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Short Communication

Theta-Point Exponent for Polymer Chain in Random Media

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Using field-theoretic arguments for self-avoiding walks on dilute lattices with site occupation concentration p, we show that the θ-point size exponent ϑ_p^θ of polymer chains remains unchanged for small disorder concentration ($p > p_c$). At the percolation threshold $p = p_c$, using a Flory-type approximation, we conjecture that $\vartheta_{p_c}^\theta = 5/(d_B + 7)$, where d_B is the percolation backbone dimension. It shows that the upper critical dimensionality for the θ-point transition at $p = p_c$ shifts to a dimension $d_c > 3$. We also propose that the θ-point varies practically linearly with p for $1 > p \geqslant p_c$.

KEY WORDS: θ-point; self-avoiding walks; percolation; fractals; renormalization group; Flory approximation.

1. INTRODUCTION

The statistics of self-avoiding walks (SAW) on lattices with quenched random impurities is presently being investigated with keen interest.[(1-7)] Apart from some extensions to correlated disorder,[(6)] or to more elaborate (log) configurational averagings,[(7)] most of these studies investigated the end-to-end size exponent of the SAWs on percolation clusters (see, e.g., ref. 8). In the context of polymers in, say, a porous medium (a realization of a quenched random medium), such walk statistics corresponds to the infinite-temperature situation; or, more specifically, to a temperature T above the polymer–solvent theta point θ (appropriate for the porous media), below which a collapse transition takes place.[(9,10)] The essential

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finding, so far, for this swollen chain phase ($T > \theta$), has been that the polymer size exponent $\vartheta_p^{\mathrm{SAW}}$ does not change from the pure SAW exponent $\vartheta_0^{\mathrm{SAW}}$ for any amount of disorder concentration $c = 1 - p$ below the percolation threshold value $c_c = 1 - p_c$.(11-13) At $p = p_c$, the exponent crosses over to a new value $\vartheta_{p_c}^{\mathrm{SAW}}$ ($> \vartheta_0^{\mathrm{SAW}}$), determined by the excluded volume effect on the percolation fractal.(13–15,4,5) The upper critical dimensionality also shifts to $d_c = 6$ ($\vartheta_{p_c}^{\mathrm{SAW}} = 1/2$ for $d \geqslant 6$(2,4)). These theoretical estimates for the $\vartheta_{p_c}^{\mathrm{SAW}}$ value are, however, considerably higher than the Monte Carlo estimates,(3,14) except for a recent enumeration result on percolation clusters which agrees with the analytical results.(4)

As mentioned before, all these studies on SAW statistics on random lattices correspond to the swollen polymer chain phase at $T > \theta(p)$, where $\theta(p)$ denotes the polymer solvent θ-point appropriate to the porous medium. In this paper, we consider the behavior of the polymer chain at and below the theta point.

2. SIZE EXPONENT AT THE THETA POINT FOR $p > p_c$

For studying SAW statistics on site diluted lattices, we start with the standard n-vector magnetic model with dilution

$$H = -\sum_{(ij)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \qquad J_{ij} = J_0 c_i c_j, \qquad c_i = 0, 1 \tag{1}$$

and write the effective continuous spin Hamiltonian as(12)

$$\begin{aligned} H = {} & \sum_q \sum_\alpha (r + q^2)\, \mathbf{S}_q^\alpha \cdot \underline{\mathbf{S}}_q^\alpha \\ & + \sum_{q_1} \sum_{q_2} \sum_{q_3} \sum_{q_4} \sum_{\alpha, \beta} (u\delta_{\alpha\beta} - v) \\ & \times \mathbf{S}_{q_1}^\alpha \cdot \mathbf{S}_{q_2}^\alpha \mathbf{S}_{q_3}^\beta \cdot \mathbf{S}_{q_4}^\beta \delta(q_1 + q_2 + q_3 + q_4) \end{aligned} \tag{2}$$

Here S is the n-component spin vector, $\alpha = 1, 2, \ldots, m$ is the replica index coming from averaging over the quenched randomness, u is generally a measure of the two-body (repulsive) interaction, and $v = J_0^2 c(1 - c)$. To get the polymer (SAW) statistics from this n-vector model, we have to take the $n \to 0$ limit,(9) and for the quenched configurational averaging, we need the $m \to 0$ limit. However, as shown by Kim,(12) because of the simultaneous appearance of n and m, both going to zero, the replica coupling effectively disappears in this limit. The sole effect of the disorder is to reduce the two-body interaction term to $u_{\mathrm{eff}} = u - v$. Writing $u_{\mathrm{eff}} = [T - \theta(p)]/\theta(p)$, one therefore finds that the critical behavior is governed by the excluded-volume fixed point of pure SAWs for $T > \theta(p)$, giving $\vartheta_p^{\mathrm{SAW}} = \vartheta_0^{\mathrm{SAW}}$ for $p > p_c$.(12) However, as T is reduced, u_{eff} will cross the zero value, giving a tricritical behavior at the theta point.(9,16) The critical exponents for the theta point (since $u_{\mathrm{eff}} = 0$, the S^6 term is necessary for stability) and for the collapse phase ($u_{\mathrm{eff}} < 0$) should be identical to those of the polymer chain in pure solvent.

