as does a reanalysis of exact data for two-dimensional lattices.

A polymer chain is self-avoiding due to the excluded volume effect between monomer units which causes an expansion or "swelling" of the chain when compared to the free random walk. The central quantity of interest is therefore the mean square end-to-end length $\langle R_N^2\rangle$. This is believed to have the form

$$\langle R_N^2\rangle = AN^{2\nu}(1+BN^{-\Delta_1}+CN^{-1}+\cdots), \tag{1}$$

where N is the number of chain links, ν is the leading scaling exponent, A,B,C are excluded volume-dependent coefficients, and Δ_1 is the leading correction-to-scaling exponent. It is now firmly established[1–4] that in two dimensions (2D) $\nu = 3/4$ is exact. Despite this, there is very little agreement about the value of Δ_1. Nienhuis[1] predicts $\Delta_1 = 3/2$, while Rapaport[5] has argued that there is no need for a correction term other than the analytic correction, i.e., $\Delta_1 = 1$. However, many numerical studies have disagreed with these results, with estimates for Δ_1 of 1.2,[6] 0.84,[7] and 0.65.[3,4,8] These numerical estimates are based on results obtained from self-avoiding walks on 2D lattices. With the exception of a very few authors[9,10] (these studies however were not concerned with the correction to scaling terms), it appears that little work has been done in the continuum. Theoretical results are also in disagreement. Besides Nienhuis's prediction, which relies on a mapping to an exactly solvable solid-on-solid model on the honeycomb lattice, Baker *et al.*[11] predict $\Delta_1 = 1.18$ using renormalization-group arguments, while Saleur[12] predicts $\Delta_1 = 11/16$ by conformal invariance. Interestingly, Saleur also gives evidence for a term $\Delta_1 = 1/2$, but he then rejects this result. Perturbation expansion techniques,[13,14] which start from the free random-walk solution, have also been used to predict $\langle R_N^2\rangle$, but these methods have resulted in series which are divergent in N and v, the excluded volume parameter, and hence a value for Δ_1 cannot be predicted. The obvious confusion in both the numerical and theoretical estimates for Δ_1, lack of corresponding data for the continuum, and the possibility of using a better perturbation expansion to determine $\langle R_N^2\rangle$ form the motivation of this study.

We have used a perturbation method, which unlike previous studies, starts from a ground state that already correctly predicts the *exact* large N behavior in 2D, namely the Edwards self-consistent solution.[15] Although it has been shown[16] that the Edwards solution cannot be the correct form for the self-avoiding random walk end-to-end distribution function,[17] it has mathematically convenient features that enable a perturbation expansion to be performed. We believe its use here underpins the essential physics and that Δ_1 thus obtained may well be exact in 2D. In path-integral representation,[18] the exact distribution function, or Green's function, for the end-to-end distance $\mathbf{R}$ is

$$G(\mathbf{R},L) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[\mathbf{r}]\exp\left[-\frac{1}{l}\int_0^L ds\left(\frac{\partial\,\mathbf{r}(s)}{\partial s}\right)^2 - \frac{v}{l^2}\int_0^L ds\int_s^L ds'\,\delta^2[\mathbf{r}(s)-\mathbf{r}(s')]\right], \tag{2}$$

where L is the total chain length $L = Nl$, l being the step length of one link, and v is the excluded volume. Two problems arise in dealing with this intractable path integral. Firstly, divergences appear in the calculation which must be handled carefully, and secondly, the resulting series expansion is a power series of increasing L and v. This leads to a divergent result unless the value of v is assumed to be very small. This divergent property is the hallmark of modern critical phenomena theory whose resolution was offered by the renormalization-group approach.[19,20] Historically Edwards avoided the divergence problems of such an approach by replacing the point contact potential by a self-consistent field $W(r)$ which in 2D is equal to $v\tilde{p}(r)/l$, where $\tilde{p}(r)$ is the one-particle potential proportional to $r^{-2/3}$.[15,21] Therefore

$$W(r) = \mathscr{C}v^{2/3}r^{-2/3}, \tag{3}$$

where $\mathscr{C} = (\sqrt{3}/4\pi l)^{2/3}$. Thus the Edwards Green's function $G_E(\mathbf{R},L)$ becomes

$$G_E(\mathbf{R},L)=\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[\mathbf{r}]\exp\left[-\frac{1}{l}\int_0^L ds\left(\frac{\partial\mathbf{r}(s)}{\partial s}\right)^2-\int_0^L W(s)ds\right]. \quad (4)$$

