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LETTER TO THE EDITOR

Scaling at the conformational rod-to-coil transition

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Abstract. We present evidence for the partial suppression of self-avoidance effects in the rod-to-coil transition scaling, observed recently in numerical simulations. The scaling ansatz is examined critically, and also checked explicitly in a soluble model on a partially directed lattice.

In this letter, we focus on aspects of the scaling behaviour in the simplest lattice model of a single chain rod-to-coil transition (Halley *et al* 1985, Lee and Nakanishi 1986). Thus we consider biased self-avoiding walks (BSAW) of N steps on hypercubic lattices. For each 90° turn of a walk, a statistical weight w is assigned, where w is positive and *small*. If $w \to 0$ for fixed N, the statistical averages over N-step walks will be dominated by elongated, rod-like configurations.

The above model is a simple theoretical abstraction. Indeed, the concept of *persistency* has played an important role since the early, effective-field theories of polymer conformation (see, e.g., Odijk (1983) and references therein). However, in real systems studied experimentally, the pattern is typically complicated, the persistency being both *linear* and *planar* (Chance *et al* 1979, Lim *et al* 1983, Lim and Heeger 1985), or having a more involved structure (Mattice and Scheraga (1984) and references therein). More realistic theoretical models of persistency effects within the scaling framework (see, e.g., Schroll *et al* 1982) failed to allow fully for the self-avoidance. Other studies explored the interplay between the intra-chain semiflexibility and the inter-chain interactions and/or the anisotropy of the surrounding medium (see Warner *et al* (1985), Nagle *et al* (1984) and literature quoted therein).

Armed with the concept of universality, we turn to the simplest lattice model which we consider in general dimensionality, d. Halley *et al* (1985) proposed the following scaling relation for the mean-squared end-to-end distance of N-step walks

$$\langle R_N^2(w)\rangle \approx N^2 G(wN^{\phi}). \qquad (1)$$

(Note that we use a different notation which is more suited to our discussion.) This relation was checked through extensive Monte Carlo calculations by Lee and Nakanishi (1986). Both numerical studies in $d = 2, 3$, and some analytical arguments suggest

$$\phi_{\mathrm{BSAW}} = 1. \qquad (2)$$

However, the standard scaling prediction for the large argument behaviour,

$$G(x) \sim x^{(2\nu-2)/\phi} \qquad \text{as } x \to \infty \qquad (3)$$

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where $\nu \equiv \nu_{SAW}$, was not observed in $d=3$ dimensions even for rather large values of the scaling combination

$$x \equiv wN^{\phi}. \tag{4}$$

Instead, Lee and Nakanishi (1986) found that for an unexpectedly large range of x values,

$$G_{BSAW}(x) \simeq G_{BRW}(x) \tag{5}$$

where BRW denotes biased random walks with no *immediate* returns (but revisits are otherwise permitted). The approximate equality (5) extends well into the regime of the large-x asymptotic behaviour of $G_{BRW}(x)$, which is of the form (3) but with $\nu = \frac{1}{2}$. In the present work, we carry out a perturbative study of this anomalous behaviour, to the leading non-trivial order in the small-x expansion. We also report *exact* results for the *partially directed* BSAW on the square lattice. For this non-Gaussian model, the scaling ansatz is found to hold, with $\phi = 1$.

Let $c(k, N)$ denote the total number of N-step walks having exactly k turns. Then the generating function,

$$C(w, N) \equiv \sum_{k=0}^{N-1} c(k, N) w^k \tag{6}$$

must *scale* according to

$$C(w, N) \approx F(wN^{\phi}). \tag{7}$$

For random walks with no immediate returns

$$F_{BRW}(x) = 2d \exp[2(d-1)x] \tag{8}$$

and $\phi_{BRW} \equiv 1$. Corrections to (7) are of relative order w or $1/N$, for the BRW case. The scaling function F measures the *multiplicity* of walks, weighted by the appropriate powers of w. We focus on this quantity since it is easier to handle than the radii. The asymptotically exponential form of $F_{BRW}(x)$ for large x reflects a finite entropy (per step) in the 'coil' limit.

Consider now the relation

$$C_{BSAW}(w, N) = C_{BRW}(w, N) - C_C(w, N) \tag{9}$$

where the subscript C denotes the generating function for walks with *at least one* revisited site (contact). If we *assume* that all three quantities scale according to (7), with the same $\phi = \phi_{BRW} \equiv 1$, then

$$F_{BSAW}(x) = F_{BRW}(x) - F_C(x). \tag{10}$$

For small x,

$$F_{BRW}(x) = 2d + 4d(d-1)x + 4d(d-1)^2x^2 + \tfrac{8}{3}d(d-1)^3x^3 + \cdots. \tag{11}$$

