Journal of Statistical Physics, Vol. 61, Nos. 3/4, 1990

Theta-Point Exponent for Polymer Chains on Percolation Fractals

A. K. Roy,[1,2] **B. K. Chakrabarti,**[3] **and A. Blumen**[1]

Received May 25, 1990; final June 1, 1990

We derive a new expression for the Flory exponent describing the average radius of gyration of polymer chains at the theta point. For this we make use of the appropriate distribution function for the radius of gyration. We start from Euclidean lattices and extend the results to percolation fractals, by taking into account the basic geometry and the topology of such structures. We show that such basic features have a very prominent effect on the Flory exponent of the chain polymer on fractals at the theta point.

KEY WORDS: Theta point; self-avoiding walks; percolation; fractals; random walks; Flory approximation.

The manifestation of the excluded-volume effect on polymer chains on percolation fractals in the high-temperature self-avoiding-walk (SAW) limit ($T > \theta$) is still being debated,[1-3] principally because the effect seems to be very small.[2] Recently, the question of the effect on the tricritical size exponent ν^θ for polymers on percolation fractals (at temperatures around and at $T = \theta$) has been addressed[4]: in this work, using a straightforward derivation, the authors find a somewhat pronounced effect on ν^θ. In this paper we obtain, using a scaling method, a generalized Flory formula for ν^θ: we derive the expressions for ν^θ both for Euclidean spaces and also for percolation fractals. Comparison of our results leads us to find clear differences between the corresponding ν^θ values.

Now, for two-dimensional Euclidean spaces ν^θ was obtained by de Queiroz[5]; his derivation incorporates the screening effect[6] of the

---

[1] Physikalisches Institut and BIMF, University of Bayreuth, D-8580 Bayreuth, Germany.

[2] Santipur College, Nadia 741404, India.

[3] HLRZ, c/o KFA Jülich, D-5170 Jülich, Germany, and Saha Institute of Nuclear Physics, Calcutta 700009, India.

long-range three-body repulsion term (the two-body terms are zero at the theta point). Here we study the θ-point transition by using a phenomenological approach which takes into account the basic geometry of the polymer chain. We show that de Queiroz$^{(5)}$ result can be obtained by an independent argument from a Flory-type formula, which makes use of very general distribution function forms for the radius of gyration.$^{(7-9)}$ This Flory expression is then extended to percolation fractals, essentially following the same procedure as for the SAW limit$^{(8)}$ and for branched polymers on percolation fractals.$^{(9)}$ In refs. 8 and 9 such extensions have been shown to be quite accurate and to agree with the existing results for SAW$^{(10)}$ and branched polymers$^{(11)}$ on regular and nonrandom fractals.

We start from the pure lattice case. Let $G_N(r)$ denote the number of configurations of a polymer chain of N monomers at the θ point, where r is the *radius of gyration* (*not* the end-to-end distance). We follow the spirit of the arguments given by Lhuillier$^{(7)}$ and Roy and Blumen.$^{(8)}$ Thus, $G_N(r)$ must be exceedingly low in two extreme situations:

(a) When $r < N^{1/d}$, because then the minimum radius of gyration corresponds to that of a collapsed chain.

(b) For very extended chains, where $r > N^x$. The Monte Carlo calculations$^{(6)}$ for polymer chains at the θ point indicated that the short-range SAW condition remains intact, though the two-body attractions cancel the long-range two-body repulsions at $T = \theta$. We take into account this fact with the help of our parameter x above. We know that $d = 3$ is the upper critical dimension of polymer chains at the θ point, i.e., for $d = 3$ there does not exist any excluded-volume condition and the chain behaves in a mean-field-like way. Therefore, for $d = 3$ at $T = \theta$ the short-range SAW condition can have no effect on polymer chain topology, as the long-range three-body term is already irrelevant and thus the chain can be stretched to its maximal length N. This means the parameter x equals 1 for $d \geqslant 3$. But for $d < 3$ the topology of the chain for large r at $T = \theta$ is affected by the short-range SAW condition because there prevails a long-range excluded-volume effect and thus the chain at $T = \theta$ for $d < 3$ cannot be stretched more than its average SAW ($T > \theta$) radius ($\approx N^{\nu^{\mathrm{SAW}}}$). The parameter x then changes discontinuously from 1 (for $d \geqslant 3$) to ν^{SAW} (for $d < 3$). This type of situation at $T = \theta$ was also considered by de Queiroz$^{(5)}$ in an usual Flory-type calculation, by making the long-range three-body repulsive energy screened by the short-range SAW condition for $d = 2$.

