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LETTER TO THE EDITOR

Polymer statistics on a Cayley tree†

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Abstract. We study linear and branched polymers on a Cayley tree. We obtain the values of the critical monomer fugacity in closed form, for any value of the branching-point fugacity. The correlation-length exponent ν is found to be $\frac{1}{2}$, through finite-size scaling arguments. This gives independent support to the idea that mean-field and Cayley-tree approximations are not equivalent. A proposal is made for the behaviour of ν against branching-point fugacity.

1. Introduction

The connection between statistics of polymers and scaling theory of critical phenomena has been extensively studied in recent years (see e.g. McKenzie (1976) and references therein). Specifically, de Gennes (1972) has shown the equivalence of the $n \to 0$ limit of the n-vector model to the statistics of linear polymers, with $1/N$, the inverse number of monomers, playing the role of $T - T_c$. Since this correspondence has been established, researchers have been provided with further confidence to apply methods initially devised for the description of thermal critical phenomena to the study of the large-N properties of polymers. In particular, models in which no explicit reference is made to the $n \to 0$ trick have been successful in accounting for properties of both linear (Shapiro 1978, de Queiroz and Chaves 1980) and branched (Family 1980) polymers, in the high-temperature, zero-concentration limit. In this limit, one has a single polymer subject only to geometrical constraints expressed by the non-intersecting or self-avoiding walk (SAW) condition (McKenzie 1976). The grand canonical partition function, or generating function, is given by

$$\Gamma(p) = \sum_n a_n p^n \tag{1}$$

for a linear polymer, where a_n is the number of n-step SAWs starting at a given point of a regular lattice, and p is the fugacity per monomer. For branched polymers, one has to take into account the existence of branching points, and this can be done in two ways, either by assigning a branching *probability* to each site on the lattice (Family 1980) or by introducing a *fugacity* for branching points (Lubensky 1978). Here we make use of the latter approach, and shall comment on it below.

The Cayley tree (CT) is not a realistic lattice, in the sense that its topology does not allow the existence of rings of bonds; in what concerns polymer statistics, the SAW condition is already fulfilled from the beginning, provided we do not take backward steps into account. However, it makes perfect sense to define structures governed by

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generating functions such as equation (1) and ask questions as to what happens in the large-N limit. The answers to these questions may provide us with useful insight into the behaviour of similar systems constrained to physically realisable lattices.

Further, it is interesting to discuss the usually accepted statement that a Cayley tree is equivalent to an infinite-dimensional lattice, whence mean-field (MF) results would apply. This is true for critical exponents in the percolation problem (Stauffer 1979), although Nakanishi and Stanley (1981) have already pointed out differences in the scaling function for percolation on the Cayley tree and in the MF approximation, the former becoming equivalent to the latter only as the coordination number approaches infinity. For linear polymers, it is known that critical exponents differ in either case (McKenzie 1976), and as we shall show below, we expect this distinction to hold also for branched polymers.

We now review briefly the statistics of linear polymers as a Cayley tree. We denote by 'σ-tree' a Cayley tree in which each site is connected to $\sigma+1$ sites. In this case, equation (1) is written

$$\Gamma(p)=p+\sigma p^2+\sigma^2 p^3+\ldots=p/(1-\sigma p). \tag{2}$$

Criticality is identified with the divergence of $\Gamma(p)$, so the critical fugacity is

$$p_c=1/\sigma. \tag{3}$$

This is the same as the critical *probability* for the percolation problem on a Cayley tree (Fisher and Essam 1961). The coincidence arises because, in what concerns the infinite percolation cluster, it does not matter whether 'dangling' bonds are present or absent.

We define the critical exponent γ through

$$\Gamma(p)\sim(p_c-p)^{-\gamma} \qquad (p\to p_c^-) \tag{4}$$

(Redner and Reynolds 1981), and the correlation-length exponent ν, which measures the divergence of the average end-to-end distance $R(p)$ as

$$R(p)\sim(p_c-p)^{-\nu} \qquad (p\to p_c^-) \tag{5}$$

(Shapiro 1978, de Queiroz and Chaves 1980). A suitable definition for end-to-end distance of linear polymers on a Cayley tree is simply the number of monomers present in the chain, so that we have in this case

$$R(p)=p\frac{\mathrm{d}}{\mathrm{d}p}\ln\Gamma(p). \tag{6}$$

Hence we obtain from (2) and (6)

$$\gamma=\nu=1. \tag{7}$$

Results (3) and (7) are quoted in McKenzie (1976).

We now turn to branched polymers and allow for the existence of branching units. Following Lubensky (1978), a fugacity Λ is attributed to each f-functional unit, so that the corresponding weight Λp^f is included in the generating function. We have performed calculations with different functionalities, all yielding the same qualitative results, hence we shall restrict ourselves to $f=\sigma$ in what follows.

