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LETTER TO THE EDITOR

On the apparent failure of a Flory approximation for directed linear polymers

S L A de Queiroz†

Department of Theoretical Physics, 1 Keble Road, Oxford OX1 3NP, UK

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Abstract. We discuss the apparent failure of a Flory approximation for directed linear polymers, commenting on the details implicit in this type of picture. The relationship of a standard Flory viewpoint to a simplified application of fractal theory is explored, and a correspondence is drawn between aspects of both theories.

Directed self-avoiding walks (SAWs) are defined as SAWs in which steps in certain directions are not allowed. Directed SAW models were discussed by Fisher and Sykes (1959) in an attempt to establish rigorous lower bounds for the connective constant of isotropic SAWs, following the early work of Temperley (1956). However, it is only in the past couple of years that the asymptotic properties of these models have received further attention; this renewed interest stems from the recently established finding that the introduction of a directional bias changes the overall critical properties of geometrical models (for a review of directed percolation, see e.g. Kinzel (1983); for directed animals see Nadal *et al* (1982)). Directed SAWs describe the configurational properties of linear polymers under anisotropic conditions, e.g. under traction (de Gennes 1979).

The critical behaviour of directed SAWs is very simple; most surprising is the fact that a standard Flory approximation (Flory 1971, de Gennes 1979), which works remarkably well for a number of both isotropic and directed models (Isaacson and Lubensky 1980, Redner and Coniglio 1982, Lubensky and Vannimenus 1982, Family and Daoud 1984, Daoud *et al* 1984), seems to give erroneous results when applied to this problem. This fact has been noticed by Lubensky and Vannimenus (1982); however, those authors do not try to work out an explanation for it. It is currently accepted that the theoretical grounds of the Flory approximation are somewhat shaky, its relatively accurate numerical results being due to a fortuitous cancellation of errors (de Gennes 1979); thus it seems worthwhile to discuss this apparent failure in detail, in order to check precisely how it arises from limitations intrinsic to the viewpoint of the Flory approach, which possibly do not show up in other cases. This would help provide a better understanding of the mechanisms involved in Flory-like approximations. In what follows, we first recall the properties of directed SAWs and rederive the results of a standard Flory approach to the problem; then we show how these results are corrected through the introduction of the screening of repulsive interactions, which is related to topological properties of the walks; finally we discuss the relationship of

† On leave from Departamento de Fisica, PUC, 22452 Rio de Janeiro, Brazil. Supported by CNPq.

the value of the upper critical dimensionality for this problem, as given by the standard Flory approximation, to properties of fractals.

A directed SAW can be decomposed into a forward walk along the preferred direction and a random walk perpendicular to that direction. Consequently, the average dimensions $\langle R_{\parallel}^2\rangle^{1/2}$ and $\langle R_{\perp}^2\rangle^{1/2}$ respectively along and perpendicular to the 'easy' axis are, for an N-step walk,

$$\langle R_{\parallel}^2\rangle^{1/2} \sim N^{\nu_{\parallel}}, \qquad \langle R_{\perp}^2\rangle^{1/2} \sim N^{\nu_{\perp}}, \tag{1}$$

with $\nu_{\parallel} = 1$ and $\nu_{\perp} = \frac{1}{2}$. This is self-evident for the two-choice walk on a square lattice, in which only steps in the $+x$ or $+y$ directions are allowed (figure 1). The same results have been found for the three-choice square lattice (see figure 1) by a variety of methods (Redner and Majid 1983, Szpilka 1983, Blöte and Hilhorst 1983), as well as for the five-choice triangular lattice (Redner and Majid 1983) of figure 1, in which the possibility of self-intersections is not ruled out at once by the directionality constraint (hence e.g. a transfer-matrix solution is not possible); this common behaviour is expected on universality grounds (de Queiroz 1983). Zhang *et al* (1984) showed that the same exponents are found for the five-choice simple cubic lattice (figure 1); actually, Cardy (1983) has shown from a field-theoretic approach that directed SAWs are in the same universality class as directed unrestricted random walks, and therefore should exhibit mean-field exponents $\gamma = 1$, $\nu_{\parallel} = 1$ and $\nu_{\perp} = \frac{1}{2}$ in all dimensionalities.

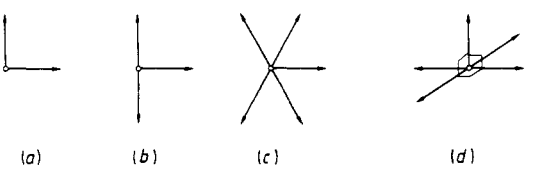

Figure 1. Directed SAW models. Allowed step directions are indicated. (*a*) Two-choice square lattice; (*b*) three-choice square lattice; (*c*) five-choice triangular lattice; (*d*) five-choice simple cubic lattice.