We thus assume that the probability distribution function $P_N(r)$, defined by $P_N(r) = G_N(r)/G_N$, where G_N is the total number of configurations, has the form$^{(7-9)}$

$$P_N(r) \approx \exp\left\{-N\left[C_1\left(\frac{N}{r^d}\right)^{\alpha} + C_2\left(\frac{r}{N^x}\right)^{\delta}\right]\right\} \qquad (1)$$

Thus, for small r the free energy of the chain is dominated by a term $(N/r^d)^\alpha$, which may be thought to arise from the three-body long-range repulsive energy (as noted, the two-body long-range repulsive energy is balanced by the two-body attractive energy at $T=\theta$). For large r the free energy is dominated by the term $(r/N^x)^\delta$, which represents the contribution of the configurational entropy. In Eq. (1), α and δ are unknown exponents, to be determined at a later stage.

Now, the most probable radius of gyration r_0 of a chain at the θ point is given by the maximum of $P_N(r)$. Thus, with ν^θ being the polymer size exponent at the θ point, $\langle r_0^2 \rangle \sim N^{2\nu^\theta}$, and therefore (with $x=1$ for $d \geqslant 3$ and $x=\nu^{\mathrm{SAW}}$ for $d<3$),

$$\begin{aligned} \nu^\theta &= \frac{1+\nu^{\mathrm{SAW}}K}{d+K} \qquad \text{for} \quad d<3 \\ \nu^\theta &= \frac{1+K}{3+K} \qquad \text{for} \quad d\geqslant 3 \end{aligned} \tag{2}$$

Here K is the (positive) exponent ratio,

$$K=\delta/\alpha \tag{3}$$

It is to be noted that ν^θ depends on the ratio K, a typical property of the radius-of-gyration distribution function, but not on the individual values of δ and α.

To the best of our knowledge, there does not exist any precise estimate for the distribution of the radius of gyration (1) for a chain at the θ point. This prevents us from having any precise values for the exponents α and δ. We are thus restricted to calculating ν^θ by using mean-field estimates for α and δ. Now, since the first term in the exponential factor in Eq. (1) represents the three-body repulsive energy, one may expect from a mean-field point of view that

$$\alpha=2$$

Similarly, the second term in the exponential factor in Eq. (1) represents the influence of the configurational entropy; following Lhuillier$^{(7)}$ we have

$$\delta=2$$

It follows that the mean-field value of K equals $\delta/\alpha=1$. Inserting this value, $K=1$, and also the Flory mean-field estimate of $\nu^{\mathrm{SAW}}=3/(2+d)$ into Eq. (2), we get

$$\nu^\theta=\frac{d+5}{(d+2)(d+1)} \qquad \text{for} \quad d<3 \tag{4a}$$

$$\nu^\theta=\frac{1}{2} \qquad \text{for} \quad d\geqslant 3 \tag{4b}$$

Equation (4a) gives a reasonably good estimate for $d=2$ ($\nu^\theta=7/12$), which is only within 2% off the conjectured exact value$^{(12)}$ $\nu^\theta=4/7$. Actually, $\nu^\theta=7/12$ for $d=2$ was also found by de Queiroz$^{(5)}$ using a generalized Flory formula. It has to be noticed that the derivation in ref. 5 incorporated the screening of the three-body long-range repulsive energy term: there the short-range SAW condition persists,$^{(6)}$ although the long-range two-body repulsive terms are canceled by long-range attractive energy terms. On the other hand, in ref. 5 the elastic energy part in the free energy of the chain at θ point was left unchanged. The ensuing free energy (in the mean-field limit) has the following structure, in which constant coefficients are omitted:

$$F_N^{\mathrm{dQ}} \approx \frac{1}{N^{d\nu^{\mathrm{SAW}}-1}}\left(\frac{N^3}{r^{2d}}\right)+\frac{r^2}{N} \tag{5}$$

According to our radius-of-gyration distribution [Eq. (1)], the free energy of polymer chains at $T=\theta$ becomes in the mean-field limit

$$F_N \approx \frac{N^3}{r^{2d}}+\frac{r^2}{N^{2\nu^{\mathrm{SAW}}-1}} \tag{6}$$

These two free energy expressions [Eqs. (5) and (6)] are very different; but the derivation of the average radius of gyration, being determined by the minimum of these two free energies with respect to r [Eqs. (5) and (6)], gives the same result for ν^θ if for ν^{SAW} the Flory mean-field value $\nu^{\mathrm{SAW}}=3/(2+d)$ is used.

