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Flory approximant for self-avoiding walks near the theta-point on fractal structures

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Abstract. — We present a Flory approximant for the size exponent and the crossover exponent of a self-avoiding walk at the theta-point on fractal structures. This approximant involves the three fractal dimensionalities for the backbone, the minimal path, and the resistance of the fractal structures.

There has been much interest in the statistics of a single linear polymer [1, 2] with quenched randomness [3–16]. At high temperature T or in good solvents, where the excluded volume interaction between two non-bonded nearest neighbor monomers prevails over their attractive interaction, usually this statistics is described by that of self-avoiding walks (SAWs) [1, 2] with the same randomness. In the presence of dilution it has been shown that for $p > p_c$ (p is the probability of each bond being occupied and p_c is the percolation threshold) SAWs on a dilute lattice belong to the same universality class of SAWs on a pure lattice [3, 5 – 7, 10, 14]. For SAWs on the incipient infinite cluster at the percolation threshold Aharony and Harris (AH) [13] presented a Flory approximant for the exponent ν describing the scaling of the mean square end-to-end distance $\langle R^2 \rangle \sim N^{2\nu}$ of SAWs of N -steps on fractal structures [12, 15]. For a long time there had been a debated question whether the randomness changes the universality class of SAWs at $p = p_c$ from that on a pure lattice. Recently Meir and Harris [14] answered this question and showed by the renormalization group theory that it is described by a fixed point different from the one on a pure lattice. Also their numerical results, obtained using series, are very close to the prediction from AH and exclude the pure lattice values for Euclidean dimensions higher than 2.

As T decreases, or the solvent becomes poor, there is a special temperature $T = \Theta$ at which the (two body) excluded volume and the attractive interaction compensate each other, therefore the three body interaction starts to play a role [1, 2, 17, 18]. As a result, the chain behaves closer to ideal. Also a single linear polymer at its Θ -point is usually modeled by self-attracting SAWs on a lattice. It is interesting to see how the quenched randomness affects the asymptotic statistical behavior of SAWs at the Θ -point (Θ -SAWs). In this paper we present a new Flory approximant for the size exponent ν_Θ and the crossover exponent ϕ of Θ -SAWs on fractal structures.

Our starting point is based on the work of AH [11, 13, 16] and follows the standard procedure for Flory formulae [1, 2]. In general one can write the probability of a single linear polymer of N monomers to have a linear dimension R as $\exp(-F)$, with

$$F = \left(\frac{R^{d_{w,B}}}{N} \right)^\alpha + \frac{1}{2}v \left(\frac{N^2}{R^{D_B}} \right) + \frac{1}{6}w \left(\frac{N^3}{R^{2D_B}} \right) + \dots \quad (1)$$

The first term is the entropic contribution due to the probability of finding a regular random walk whose end-to-end distance is R after N -steps, where $d_{w,B} = D_B + \tilde{\zeta}_R$ is the fractal dimension of random walks on the backbone and $\tilde{\zeta}_R$ is a resistance exponent. The value of α , for typical random walks, has been argued by Harris and Aharony [11] to be

$$\alpha = \frac{d_{\min}}{d_{w,B} - d_{\min}}, \quad (2)$$

where d_{\min} is the fractal dimension of the minimal (or chemical) path. The second term in equation (1) is the two body interaction contribution, which may be repulsive or attractive depending on the sign of the interaction parameter v , and the third term is the three body interaction contribution, with the interaction parameter w . The last two terms use the mean-field approximation, in the sense that one replaces a concentration c of monomers by the average concentration $\bar{c} = N/R^{D_B}$, where D_B is the fractal dimension of the backbone (the polymer is restricted to the backbone, since its self-avoidance prevents it from coming back out of dangling bonds). Both v and w contain factors of $1/k_B T$, and thus become unimportant at high T . For regular SAWs, with $v > 0$ and $w = 0$, AH [13] minimized F in equation (1) and found that

$$\nu_{\text{SAW}} = \frac{1}{D_{\text{SAW}}} = \frac{2 + \alpha}{D_B + \alpha d_{w,B}} \quad (3)$$

The same expression was also found by others [12, 15], using different arguments. At the Θ -point, v vanishes since the (two body) repulsive and attractive interactions compensate each other. Minimization of equation (1) with respect to R immediately yields our new Flory approximant,

$$\nu_\Theta = \frac{1}{D_\Theta} = \frac{3 + \alpha}{2D_B + \alpha d_{w,B}} \quad (4)$$

Note that for the non-dilute case ($p = 1$), $D_B = d$, $d_{w,B} = 2$ and $d_{\min} = 1$, and equations (2) - (4) recover the usual Flory results $\nu_{\text{SAW}} = 3/(d + 2)$ and $\nu_\Theta = 2/(d + 1)$.

In table I we list the predictions from equation(4) for Θ -SAWs on the infinite percolation cluster at $p = p_c$ together with those for SAWs from AH (Eq.(3)) for $d = 2, 3, 4$, and ≥ 6 respectively. First, we notice that $\nu_{\text{SAW}} \geq \nu_\Theta$ for every d , which makes sense physically. Second, ν_Θ is always larger than the pure lattice values ($\nu_\Theta = \frac{4}{7}$ and $\frac{1}{2}$ for $d = 2$ and ≥ 3), which tells us that the dilution of sites swells the polymer. This is to be expected: the dilution of sites increases effectively the excluded volume interaction (or introduces a long range excluded volume interaction) between monomers, since it eliminates some spatial region where a chain can be embedded. Therefore it makes a chain more swollen than a chain on a pure lattice for a given Euclidean dimension d . We also observe that the inequalities, $d_{\min} \leq D_{\text{SAW}} \leq D_\Theta \leq D_B$ hold for every d . These inequalities are exact for our approximants, and follow from the fact that $d_{\min} \leq D_B$.