It is therefore concluded, thanks to the effective disappearance of the replica coupling in the $n \to 0$ limit, that the size exponent for the theta point and the collapse phase remain the same as in pure solvents(16,17) for any small amount of disorder:

$$\vartheta_p^c = \vartheta_0^c = \frac{1}{d} \quad \text{and} \quad \vartheta_p^\theta = \vartheta_0^\theta = \frac{1}{2} + \frac{2}{3}\frac{\varepsilon^2}{121} + O(\varepsilon^3) \tag{3}$$

$$\varepsilon = 3 - d$$

for $p > p_c$. This, in fact, was observed earlier, using similar field-theoretic techniques.(18,19)

3. SIZE EXPONENT AT THE THETA POINT FOR $p = p_c$

At $p = p_c$, the collapsed structure of the polymer chain at $T < \theta(p_c)$ should have the size exponent $\vartheta_{p_c}^c = 1/d_B$, since the dangling ends of the percolation cluster cannot contribute to the statistics of long polymers, and the collapsed dimension should be identical to that of the percolation backbone. In order to estimate the θ-point size exponent $\vartheta_{p_c}^\theta$ at $T = \theta(p_c)$, we use an approximate Flory-like formula, since the small-disorder expansion of the Hamiltonian in Eq. (2) is not adequate.

In the conventional Flory approximation, the theta-point size exponent is given by $\vartheta_p^\theta = 2/(D+1)$, where D is an appropriate dimension ($D = d$ for $p > p_c$).(10) For collapse in two dimensions ($D = d = 2$), this formula overestimates the exponent, which is known exactly to be 4/7.(17) However, for $D = d = 3$, this gives 1/2, which is indeed correct for the upper critical dimension $d = 3$.(9) In order to have a better estimate of this exponent, we use the correspondence, in two dimensions, between the percolation hull and the polymer chain conformation at the theta point(20)

$$(\vartheta^\theta)^{-1} = 1 + (\vartheta^p)^{-1} \tag{4}$$

where ϑ^p is the percolation correlation length exponent. From the known values of ϑ^θ and ϑ^p, we know that this relation is correct only in two dimensions, even though the error in other dimensions is quite small.

Ignoring this small correction, if we use the Flory value $\vartheta^p = 5/(D+2)$ for the percolation exponent,(21) we get

$$\vartheta^\theta = 5/(D+7) \tag{5}$$

This gives a reasonably good value for the theta-point size exponent for pure lattices ($p > p_c$): $\vartheta_0^\theta = 5/9 \simeq 0.56$, compared to $4/7 \simeq 0.57$ in $D = d = 2$, and $\vartheta_0^\theta = 1/2$ for $D = d = 3$, which is also correct for the upper critical dimension $d_c = 3$. The error in using Eq. (4) in dimensions higher than two is somehow canceled by the error in the Flory formula for the percolation exponent. This is probably another example of the strange cancellation in the Flory approximations.

We thus conjecture that at $p = p_c$, the polymer chain size exponent at the theta point $[T = \theta(p_c)]$ will be given by

$$\vartheta_{p_c}^\theta = 5/(d_B + 7) \tag{6}$$

where d_B is the percolation backbone dimension ($d_B \simeq 1.61$ and 1.75 in two and three dimensions, respectively(8)). In two dimensions, we therefore get $\vartheta_{p_c}^\theta = 0.58$ at $p = p_c$, compared to 0.57 for $p > p_c$, and expect this estimate to be particularly accurate, since the correspondence with percolation hull in Eq. (4) may still remain exact on $d = 2$ percolation clusters. In three dimensions, $\vartheta_{p_c}^\theta \simeq 0.57$. It may be noted that the upper critical dimension is no longer 3, but has shifted to $d_c > 3$, for which the backbone dimension is 3. This corresponds to a Euclidean dimension $d \simeq 4$.(8)