It is easy to see that the following recursion relation holds between finite trees with N and $N+1$ generations respectively:

$$\Gamma_{N+1}(p,\Lambda)=p(1+\Lambda p^\sigma X_N^\sigma+\sigma p X_N) \tag{8}$$

where

$$X_N = 1 + \Lambda p^\sigma X_{N-1}^\sigma + \sigma p X_{N-1}, \qquad X_0 = 0, \tag{9}$$

and $\Gamma_N(p, \Lambda)$ is the generating function for a finite, N-generation tree. This can be visualised by recalling that

$$\Gamma_1(p, \Lambda) = p, \Gamma_2(p, \Lambda) = p(1 + \Lambda p^q + qp), \Gamma_3(p, \Lambda)$$
$$= p[1 + \Lambda p^\sigma (1 + \Lambda p^\sigma + \sigma p)^\sigma + \sigma p(1 + \Lambda p^\sigma + \sigma p)]$$

etc. Here the zero-bond cluster, which does not contribute to the non-analyticities of $\Gamma(p, \Lambda)$, is not taken into account. We have

$$\Gamma(p, \Lambda) = \lim_{N\to\infty} \Gamma_N(p, \Lambda) \tag{10}$$

and

$$\Gamma(p, 0) = p/(1 - \sigma p) \tag{11}$$

in accordance with (2).

Criticality is given by regarding p and Λ as parameters for $X(p, \Lambda)$ and imposing

$$X_{N+1}(p_c, \Lambda) = X_N(p_c, \Lambda) = X^* \qquad (N \to \infty) \tag{12}$$

and

$$\frac{\partial}{\partial X}(1 + \Lambda p_c^\sigma X^\sigma + \sigma p_c X)|_{X^*} = 1$$

where we take Λ as fixed; (9) and (12) then yield

$$p_c = \sigma\left[1 + \left(\frac{\Lambda}{(\sigma - 1)^{\sigma-1}}\right)^{1/\sigma}\right]^{-1}. \tag{13}$$

Again we have $p_c(\Lambda = 0) = 1/\sigma$. Further, for $\sigma = 2$, the coefficients of $\Gamma(p, 1) = \Sigma\, a_s p^s$ give the number of s-bond Cayley trees per bond of a Bethe lattice, which approaches $[\sigma^\sigma/(\sigma - 1)^{\sigma-1}]^s$ as $s \to \infty$ (Fisher and Essam 1961, Essam and Gwilym 1971). Indeed, (13) gives $p_c = \frac{1}{4}$ in this case, in agreement with the criticality condition $\mu p_c = 1$, where μ is the effective connective constant of the lattice (McKenzie 1976).

We now turn to the calculation of the critical exponent ν. Applying finite-size scaling arguments (Fisher 1971, Sur *et al* 1976, Reynolds *et al* 1980) to the present case, the critical fugacity for a finite tree with N generations varies with N as

$$(p_c(N) - p_c) \sim N^{-1/\nu} \tag{14}$$

where $p_c = \lim_{N\to\infty} p_c(N)$ is given by (13). $p_c(N)$ is defined as the value of p for which Γ_N diverges, the Λ-dependence being implicitly understood, and can be located within very good accuracy. For example, $\Gamma_{100}(p, 0.5)$ goes from $\sim 10^5$ to $\sim 10^{18}$ for a p-variation of 6×10^{-5}, close enough to $p_c(100)$. At greater values of N, the divergence is far steeper, allowing a precise location of $p_c(N)$ to one part in 10^7. As can be seen from figure 1, $p_c(N)$ indeed approaches p_c quite rapidly as N increases.

Our data are consistent with a value of $\nu = \frac{1}{2}$, which differs from the MF result for branched polymers (Lubensky 1978, Redner 1979), $\nu_{MF} = \frac{1}{4}$. As in the case of linear polymers, where $\nu = 1$ for Cayley trees and $\nu_{MF} = \frac{1}{2}$ (McKenzie 1976), the CT value of ν