Our approach relies on obtaining a better first-order perturbation expansion by starting from the Edwards ground state and then perturbing this with the *difference* between the self-consistent field and the true point contact potential.[22] Thus

$$G(\mathbf{R},L)=\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} D[r]\exp\left[-\frac{1}{l}\int_0^L ds\left(\frac{\partial\mathbf{r}(s)}{\partial s}\right)^2-\int_0^L W(s)ds\right]$$
$$\times\exp\left(\int_0^L W(s)ds-\frac{v}{l^2}\int_0^L ds\int_s^L ds'\,\delta^2[\mathbf{r}(s)-\mathbf{r}(s')]\right), \quad (5)$$

where the difference potential in the second exponential term is now being treated as a perturbation. The Fourier transform of Eq. (5) thus becomes

$$\hat{G}(\mathbf{k},L)=\hat{G}_E(\mathbf{k},L)+\hat{G}_1(\mathbf{k},L)+\hat{G}_2(\mathbf{k},L)+\cdots, \quad (6)$$

where $\hat{G}_1(\mathbf{k},L)$ and $\hat{G}_2(\mathbf{k},L)$ are the first-order terms in the perturbation expansion. By using the method of Fourier and Laplace transformation as in Ref. 14, we derive the following functions to leading order in L:

$$\hat{G}_E(\mathbf{k},L)=1-\frac{k^2}{4}\left(\mathscr{A}^2L^{3/2}+\frac{3}{2\mathscr{B}}L+\cdots\right),$$

$$\hat{G}_1(\mathbf{k},L)=\frac{3}{16}k^2\mathscr{A}^2L^{3/2}+\cdots, \quad (7)$$

$$\hat{G}_2(\mathbf{k},L)=2L\Phi-2\Psi-k^2\left(\frac{2\mathscr{A}^2\Phi}{5}L^{5/2}+\frac{3\Phi}{4\mathscr{B}}L^2\right.$$
$$\left.-\mathscr{A}\Psi L^{3/2}+\cdots\right),$$

where $\mathscr{A}$ and $\mathscr{B}$ are excluded volume and step-length-dependent quantities that appear in the 2D Edwards solution, and Φ and Ψ, which also depend on $\mathscr{A}$ and $\mathscr{B}$, are well behaved convergent integrals in the large L limit.[21] The calculation of these functions required the exact form of the L-dependent normalization factor of the 2D Edwards solution. However, unlike the normalization for the free walk solution which leads to logarithmic divergences and hence the introduction of a cutoff ϵ, see Ref. 14, the normalization for the 2D Edwards solution has a form such that a term corresponding to ϵ appears naturally. As we know its exact L dependence, integrals which would otherwise diverge remain controlled. The subsequent calculation of $\langle R^2\rangle$ from these results gives[21]

$$\langle R^2\rangle=\frac{4}{5}\mathscr{A}^2L^{3/2}\left[1+\frac{15}{8\mathscr{A}^2\mathscr{B}}L^{-1/2}\right.$$
$$\left.-\left(\frac{5}{4}\,\frac{16w\Psi+1}{8w\Phi}\right)L^{-1}+\cdots\right]. \quad (8)$$

