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Series studies of self-avoiding walks near the θ-point on 2D critical percolation clusters

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Abstract. The thermally weighted average end-to-end distance $\langle R_N \rangle$ of interacting self-avoiding walks (SAWs) are obtained here enumerating all the (finite) N-stepped SAW configurations on the infinite percolation cluster of bond diluted square lattice at the percolation threshold. Averaging over 250 percolation clusters and enumerating all the possible SAWs on them for N up to 31, $\langle \overline{R_N} \rangle$ is fitted to a scaling form $\langle \overline{R_N^2} \rangle \sim N^{2\nu^\theta} f(N^\phi \tau)$, where $\tau = (T-\theta)/\theta$ is the temperature interval away from the θ-point, ϕ is the crossover exponent and ν^θ is the tricritical size exponent. The best fit is obtained for $\theta \simeq 0.71$ (compared to $\theta_0 \simeq 1.54$ on a pure square lattice), $\nu^\theta \simeq 0.74$ (compared to $\nu_0^\theta = \frac{4}{7} \simeq 0.57$ in two dimensions) and $\phi \simeq 0.20$. We also obtain an estimate of the SAW size exponent ν^C for collapsed phase on the percolation cluster.

1. Introduction

The manifestation of the excluded volume effect of polymer chains trapped in a porous medium, modelled by self-avoiding walks (SAWs) on a quenched random lattice, has recently been studied with much interest [1–8]. While at high temperatures (or in good solvents) the statistics are still being debated (effect of percolation fractal in the random SAW limit) [1–5], the questions regarding the effect of percolation fractal on the tricritical θ-point [6] and on the tricritical size exponent ν^θ, have already been addressed [7, 8]. Unlike in the high temperature ($T > \theta$) SAW limit, where the percolation fractal effect on the SAW size exponent ν^S seems to be small (both theoretically [3, 4] and in simulations [2, 3, 5]), the effect of percolation fractal on the tricritical excluded volume size exponent ν^θ (at $T = \theta$) has been predicted to be quite prominent. In particular, the Flory approximation for ν^θ (Roy *et al* [7]) predicted (see the appendix) $\nu^\theta \simeq 0.68$ (compared to $\nu_0^\theta \simeq 0.58$ on a pure lattice with a similar approximation) and that of Chang and Aharony [8] predicts $\nu^\theta \simeq 0.72$ (compared to $\nu_0^\theta \simeq 0.66$, with their approximation on a pure lattice; exact $\nu_0^\theta = \frac{4}{7} \simeq 0.57$) on two-dimensional (2D) percolation clusters at the percolation threshold; both indicating large deviation (increase) from the pure lattice value. Also, a recent series study of the partition function zeros [6] indicated a non-vanishing theta point value: $\theta \simeq 0.67$ (in units of non-bonding nearest neighbour monomer–monomer interaction energy) on a bond diluted square lattice at the percolation threshold (compared to $\theta_0 \simeq 1.54$ on a pure square lattice). This (non-vanishing θ-point value) is quite significant in view of the ramified structure of the percolation cluster, and for observing the tricritical (at $T = \theta$) as well as the collapsed phase (at $T < \theta$) of SAWs on the percolation cluster.

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We report here the results of a series study of SAWs on a Monte Carlo generated percolation cluster on a bond diluted square lattice. The average end-to-end distance $\langle R_N \rangle$ of N-stepped SAWs on a critical percolation cluster, averaged using appropriate thermal weights determined by the ratio of the number of interacting bonds (with unit attractive interaction through the bonds between the nearest neighbour sites visited by the SAW) and the temperature T, is fitted, after configurational averaging over percolation clusters (denoted by overhead bar), to a scaling form

$$\langle \overline{R_N^2} \rangle \sim N^{2\nu^\theta} f(N^\phi \tau) \tag{1}$$

where $\tau \equiv (T-\theta)/\theta$, ϕ denotes the crossover exponent and f denotes the scaling function. Enumerating results for all the possible SAW configurations on the critical percolation clusters up to $N=31$, when averaged over about 250 percolation clusters, gives the best fit values as $\theta \simeq 0.71$, $\nu^\theta \simeq 0.74$ and $\phi \simeq 0.20$ for the θ-point as well as that for the tricritical behaviour at the θ-point on 2D percolation clusters. Our study also indicate $\nu^C \simeq 0.73$ (compared to $\nu_0^C = \frac{1}{2}$ in pure lattice) for the size exponent of the collapsed ($T < \theta$) SAW configuration on the critical percolation cluster.