Let us consider the contribution of $F_C(x)$ to a similar expansion for F_{BSAW}, via (10). Contact configurations are not possible for $k=0$, 1 and 2 turns. Thus to order x^2 inclusive, all the scaling functions for BSAW and BRW are identical. Since the perturbative argument by Halley *et al* (1985) for $\phi_{BSAW} = 1$ is essentially equivalent to the O(x) expansion of the scaling functions, they actually did not establish anything beyond $\phi_{BRW} = 1$! One still needs the *assumption* that the three terms in (9) scale, in a similar fashion, to imply (10). Note that the analogue of (10) for the mean-squared radii (1) is

$$(FG)_{\mathrm{BSAW}} = (FG)_{\mathrm{BRW}} - (FG)_{\mathrm{C}}. \tag{12}$$

Let us consider the leading non-trivial order, $(wN)^3$. The number of *three*-turn random walks with no immediate returns is given by

$$c(3, N) = 2d[2(d-1)]^3 \sum_{n_0=1}^{N-3} \sum_{n_1=1}^{N-n_0-2} \sum_{n_2=1}^{N-n_0-n_1-1} \sum_{n_3=1}^{N-n_0-n_1-n_2} \delta_{N,n_0+n_1+n_2+n_3} \tag{13}$$

where the n_j denote the number of steps in the four straight sections. The sums can be evaluated to yield

$$c(3, N) = 2d[2(d-1)]^3(N-1)(N-2)(N-3)/6. \tag{14}$$

For large N, the product $w^3c(3, N)$ contributes to the x^3 term in (11). Consider now *contact* configurations with three turns. There is only one topology, a rectangular loop shown in figure 1. It can have $4d(d-1)$ possible orientations. The contribution of such loops to $C_{\mathrm{C}}(w, N)$ is given by

$$4d(d-1)w^3 \sum_{j=0}^{N-4} \sum_{m=1}^{[(N-j)/2]-1} \sum_{l=1}^{[(N-j)/2]-m} 1 = d(d-1)w^3(N+n)(N-1)(N-2-n)/6 \tag{15}$$

where the brackets denote the 'integral part,' and n indicates the parity of N: $n=0$ for N even, $n=1$ for N odd. The $\mathrm{O}(N^3)$ term of this sum is

$$\tfrac{1}{6}d(d-1)(wN)^3 \propto x^3 \tag{16}$$

which provides the leading-order non-trivial check for $\phi_{\mathrm{BSAW}} = 1$. The relative number of 'contact' as opposed to general walks is

$$c_{\mathrm{C}}(3, N)/c_{\mathrm{BRW}}(3, N) \approx [16(d-1)^2]^{-1} \tag{17}$$

which is about 6% in $d=2$, but only about $1\frac{1}{2}$% in $d=3$. Notice that the number of contact walks is suppressed not only by a numerical factor, but also by the factor $(d-1)^{-2}$, which essentially reflects the constraint that the loops be *more planar* than

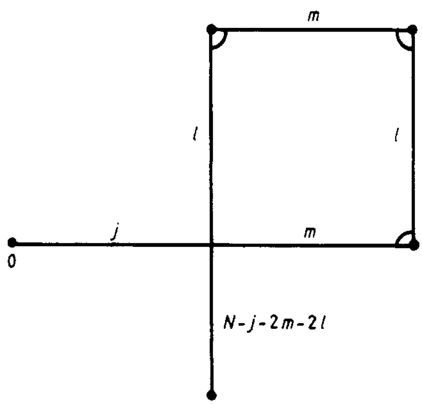

Figure 1. The only 'contact' topology with three turns. The number of steps in each straight portion is indicated.

the rest of the walk, and which becomes more effective with increasing dimensionality. Furthermore, since most of the *multi-turn* walks have sub-loops of the type of figure 1, their contribution to higher order in x will be strongly suppressed. Unfortunately, explicit calculation of the number of k-turn contact walks for higher k seems impractical. The general trend indicated by the lowest-order calculation—specifically, the stronger suppression of the self-avoidance effects in $d=3$ than in $d=2$—is consistent with the numerical results of Lee and Nakanishi (1986). Finally, note that the even-odd oscillations in the *corrections* to the leading $O(x^3)$ scaling, in (15), are reminiscent of the ordinary $(w=1)$ square lattice SAW behaviour.

In order to have some indication that the scaling (1) is applicable beyond the small-x expansion, in a non-Gaussian model, we considered *partially directed* BSAW on the square lattice. For these walks, only $\pm\hat{x}$ and $+\hat{y}$ steps are permitted. The problem can be solved exactly. We used the generating function technique described by Szpilka (1983). Only a simple extension and more bookkeeping are needed to account for the turn weights, w. Specifically, we calculated

$$C(w, N)=3[A(w, N)-A(w, N-1)]+4wA(w, N-1) \tag{18}$$

where

$$A(w, N)\equiv[(1+w\sqrt{2})^N-(1-w\sqrt{2})^N](2w\sqrt{2})^{-1}. \tag{19}$$

We also calculated the first moment of R_y:

$$\langle R_y(w, N)\rangle=\tfrac{1}{2}[N-A(w, N)/C(w, N)]. \tag{20}$$

This moment is non-zero due to asymmetry in the y direction. (Calculation of the second moments is straightforward but tedious.) The appropriate scaling form for this result is

$$\langle R_y(w, N)\rangle\approx NP(wN^{\phi}) \tag{21}$$

with

$$\phi_{\mathrm{DBSAW}}\equiv 1 \tag{22}$$

and

$$P_{\mathrm{DBSAW}}(x)=\tfrac{1}{2}-\sinh(x\sqrt{2})[2x\sqrt{2}F_{\mathrm{DBSAW}}(x)]^{-1} \tag{23}$$

where $x\equiv wN$. Here, as in (7),

$$F_{\mathrm{DBSAW}}(x)=3\cosh(x\sqrt{2})+2\sqrt{2}\sinh(x\sqrt{2}) \tag{24}$$

is the scaling function for the generating function $C(w, N)$.

For this partially directed walk model, then, the expected scaling indeed holds, and both the small-x and large-x scaling function behaviours are 'normal,' as can be checked explicitly.

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