It should be noted that in deriving this result, unlike previous perturbation calculations, no divergences are encountered, and no restriction is placed on the value of v since the series is convergent in L. When comparing Eq. (8) with Eq. (1), we see that it predicts a value $\Delta_1=1/2$, as well as a *negative* value of the coefficient C. If we assume $a/l=0.5$, corresponding to the maximum excluded volume $v=\pi a^2$, we calculate $\mathscr{A}\approx0.793$, $\mathscr{B}\approx1.13$, $\Psi\approx0.107$, and $\Phi\approx0.226$. Substituting these into Eq. (8) the scaling amplitudes of Eq. (1) become $A\approx0.50$, $B\approx2.65$, and $C\approx-2.07$. However these ''mean field'' values for the amplitudes are not expected to agree well with numerical or exact results.[23]

We now turn to numerical studies. In order to create 2D self-avoiding chains in the continuum we have used a *biased* sampling Monte Carlo method dating back to Rosenbluth and Rosenbluth.[24] Although more efficient algorithms exist for creating longer chains[25] we are unsure about their reliability for studying the correction-to-scaling terms in the continuum. As our chains are in the continuum, the simulation procedure is considerably more complicated than that in Ref. 24. Given a chain consisting of n circles, the area available to the $(n+1)$th circle must be determined. If no areas are large enough, the chain is discarded and a new one started, otherwise the position of the next circle is picked randomly from the available areas and the chain at that position weighted with a factor $\theta/(2\pi-\beta)$, where θ is the total available angle and β is the angle excluded by the $(n-1)$th circle as no doubling back is permitted. This weighting factor distinguishes polymer statistics from the ''true'' self-avoiding walk.[26] In this way relatively long chains can easily be built even with the maximum excluded volume. We have checked the program against the analytic solution for the three step walk[27] and against a similar simple sampling program up to much longer chain lengths, with satisfactory results. The method has also been tested against Guttman's exact enumeration data on the lattice.[2]

To analyze our data, we have used the finite-size scaling method of Privman and Fisher[28] which is based on the cancellation of leading terms. We plot the estimating function

$$A_{N,k}(\Delta)=\frac{N^{\Delta-2\nu}R_N^2-(N-k)^{\Delta-2\nu}R_{N-k}^2}{N^{\Delta}-(N-k)^{\Delta}}. \quad (9)$$

Assuming Eq. (1) with $\nu=3/4$, then

$$A_{N,1}(\Delta)=A+(1-1/\Delta_1)ACN^{-1}+\cdots, \quad (10)$$

when $\Delta=\Delta_1$. The curves for different N will thus cross at a point close to the correct value of A and Δ_1 *assuming* $|C|$ *is small compared to* $|A|$. Figure 1(a) shows this technique ap-