2. Simulation and results

In the simulation we take an 80×80 square lattice. Using a Monte Carlo program we first generate the bond diluted lattice configuration and with bond occupation concentration $p = \frac{1}{2} = p_c$, the percolation threshold. We search for the cluster which connects the upper boundary to the lower boundary on the lattice and if there is a break, we discard that cluster and start searching for a new one. As soon as we get a connected cluster we isolate that cluster as the infinite (spanning) percolation cluster. Since at the percolation threshold the probability for the existence of the infinite percolation cluster is precisely zero, the probability of coming across a spanning cluster becomes increasingly lower with increasing lattice size and we actually simulate a rather small lattice size (80×80). The choice of the origin is immaterial as we check the cluster connectivity incorporating the periodic boundary condition. Let $C_{NM}(x, y)$ be the number of N-stepped SAWs having M nearest neighbours between non-consecutive vertices which terminate at the point (x, y), starting at $(0, 0)$. The average end-to-end distance for a particular configuration is given by

$$\langle R_N^2 \rangle = \frac{\Sigma_M \Sigma_x \Sigma_y (x^2+y^2) C_{NM}(x, y) \varepsilon^M}{\Sigma_M \Sigma_x \Sigma_y C_{NM}(x, y) \varepsilon^M} \tag{2}$$

where $\varepsilon = \exp[1/kT]$, with unit interaction between the nearest neighbour sites visited by a SAW.

On the critical percolation cluster, we enumerate exactly all the $C_{NM}(x, y)$ SAWs, starting from a suitable origin on the cluster. Then we evaluate the square of the average end-to-end distance $\langle R_N^2 \rangle$ from equation (2) for a particular configuration of the cluster. The values of $\langle R_N^2 \rangle$ are then evaluated over a wide range of temperatures T. We repeat this operation for 250 different configurations and vary the step size from $N=9$ to 31 (total CPU time used is 70 hours on an Intel 80486-based computer). The range of ε ($\equiv \exp[1/kT]$) is taken from 1.5 to 20.0. Finally we take the configurational average of the end-to-end distance squared $\langle R_N^2 \rangle$ at different temperature for each step.

$\langle R_N^2 \rangle$ for a pure square lattice is also estimated for SAWs with step size from 7 to 18 (the CPU time used is 9 hours for $N=18$ using the same computer) in the above

range of temperatures. Since the values of ν, ϕ and θ are well known for a pure lattice [9], we determine the values of those quantities as a check of the scaling law fitting procedure.

To obtain the values of ν^θ, ϕ and θ we proceed as follows. For best choice of the quantities ν^θ, ϕ and θ in the scaling relation (1), we expect that all experimental points collapse on to a single curve. For this purpose we plot $f(x)$ $[\equiv \langle \overline{R_N^2} \rangle / N^{2\nu^\theta}]$ as a function of x $[\equiv N^\phi \tau]$ for various combinations of ν^θ, ϕ and θ. For the percolation cluster series data, the optimal choices for these quantities are $\nu^\theta = 0.74 \pm 0.02$, $\phi = 0.2 \pm 0.1$ and $\theta = 0.71 \pm 0.08$ (see figure 1). It may be noted that the curve shown in figure 1 comes from the collapse of about 874 points (coming from 23 N values for $9 \leqslant N \leqslant 31$ at every temperature with 38 different temperatures considered). It may also be mentioned that, although the fitting is not very sensitive to minor changes in the value of ϕ, it is very sensitive to the values of θ and ν^θ. In fact, we find the fitting curve to be visibly destroyed for $\theta > 0.8$ and $\theta < 0.6$ and for $\nu^\theta > 0.76$ and $\nu^\theta < 0.72$. As a check and for comparison, the same fitting is repeated for the series data on a pure square lattice. The combination of $\theta = 1.4 \pm 0.1$, $\nu^\theta = \nu_0^\theta = 0.6 \pm 0.2$ and $\phi = 0.4 \pm 0.1$ gave the best fit (see inset figure 1). These values for the pure lattice case, obtained here using this scaling fit method, agree fairly well with the previous known estimates [9], the deviations being due to the small step size ($N \leqslant 18$) considered.