Next we study ν^θ for percolation fractals. At the start we mention that for percolation fractals in two dimensions a collapse transition can occur at finite temperatures.$^{(13)}$ Furthermore, this transition temperature is quite different from that for the pure lattice case. Thus, it is very important to establish the effect of percolation fractal characteristics on ν^θ.

We consider the backbone of the percolation fractal; note that the polymer chain is restricted to the backbone, otherwise it would be trapped in the dangling ends. The chain, in the SAW limit ($T>\theta$), is at its upper critical dimension if $d_S^B \geqslant 4$ (see, e.g., ref. 8), where d_S^B is the fracton (or spectral) dimension of the backbone of the percolation fractal.$^{(14)}$ Using similar reasoning, we can say that polymer chains at the θ point reach their upper critical dimension on percolation fractals if $d_S^B \geqslant 3$.

Let us again determine the distribution $P'_N(r)$ of the radius of gyration: we use the prime to distinguish the expression from the pure lattice case. Following ref. 8 and the previous discussion for chains on pure lattices, we observe that $P'_N(r)$ must decrease strongly (a) for $r<N^{1/d_B}$, where d_B is the fractal dimension of the backbone,$^{(15)}$ and (b) for $r>N^{\nu}$.

For $d_S^B < 3$, $y = \nu_c^{\mathrm{SAW}}$, where ν_c^{SAW} is the polymer size exponent (in the SAW limit, $T > \theta$) on the percolation fractal; and $y = 1/d_{\min}$ for $d_S^B \geqslant 3$, where $d_{\min}$ is the fractal dimension of the shortest (chemical) path on the percolation fractal.(14)

Thus we have

$$P'_N(r) \approx \exp\left\{-N\left[C_1\left(\frac{r}{N^{d_B}}\right)^{\alpha'} + C_2\left(\frac{N}{r^y}\right)^{\delta'}\right]\right\} \tag{7}$$

Maximizing with respect to r, we obtain

$$\begin{aligned} \nu_{p_c}^{\theta} &= \frac{1 + \nu_{p_c}^{\mathrm{SAW}} K'}{d_B + K'} && \text{for} \quad d_S^B < 3 \\ \nu_{p_c}^{\theta} &= \frac{1}{d_B}\,\frac{d_B + K' d_L^B}{d_B + K'} && \text{for} \quad d_S^B \geqslant 3 \end{aligned} \tag{8}$$

where $\nu_{p_c}^{\theta}$ is the polymer size exponent at $T = \theta$ on the percolation fractal; in Eq. (8), K' $(=\delta'/\alpha')$ is a (positive) exponent ratio and d_L^B $(=d_B/d_{\min})$ is the spreading (or connectivity) dimension of the backbone of the percolation fractal.(14)

Next we calculate the mean-field estimate of $\nu_{p_c}^{\theta}$. The mean-field values for δ' and α' are, respectively, $\delta' = 2d_B/(2d_L^B - d_S^B)$ (ref. 8) and $\alpha' = 2$ (ref. 7); from this mean-field estimate K' turns out to be $K' = d_B/(2d_L^B - d_S^B)$. Taking from Roy and Blumen(8) the value of $\nu_{p_c}^{\mathrm{SAW}} = (4d_L^B - d_S^B)/d_B(2 + 2d_L^B - d_S^B)$, we have from Eq. (8)

$$\nu_{p_c}^{\theta} = \frac{1}{d_B}\,\frac{2 + (2d_L^B - d_S^B)(3 + 2d_L^B - d_S^B)}{(2 + 2d_L^B - d_S^B)(1 + 2d_L^B - d_S^B)} \qquad \text{for} \quad d_S^B < 3 \tag{9a}$$

$$\nu_{p_c}^{\theta} = \frac{1}{d_{W,B}} \qquad \text{for} \quad d_S^B \geqslant 3 \tag{9b}$$

where $d_{W,B}$ $(=2d_B/d_S^B)$ is the fractal dimension of random walks on the backbone of percolation fractals.(15)