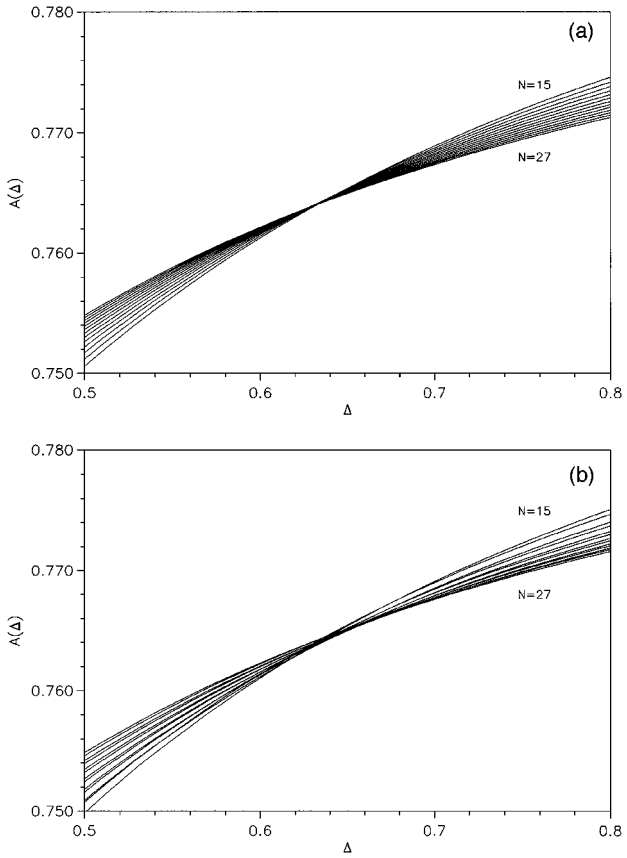

FIG. 1. (a) Plot of $A_{N,2}(\Delta)$ vs Δ for simulated square lattice data with $A=0.760$, $B=0.227$, $C=0.18$, and $\Delta_1=0.5$. (b) shows the same plot for the exact square lattice data of Ref. 2.

plied to the exact square lattice data of Guttmann[2] for values $N=15$ to $N=27$. In this case $k=2$ is used and the resulting $A_{N,2}(\Delta)$ data averaged with the $A_{N-1,2}(\Delta)$ data to eliminate the odd-even effect. As can be seen the curves cross at a value $\Delta\approx 0.65$ and $A\approx 0.765$, in agreement with Ishinabe,[3] while $\Delta_1=0.65$ was also reported by Privman[8] using the same technique on the triangular lattice data of Grassberger.[29] However, these authors assumed $|C|\ll|A|$, even though no clear evidence was given to support this assumption. Figure 1(b) also shows the results obtained using the same method on data calculated from Eq. (1) (hereafter called "simulated data") with $A=0.760$, $B=0.227$, $C=0.18$, and $\Delta_1=0.5$. These values of A, B, and C were obtained from a least-squares fit to the data[2] having set $\Delta_1=0.5$. The resulting curves are virtually indistinguishable from the exact data even though the values of Δ_1 differ. We have confirmed that any positive value of C will shift the crossing point to higher values of Δ. It thus appears that for the lattice Δ_1 could be as large as 0.66, but $\Delta_1=0.5$ is possible. The same procedure using exact triangular lattice data[29] yielded excellent agreement with simulated data for $A=0.704$, $B=0.175$, $C=0.128$, and $\Delta_1=0.5$.

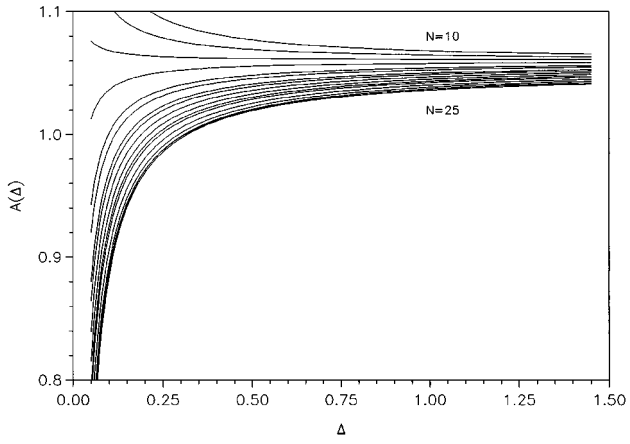

FIG. 2. Plot of $A_{N,1}(\Delta)$ vs Δ for our Monte Carlo 2D continuum data, with maximum excluded volume.

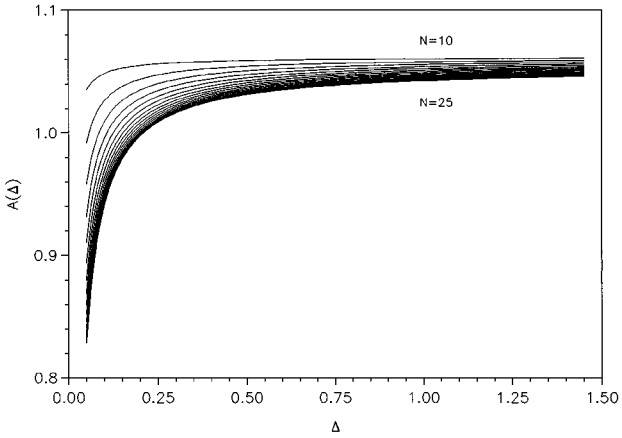

FIG. 3. Plot of $A_{N,1}(\Delta)$ vs Δ for simulated continuum data with $A=1.023$, $B=0.491$, $C=-0.681$, and $\Delta_1=0.666$.