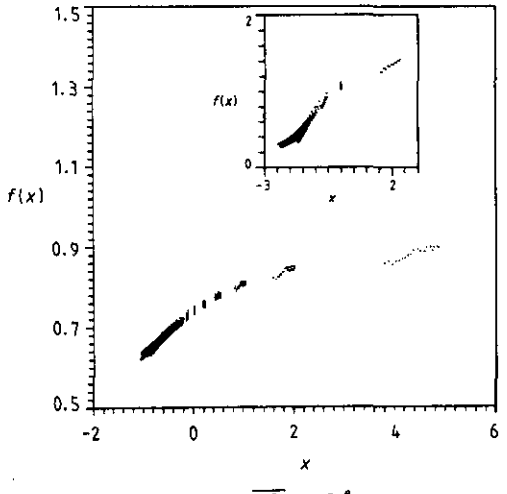

Figure 1. Plot of $f(x)$ $(\equiv \langle \overline{R_N^2} \rangle / N^{2\nu^\theta})$ against x $(\equiv N^\phi \tau)$ for the series data of SAWs on a bond diluted square lattice at the percolation threshold, with the best fit choice $\nu^\theta = 0.74$, $\phi = 0.2$ and $\theta = 0.71$. The inset is for a pure lattice (with $\nu_0^\theta = 0.6$, $\phi = 0.4$ and $\theta = 1.4$).

We also plot $\ln(\langle \overline{R_N^2} \rangle)$ against $\ln N$ at different temperatures. Since the variation in N covers a wide range ($9 \leqslant N \leqslant 31$; for percolation cluster series data), the slope of the straight line fit is expected to give a reasonable estimate of the effective size exponent ν at different temperatures (see inset figure 2). In figure 2 we plot these ν values as a function of temperature. At low temperatures ($0.5 < T < 0.6$) ν is seen to saturate to a (collapsed phase) value $\nu^C = 0.73$, while saturation at the high temperature region is not obtained for the temperature range studied ($T \leqslant 2.5$). Since no saturation in ν value is observed in the high temperature range and the ν value already reaches about 0.76 for the highest temperature considered, we believe $\nu^S \geqslant 0.76$ on a 2D critical percolation cluster.

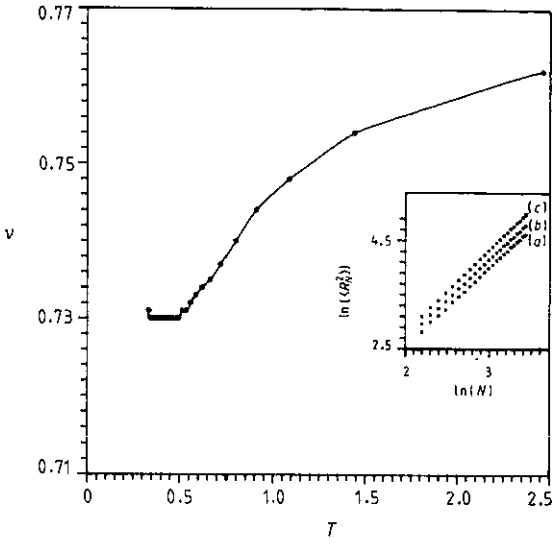

Figure 2. The effective size exponent ν as a function of temperature T from series data for SAWs on a bond diluted square lattice at the percolation threshold. The inset shows the plot of $\ln(\langle R_N^2 \rangle)$ against $\ln(N)$ for three different temperatures: (*a*) 0.34, (*b*) 0.72 and (*c*) 2.5.

The collapse of data as shown in figure 1 is an optimum one and the best-fit values for the parameters ν^θ, θ and ϕ (given above) have some spread which could not be eliminated because of the configurational fluctuations in the values of $\langle R_N^2 \rangle$. These fluctuations are, however, not much as can be seen from the raw data for $\langle R_N^2 \rangle$ for some typical temperatures, shown in the inset figure 2. Here, of course, the plots being on a log scale, fluctuations become less than the symbol size.