Dhar and Vannimenus(16) solved exactly the θ point chain problem on Sierpinski gaskets in 3 dimensions and they found $\nu_{p_c}^{\theta} = 0.529\ldots$; our Eq. (9a) yields $\nu_{p_c}^{\theta} = 0.565$, only 6.7% off the exact value. Thus, using Eq. (9a), we predict that one should have $\nu_{p_c}^{\theta} \cong 0.678$ and $\nu_{p_c}^{\theta} \cong 0.611$ for percolation fractals in $d = 2$ and $d = 3$. By comparison, we see that these $\nu_{p_c}^{\theta}$ values are very different from the corresponding values for the pure lattices, where $\nu^{\theta} = 4/7$ and $\nu^{\theta} = 1/2$, respectively. Thus, we infer that the percolation fractal characteristics should influence strongly the behavior of chain polymers at $T = \theta$. Moreover, from Eq. (9a) we see that $\nu_{p_c}^{\theta} = 1/2$ on $d = 6$

percolation fractals, which supports the conjecture of Roy and Blumen(8) that there will be no finite-temperature collapse transition (i.e., $\theta = 0$) of polymer chains on $d = 6$ percolation fractals, a fact which stems from the topology of the fractal structure itself.

In conclusion, we have shown that, using the radius-of-gyration distribution function, one obtains a good Flory approximant for polymer chains at $T = \theta$ in Euclidean spaces. We have extended this method to percolation fractals and we found that the geometry and topology of percolation fractals strongly influence the size exponent of polymer chains at $T = \theta$. It would be interesting to compare our formula (9a) with accurate Monte Carlo simulations or exact enumeration calculations.

ACKNOWLEDGMENTS

We are grateful to Prof. D. Stauffer for helpful comments. B.K.C. is grateful to the Physics Department, University of Bayreuth for hospitality, where this work was finished. A.K.R. thanks the Deutscher Akademischer Austauschdienst (DAAD) for financial support through the award of a research fellowship. Grants from the Deutsche Forschungsgemeinschaft (SFB 213) and from the Fonds der Chemischen Industrie are gratefully acknowledged.

REFERENCES

1. A. K. Roy and B. K. Chakrabarti, *J. Phys. A* **20**:215 (1987).
2. S. B. Lee and H. Nakanishi, *Phys. Rev. Lett.* **61**:2022 (1988); S. B. Lee, H. Nakanishi, and Y. Kim, *Phys. Rev. B* **39**:9561 (1989).
3. Y. Meir and A. B. Harris, *Phys. Rev. Lett.* **63**:2819 (1989).
4. B. K. Chakrabarti and S. M. Bhattacharjee, *J. Stat. Phys.* **58**:383 (1990).
5. S. L. A. de Queiroz, *Phys. Rev. A* **39**:430 (1989).
6. K. Kremer, A. Baumgärtner, and K. Binder, *J. Phys. A* **15**:2879 (1981).
7. D. Lhuillier, *J. Phys.* (Paris) **49**:705 (1988).
8. A. K. Roy and A. Blumen, *J. Stat. Phys.* **59**:1581 (1990).
9. A. K. Roy and A. Blumen, *J. Chem. Phys.*, in press.
10. A. Aharony and A. B. Harris, *J. Stat. Phys.* **54**:1091 (1989).
11. M. Knežević and J. Vannimenus, *Phys. Rev. B* **35**:4988 (1987).
12. B. Duplantier and H. Saleur, *Phys. Rev. Lett.* **59**:539 (1987); P. H. Poole, A. Coniglio, N. Jan, and H. E. Stanley, *Phys. Rev. Lett.* **60**:1203 (1988).
13. K. Barat, S. N. Karmakar, and B. K. Chakrabarti, SINP preprint (1990).
14. H. E. Stanley, in *On Growth and Form*, H. E. Stanley and N. Ostrowsky, eds. (NATO ASI Series E, No. 100, 1986).
15. D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).
16. D. Dhar and J. Vannimenus, *J. Phys. A* **20**:199 (1987).

Communicated by D. Stauffer