Figure 2 shows the resulting curves when the estimating function Eq. (9) is applied to our continuum data for chain lengths of $N=10$ to $N=25$ with the maximum excluded volume ratio of 0.5. The estimate of $\langle R_N^2\rangle$ for $N=25$ comes from averaging approximately 1.87×10^8 walks, resulting in an error of less than 0.1%. Clearly the data show no sign of crossing, and we suggest that this is due to a large negative C. An estimator, similar to Eq. (9), but which gives simultaneous estimates of B and Δ_1,[3] was also studied, but it too showed no evidence of crossing. Due to the large C value and small random errors in our Monte Carlo continuum data it is difficult to use other graphical techniques[4,7] to determine

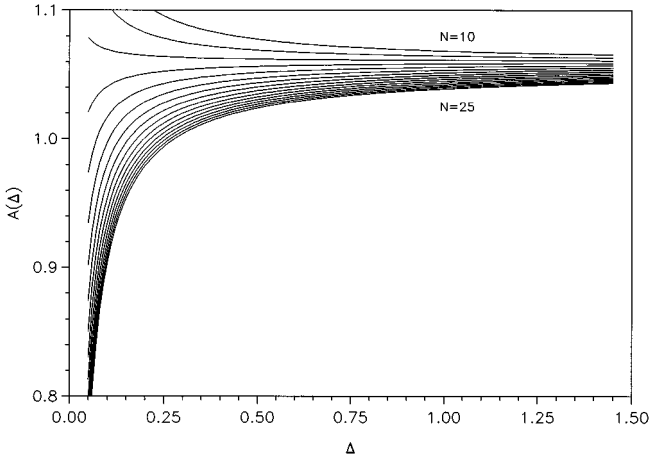

FIG. 4. Plot of $A_{N,1}(\Delta)$ vs Δ for simulated continuum data with $A=0.990$, $B=0.489$, $C=-0.839$, and $\Delta_1=0.5$.

Δ_1. We therefore use the above method of comparison between simulated and Monte Carlo data.

We first assumed a value of $\Delta_1 = 0.666$, in agreement with Ref. 4, and using a least-squares curve fit to our data from $N = 10$ to $N = 25$, we found a best fit with coefficient values of $A = 1.023$, $B = 0.491$, and $C = -0.681$. We then used these values to create simulated $\langle R_N^2 \rangle$ data to which we applied the $A_{N,1}(\Delta)$ vs Δ analysis. The resulting curves are shown in Fig. 3. They are very different from those of the Monte Carlo continuum data. We then assumed a value of $\Delta_1 = 0.5$ from which we obtained a best fit with coefficient values of $A = 0.990, B = 0.489$, and $C = -0.839$. The resulting curves, as shown in Fig. 4, are in excellent agreement with the continuum data. The large negative C should be noted. Thus to assume C is negligible, as has often been done when analyzing 2D lattice data,[3,4,8] is a mistake and could lead to poor estimates of Δ_1.

In conclusion, we have presented strong evidence that $\Delta_1 = 1/2$ for 2D chains in the continuum. Although this value does not agree with any of those suggested by other authors for 2D chains on the lattice,,[3,4,7,8] their data are compatible with $\Delta_1 = 0.5$ when the effects due to the next order term in Eq. (1) are considered. Unless there is a breakdown of the universality of both ν and Δ_1,[20,30] we suggest that Saleur's[12] rejection of $\Delta_1 = 1/2$ should be reexamined. Since our perturbation method and our Monte Carlo analysis agree, we suggest that the leading correction-to-scaling term in two-dimensions is $\Delta_1 = 1/2$.

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