The Flory argument for directed systems with dominant two-body interactions is as follows (Redner and Coniglio 1982, Lubensky and Vannimenus 1982): in d dimensions, the repulsive energy is approximated as the integral of the square of the monomer concentration over the spatial extent of the polymer; this gives

$$\varepsilon_{\text{rep}} \sim N^2 / R_{\parallel} R_{\perp}^{d-1}. \tag{2}$$

The entropy term is written as the sum of two contributions, respectively from degrees of freedom in the 'easy' direction and in directions perpendicular to it:

$$S \sim (R_{\parallel}/R_{\parallel}^{\circ})^2 + (R_{\perp}/R_{\perp}^{\circ})^2 \tag{3}$$

where $R_{\parallel}^{\circ}$ and $R_{\perp}^{\circ}$ are the dimensions of the object as given by mean-field theory. For directed linear polymers, one has $R_{\parallel}^{\circ} \sim N$ and $R_{\perp}^{\circ} \sim N^{1/2}$. The upper critical dimensionality d_c, above which mean-field theory holds, is found by requiring $\varepsilon_{\text{rep}}(R_{\parallel}^{\circ}, R_{\perp}^{\circ}) \sim 1$. Below d_c the critical exponents $\nu_{\parallel}$ and $\nu_{\perp}$ are found by minimising the free energy with respect to $R_{\parallel}$ and $R_{\perp}$. From (2) and (3) one finds for directed SAWs:

$$d_c = 3, \qquad \nu_{\perp} = 5/(2d+4), \qquad \nu_{\parallel} = (d+7)/(2d+4). \tag{4}$$

Two points can be raised as concerns the above results: (i) the value of $d_c = 3$ is certainly wrong, as it is inconsistent with the numerical and analytical findings quoted above, in particular with the field-theoretical result of Cardy (1983); and (ii) one has $\nu_\parallel > 1$ for $d < 3$ (this was already noted by Lubensky and Vannimenus (1982)).

Actually, (ii) is a direct consequence of (i), for within the context of a Flory approximation one always obtains exponents greater than the classical ones below d_c; this is because the energy term (which is relevant at $d < d_c$) tends to swell the chain relative to its Gaussian dimensions, in all directions (although, for anisotropic systems, at different rates respectively in the 'easy' and perpendicular directions). It does not seem possible to obtain a consistent approach for this problem in which the swelling does not extend to the 'easy' direction; however, this should not be a matter for concern because, as we shall see below, point (ii) will no longer arise once (i) has been correctly addressed.

The reason why one usually gets correct critical dimensionalities from a Flory approach is that above d_c an essentially non-interacting, entropy-governed, picture strictly holds and, accordingly, the Flory (mean-field) repulsive energy (e.g. equation (2) above) as obtained with classical values for the exponents is negligible; that is to say, the Flory estimate for the energy is correct only as long as it is of order zero. This is typical of mean-field theory: a system with only short-range interactions can be represented in the disordered (paramagnetic) phase by a mean-field picture (which is equivalent to infinitely ranged forces) because in that regime whatever interactions exist are negligible anyway. Below d_c, both energy and entropy are overestimated in the Flory approximation, but the errors cancel to a great extent and the resulting non-classical exponents are fairly accurate numerically (de Gennes 1979).

In the present case, we obtain the wrong critical dimensionality because equation (2) fails to represent the repulsive energy of the directed SAW even in the classical regime. The key point is that, since the walk is topologically one-dimensional, each step taken in the 'easy' direction effectively prevents the following steps from interacting with the previous ones, and this must be accounted for in a mean-field description. Notice that no similar effects arise for directed lattice animals or directed percolation because in these problems the clusters (however highly anisotropic in shape) are more connected, therefore a mean-field picture, where every bond (or site) directly feels the presence of all others, is not drastically wrong (at least in high space dimensionalities).

We now show how the inclusion of this effective 'screening' of interactions corrects the previous results. If there are $N_\parallel$ steps in the preferred direction, each monomer only 'sees' a fraction $1/N_\parallel$ of the total number of monomers; this means that the effective concentration appearing in the Flory energy is only a fraction $1/N_\parallel$ of the total concentration, and the energy is (effective concentration)$^2 \times$(volume) $= (1/N_\parallel)^2 (N^2/R_\parallel R_\perp^{d-1})$. Now, within a mean-field context, $N_\parallel \sim N$ (more precisely $N_\parallel = N/\mu$, where μ, the effective connective constant, is a number of order one (de Gennes 1979)). Therefore, one has

$$\varepsilon_{\text{rep}}(R_\parallel^\circ, R_\perp^\circ) \sim N^{-(d+1)/2}. \tag{5}$$

That is, the mean-field repulsive energy is negligible for all d and we recover the result of Cardy (1983): there is no critical dimensionality for the problem, and the exponents stick to their classical values for any d.

We see then that the directionality constaints are so strong in this case that the average number of two-particle encounters is drastically cut down from what is predicted by (2) above. We now discuss a simplified application of the theory of

fractals (Mandelbrot 1982) to the present case and show that it exhibits the same shortcomings as the standard Flory approach; this will give us further insight into the relationship of directional bias to the effective lowering of the degree of randomness in this problem.

We begin by recalling two rules that are applicable to *random* fractals (Mandelbrot 1982, Turban 1983).