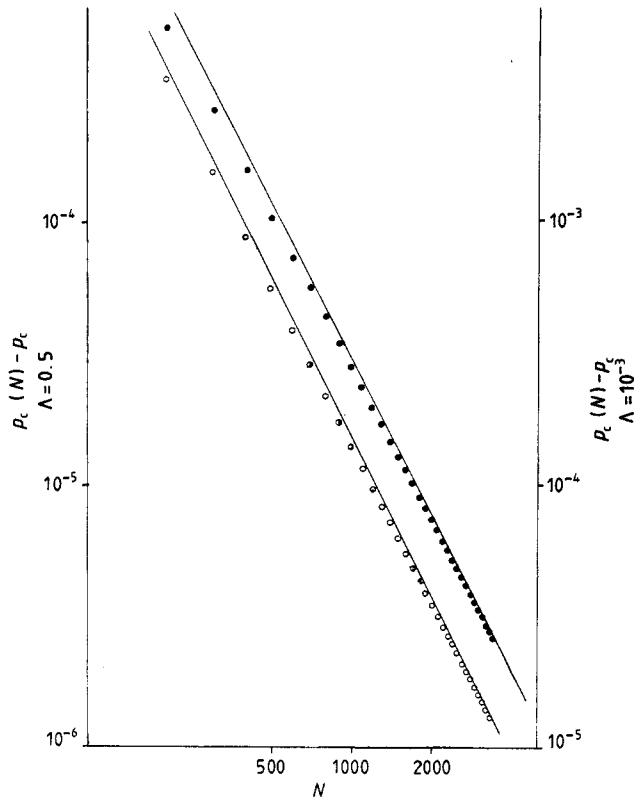

Figure 1. $p_c(N)-p_c$ against N for $\Lambda=10^{-3}$ (full circles) and $\Lambda=0.5$ (open circles). The straight lines have slope $=-2$ and serve as guides for the eye. Here $\sigma=2$. Errors are of the order of the size of the circles, or smaller.

doubles the mean-field result. Although it is not surprising that MF and CT approximations give different results, it remains to be explained why $\nu_{CT}/\nu_{MF}=2$ *both* for linear and branched polymers.

It can be seen from figure 1 that $\nu=\frac{1}{2}$ fits our finite-size scaling results very well. We have plotted data for $\Lambda=10^{-3}$ and $\Lambda=0.5$, which are the extreme values used in our calculations, corresponding roughly to 'low' and 'high' degrees of branching. Note that the curve for $\Lambda=10^{-3}$ approaches the straight line with slope -2 slower than the $\Lambda=0.5$ curve: it takes greater values of N until the effect of branching appears explicitly in the former case rather than in the latter. As the behaviour of the curves is continuous in Λ, we have not plotted data for intermediate values of the branching-point fugacity.

Further, we should like to note that, as $\Lambda\to\infty$, only configurations that cover the lattice entirely are present, hence the number of bonds necessary in order to build an N-generation tree is

$$N_b=(\sigma^N-1)/(\sigma-1). \tag{15}$$

As the end-to-end distance of an N-generation tree is $R=N$ (see the paragraph preceding equation (6) above), one has

$$R\sim\lg N_b \qquad (N, N_b\to\infty). \tag{16}$$

As $R\sim N_b^{\nu}$ (McKenzie 1976), we can say that $\nu=0$ $(\Lambda\to\infty)$.

Since we have not found evidence that ν varies for finite, non-zero values of Λ, it is reasonable to conjecture that the behaviour of the correlation-length exponent for polymers on a Cayley tree is

$$\nu = \begin{cases} 1 & \Lambda = 0 \\ \frac{1}{2} & \Lambda \neq 0, \text{ finite} \\ 0(\lg) & \Lambda \to \infty. \end{cases} \tag{17}$$

We note that a discontinuous change in ν as one goes from linear to branched polymers has also been found by Family (1980) for a two-dimensional lattice, within the context of a two-parameter position-space renormalisation group. In other words, linear and branched polymers belong to different universality classes.

We have studied the statistics of linear and branched polymers on a Cayley tree. The existence of branching points has been included through a branching-point fugacity, Λ. Although in the limit of low degree of branching, this coincides to first order with a probabilistic interpretation, it is not clear whether both approaches yield the same results for higher concentrations of polyfunctional units. In particular, for finite-dimensional lattices the possibility arises that an uncorrelated probabilistic treatment of branching leads implicitly to the inclusion of loop formation in the statistics. In the present case, a fugacity approach yields correct results in the $\sigma = 2$, $\Lambda = 1$ limit discussed above, which would not happen had we treated branching points probabilistically and considered the limit of branching probability $= \frac{1}{2}$.

We have made use of finite-size scaling arguments in order to find the correlation-length exponent ν for branched polymers on a Cayley tree. Our results are consistent with $\nu = \frac{1}{2}$, different from the mean-field value $\nu_{MF} = \frac{1}{4}$. This gives independent support to the idea that MF and CT approximations are not equivalent in principle, although in some cases they may give the same results, as happens for the critical exponents of percolation.

Finally, we propose that the value of ν on a Cayley tree changes abruptly from $\nu = 1$ ($\Lambda = 0$, linear polymers) to $\nu = \frac{1}{2}$ ($\Lambda \neq 0$, finite, branched polymers) and that it equals zero (logarithmic divergence) as Λ grows infinitely large.

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