4. THETA POINT IN RANDOM MEDIUM

Up to now our analysis is based on the assumption of the existence of the theta point $[\theta(p) > 0]$ on the percolation cluster. To be concrete, we consider the problem of an interacting self-avoiding walk on random lattices, where there is an attractive energy for each pair of nonbonded nearest neighbors. A simple mean field estimate for the transition temperature for a pure lattice would be $\theta_0 = z - 1 - \mu_0$, where z is the coordination number of the lattice and μ_0 is the connectivity constant for the SAW. This comes from an estimate(22) for the average number of nearest neighbors of a site on a SAW. For dilute lattices the modification of this formula would be $\theta(p) = p(z-1) - \mu(p)$. It is, however, observed(23,13,4) that to a sufficiently good accuracy $\mu(p) = p\mu_0$, so that $\theta(p) = p\theta_0$. Even though the estimate for the theta point for pure lattices is not good compared to the well-known estimates,(24) we expect the p dependence of $\theta(p)$ [through $\mu(p)$] to be the right one. This suggests a nonzero value for the theta point even for $p = p_c$, given by $\theta(p_c) = p_c\theta_0$. This should be contrasted with the Ising model problem, for which there is no (finite-temperature) transition on a percolating cluster; a Peierls-type domain wall argument there generally shows the absence of a transition. Such is not the case for the collapse transition because of the nonexistence of a finite number of ground states.

5. SUMMARY AND DISCUSSION

We now summarize the results.

1. The theta-point behavior on dilute lattices $(1 > p > p_c)$ is similar to the pure $(p = 1)$ case.

2. At $p = p_c$, the theta-point behavior changes, giving $\vartheta^{\theta}_{p_c} = 5/(d_B + 7)$, and for the collpased phase $\vartheta^{c}_{p_c} = 1/d_B$. The upper critical dimension for the theta transition increases to $d_c > 3 (d_c \simeq 4)$. This change in d_c should be observable in real experiments such as those on polymers in porous medium.

3. The theta-point decreases almost linearly with p in the range $1 > p \geqslant p_c$. This, we believe, can also be checked in real experiments in porous medium and in computer simulations, even above the percolation threshold.

REFERENCES

1. B. K. Chakrabarti and J. Kertesz, *Z. Phys. B* **44**:221 (1981).
2. A. K. Roy and B. K. Chakrabarti, *J. Phys. A* **20**:215 (1987).
3. 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).
4. Y. Meir and A. B. Harris, Weizmann Institute preprint (1989).
5. S. Havlin and D. Ben-Avraham, *Adv. Phys.* **36**:695 (1987); A. Aharony and A. B. Harris, *J. Stat. Phys.* **54**:1091 (1989); J. P. Bouchaud and A. Georges, *Phys.* Rev. *B* **39**:2846 (1989); A. K. Roy and A. Blumen, *J. Stat. Phys.* (Submitted)
6. Y. Kim, *J. Phys. A* **20**:6047 (1987).
7. M. Kardar and Y. C. Zhang, *Phys. Rev. Lett.* **58**:2087 (1987); B. Derrida and R. B. Griffiths, *Europhys. Lett.* **8**:111 (1989); J. Cook and B. Derrida, CEN Saclay preprint (1989).
8. D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).
9. P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
10. Y. Oono, *Adv. Chem. Phys.* **61**:301 (1985).
11. A. B. Harris, *Z. Phys. B* **49**:347 (1983).
12. Y. Kim, *J. Phys. C* **16**:1345 (1983).
13. A. K. Roy and B. K. Chakrabarti, *Phys. Lett. A* **91**:393 (1982); P. Lam and Z. Q. Zhang, *Z. Phys. B* **56**:155 (1984); M. Sahimi, *J. Phys. A* **17**:L379 (1984).
14. K. Kremer, *Z. Phys. B* **45**:149 (1981).

15. R. Rammal, G. Toulouse, and J. Vannimenus, *J. Phys.* (Paris) **45**:389 (1984).
16. M. J. Stephen, *Phys. Lett. A* **53**:363 (1975).
17. B. Duplantier and H. Saleur, *Phys. Rev. Lett.* **59**:539 (1987).
18. A. K. Roy and B. K. Chakrabarti, unpublished (1986).
19. E. Helfand and G. H. Fredrickson, private communication (1987).
20. A. Coniglio, N. Jan, I. Majid, and H. E. Stanley, *Phys. Rev. B* **35**:3617 (1987); B. Sapoval, M. Rosso, and J. F. Gouyet, *J. Phys.* (Paris) **46**:L149 (1985).
21. J. Isaacson and T. C. Lubensky, *J. Phys.* (Paris) **41**:L469 (1980).
22. S. Bhattacharya and B. K. Chakrabarti, *Z. Phys. B* **57**:151 (1984).
23. B. K. Chakrabarti, K. Bhadra, A. K. Roy, and S. N. Karmakar, *Phys. Lett.* **93A**:434 (1983).
24. V. Privman and D. A. Kurtze, *Macromolecules* **19**:2377 (1986).