(a) If two independent fractal sets of respective fractal dimensions D_1 and D_2 are embedded in d-dimensional Euclidean space, their intersection will be a set of dimension zero if $d \geqslant D_1 + D_2$. Otherwise, its dimension is $D_1 + D_2 - d$.

(b) 'Replica trick': for a random set S with fractal dimension D, the set of its K-multiple points has the same fractal dimension as the intersection of K replicas of S.

In the present case where the repulsive interactions arise from two-body encounters, we obtain that the energy term will be negligible (i.e. the set of double points will have zero dimension) if $d \geqslant 2D$, provided that both (a) and (b) hold literally.

As regards the fractal dimensionality D, there seems to be no unique way to extend this concept to directed problems. Here we make use of one possible approach which, as is argued below, is consistent with the Flory viewpoint leading to equation (2) for the energy. It is to be noticed that this approach has also been used by Kinzel (1983) for directed percolation.

We write

$$(\text{mass}) \sim (\text{effective radius})^D \tag{6}$$

where the 'effective radius' R_{eff} is the geometric mean of the average dimensions of the directed walk:

$$R_{\text{eff}} = (R_{\parallel} R_{\perp}^{d-1})^{1/d}. \tag{7}$$

This is the simplest way to take into account the fact that the walk has different dimensions along different directions; further, if taken together with the 'replica trick' mentioned, it amounts to the hypothesis underlying equation (2) above, namely that the directionality constraint does not influence the number of two-body encounters. To see this, recall that the 'effective radius' as defined above can be interpreted as the isotropic mean dimension of directed walks, averaged over an ensemble in which the 'easy' direction of each walk is completely randomly distributed. In order to show that equations (6) and (7) together with rules (a) and (b) correspond to a translation into fractal theory of the standard Flory approximation, we note that (6) and (7) give

$$D = d/[\nu_{\parallel} + (d-1)\nu_{\perp}] \tag{8}$$

and, substituting the classical values $\nu_{\parallel} = 1$, $\nu_{\perp} = \frac{1}{2}$,

$$D = 2d/(d+1). \tag{9}$$

From the condition $d_c = 2D$, once again one has $d_c = 3$.

Within the context of fractal theory we note that there are two problems with the above arguments, both intimately connected with the fact that anisotropy is not properly taken into account. First the 'replica trick' (rule (b) above) does not apply because the directionality constraint is much more stringent upon different steps of the same walk than upon pieces of distinct walks; as stated above, the directional bias effectively lowers the degree of randomness in the problem, therefore $d_c = 2D$ is not true. The simplest quantitative example is that of two-choice walks on a square lattice: one given

walk will never intersect itself, however, the intersection of two walks is a set of fractal dimensionality $\frac{1}{2}$. To see this, recall that the relative 'space-like' coordinate between the tips of two walks (see figure 2) performs a random walk (with three equiprobable displacements: 0, ±2), and the fractal dimension of the zero set (set of 'time' instants when the walker is at the origin) is $\frac{1}{2}$ for a one-dimensional random walk (Mandelbrot 1982).

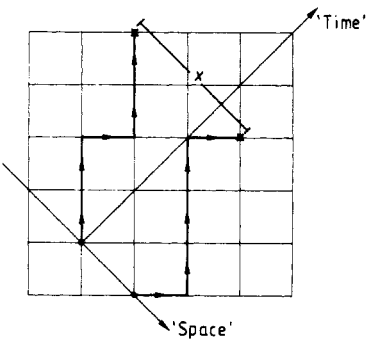

Figure 2. Two distinct two-choice directed SAWS on a square lattice; x, the relative space-like coordinate, performs a random walk in the 'space' direction.

Second, the definition of a fractal dimensionality through equation (6) above relies on the validity of the concept of self-similarity; this concept is no longer valid for a system where anisotropic scaling holds, in which case one can only talk of self-affinity (Mandelbrot 1982). Actually, since a directed SAW in d dimensions is the same as the graph, in $[(d-1)+1]$-dimensional space, of a random walk in $(d-1)$ dimensions, its fractal (Hausdorff–Besicovitch) dimensionality is $1+(d-1)/2$ (see the table at the end of Mandelbrot (1982)). We note that an approach similar in spirit to that underlying equation (6) was used by Green and Moore (1982) in an application of directed lattice animal theory to river networks, with fairly good numerical agreement between theoretical results and available data from geological surveys. What is shown by these authors is that directed animals and river networks have the same 'effective' dimensionality, which is given by a defining equation similar to equation (6); they do not suggest that this is the same as the Hausdorff–Besicovitch dimension.

In summary, we have discussed the reasons why a Flory approximation apparently fails in the case of direct linear polymers, commenting on the details implicit to this type of picture. The relationship of a standard Flory viewpoint to a simplified application of fractal theory has been explored, and a correspondence has been drawn between aspects of both theories.

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Note added in proof. For consistency, intrablob repulsion equation (6) should be multiplied by n_b, but the universality nature of the gel at the gel point seems to imply that it should be multiplied by a universal quantity which is assumed to be constant in equation (6). It is not clear how to take this into consideration to develop a consistent theory.

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