On regular lattices, the Flory formulae quoted above work only for $d \leq d_u$, with the upper critical dimensions $d_u = 4$ for SAWs and $d_u = 3$ for Θ -SAWs. For $d > d_u$, one recovers the

Table I. — Estimates for the Flory approximant for the size exponent ν_{SAW} and ν_{Θ} , and the crossover exponent ϕ on the incipient infinite percolation cluster at $p = p_c$. The values of d_{min} , D_B , and $d_{w,B}$ are cited from reference [13].

d	d_{min}	D_B	$d_{w,B}$	$D_{\text{SAW}} = 1/\nu_{\text{SAW}}$	$D_{\Theta} = 1/\nu_{\Theta}$	ϕ
2	1.13	1.62	2.61	$1.31 \simeq 1/0.76$	$1.39 \simeq 1/0.72$	0.17
3	1.36	1.83	3.14	$1.53 \simeq 1/0.65$	$1.62 \simeq 1/0.62$	0.14
4	1.62	1.94	3.53	$1.73 \simeq 1/0.58$	$1.79 \simeq 1/0.56$	0.09
≥ 6	2	2	4	$2 = 1/0.5$	$2 = 1/0.5$	0

non-interacting behavior $N \propto R^2$. In our case we never recover the analogous behavior $N \propto R^{d_{w,B}}$. However, equations (3) and (4) yield $D_{\text{SAW}} = D_{\Theta} = D_B$ for $d > 6$. This is a direct consequence from the fact that loops are irrelevant for $d > 6$, and the polymer simply follows the singly connected backbone, as in one dimension. This probably results in the absence of a Θ -point for $d > 6$, and identifies $d = 6$ as an upper critical dimension.

We now turn to the vicinity of the Θ -point, with a small $v \propto (T - \Theta)$. One can describe the crossover from the Θ -SAWs behavior to that of SAWs by minimizing equation (1) with respect to N , keeping both two body and three body interaction terms ($v \neq 0, w \neq 0$). This yields

$$R = N^{\nu_{\Theta}} \left[\frac{w}{2\alpha} + \frac{v}{\alpha} \frac{R^{D_B}}{N} \right]^{\frac{\nu_{\Theta}}{3+\alpha}} \tag{5}$$

This expression can be written as the scaling form

$$R \sim N^{\nu_{\Theta}} f [(T - \Theta) N^{\phi}] , \tag{6}$$

and the crossover exponent ϕ is identified as

$$\phi = D_B \nu_{\Theta} - 1 . \tag{7}$$

The resulting values of ϕ for the the incipient infinite percolation cluster at $p = p_c$ are also listed in table I. The scaling function $f(x)$ behaves as a constant for $x \rightarrow 0$, and as $x^{1/(D_B + \alpha d_{w,B})}$ for $x \rightarrow +\infty$. The crossover will occur when νN^{ϕ} is of order w , i.e. when $N \propto (T - \Theta)^{-1/\phi}$. For $T < \Theta$, i.e. $v < 0$, we expect a collapsed phase with $N \propto R^{d_{\text{max}}}$, where d_{max} is the fractal dimension of the longest SAWs on the cluster. However, this collapse is not contained in equation (1). The fact that $\phi > 0$ for all $d < 6$, and ϕ vanishes at $d = 6$, also identifies $d = 6$ as a border line dimension at which we may expect logarithmic corrections.

Recently Roy, Chakrabarti, and Blumen [19] attempted to construct a Flory approximant for the size exponent of SAWs and Θ -SAWs at $p = p_c$. However, they started with a particular choice of the probability distribution function based on *ad hoc* assumptions which have no convincing physical justification. In particular, their argument yields a discontinuity at $d = 3$ for SAWs and $d_s^B = 3$ for Θ -SAWs, where d_s^B is the spectral dimension on the incipient infinite percolation cluster

at $p = p_c$. Also, unlike our expression, their results do not reproduce the correct entropic behavior (the first term in Eq.(1)) at high T .

Finally we consider Θ -SAWs on the Sierpinski gasket (SG) in two and three dimensions. Real-space renormalization group calculations were used to show that no Θ -point exists on the two dimensional SG [20, 21]. On the three dimensional SG, these calculations yielded $\nu_\Theta \simeq 0.529$, and 0.507 for a length rescaling parameter $b = 2$, and 3 respectively [20, 22]. Our equation (4), for the SG, yields $\nu_\Theta \simeq 0.762$, and 0.749 in two dimensions, and $\nu_\Theta \simeq 0.645$, and 0.622 in three dimensions for $b = 2$, and 3 respectively.

At present, we are not aware of any numerical evaluations of ν_Θ on the incipient infinite percolation cluster at $p = p_c$, with which we can compare our results. We are currently carrying out exact series enumeration calculations, which may yield some such comparison in the future.

In conclusion, we have presented a new Flory approximant for the vicinity of the Θ -point on fractals, based on an approach which unifies the treatment of SAWs and Θ -SAWs.

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