3. Discussion

First, we note that the best-fit estimate of θ, $\theta = 0.71 \pm 0.08$, agrees very well with the estimate ($\theta = K_\theta^{-1} \simeq 0.67 \pm 0.06$) from a similar study for the partition function zeros on the same lattice [6]. In fact, as mentioned before, this fitting procedure is quite sensitive to the choice of the θ-value. Also, a non-vanishing value of the θ-point on the critical percolation cluster is quite significant in view of the extremely ramified structure of the percolation cluster and indicates the significance of the blobs (multiply connected regions) [10] of the fractal structures for the SAW statistics. Also, it shows the collapse phase of the SAWs on the critical percolation cluster at $T < \theta$ where we find the size exponent ν^C to be around 0.73. However this estimate (from figure 2) is not expected to be accurate, the exponent value being considerably larger than the inverse of the fractal dimension d_B^{-1} ($\simeq 0.62$) [11] of the percolation cluster backbone, it indicates considerable frustration problem [12] of compactification in the collapsed phase. The same kind of estimate (see figure 2) suggests $\nu^S > 0.76$ for SAW size exponent for $T > \theta$, as no saturation could be observed for the temperature range considered ($T \leq 2.5$). This trend for an increased value of ν^S is also consistent with other series study estimates [3, 5], which indicate $\nu^S \simeq 0.8$, compared to $\nu_0^S = \frac{3}{4} = 0.75$ for a pure 2D lattice (however, see [13]). Of course, Monte Carlo studies [2] do not indicate a similar

increase in ν^S. The reason [12] for such discrepancies seems to be the fact that the percolation fractal contains self-similar blobs of all sizes (length scale) connected by linearly or singly connected links [10], through which the diffusion of the SAW in the Monte Carlo method becomes extremely difficult (effective barrier height increases exponentially with the link length). This forces the Monte Carlo generated SAWs on the percolation cluster to be confined practically to a single blob and the SAW misses the enormous amount of configurational entropy in the next blob, which would be available once it diffuses through the link barrier. For small step sizes, therefore, the SAW sees the fractal structure of the typical blob (in which the SAW finds itself), giving effectively the ν^S for its size exponent. As it grows beyond the length scale up to which the blob appears as fractal (which, in turn, depends on the size of the percolating lattice considered), the size exponent crosses over to that (ν_0^S) for the compact Euclidean lattice, and when step size increases further the SAW makes a further crossover to an even smaller size exponent ν^C ($\simeq 0.73$ in 2D, as obtained here) for the collapsed phase. In exact enumeration, however, the SAW is forced to see the fractal beyond a single blob in which a Monte Carlo generated SAW becomes typically localized due to the exponentially large entropic barrier trap.

Most importantly, the scaling fit of these series results given $\nu^\theta = 0.74 \pm 0.02$, which is considerably higher than its pure lattice value ν_0^θ ($=\frac{4}{7} \simeq 0.57$) in 2D. Although a significant increase in the tricritical size exponent was predicted by the Flory approximations for ν^S [7, 8], the predicted values do not compare well. The approximation of Roy *et al* [7] suggests a change from $\nu_0^\theta \simeq 0.58$ (on a pure lattice) to $\nu^\theta \simeq 0.68$ on a 2D critical percolation cluster (and $\nu^\theta = \frac{1}{2}$ at $d \geqslant 2.4$ on the pure lattice and at $d \geqslant 6$ on the percolation cluster; see the appendix). The approximation of Chang and Aharony [8] gives $\nu^\theta \simeq 0.72$. However, since the same approximation gives $\nu_0^\theta \simeq 0.66$ for the pure lattice (compared to $\nu_0^\theta = \frac{4}{7} \simeq 0.57$ in the two-dimensional case), the agreement of this predicted value with our series study estimate of ν^θ may be accidental.

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Appendix

Radius of gyration distribution and Flory approximant for ν^θ

Let us consider, following Lhuiller [14] and Roy *et al* [7, 12], the form of the polymer radius of gyration (R) distribution $P(R)$ such that the distribution vanishes if R is outside the bonds $N^a \leqslant R \leqslant N^b$

$$P(R) \sim \exp[-N\{(N^a/R)^\alpha + (R/N^b)^\delta\}] \qquad \alpha, \delta > 0. \tag{A1}$$

This form for $P(R)$ ensures that $P(R)$ decays exponentially to zero as R crosses the above bounds. The maximum value of $P(R)$ occurs at the most probable size R_N of the polymer:

$$\partial P(R_N)/\partial R_N = 0 \qquad \text{at } R_N \sim N^\nu \tag{A2}$$

where

$$\nu = (a + \kappa b)/(1 + \kappa) \qquad \kappa = \delta/\alpha.$$

(*a*) For SAWs on a pure lattice in the high temperature limit (random SAW limit) $N^{1/d} \leqslant R \leqslant N$. In this case $\alpha = d$ ensures the proper two-body interaction term in the Flory free energy $F(R) \sim \ln P(R)$. Similarly $\delta = 2$ gives the elastic term in $F(R)$.

One thus gets [14] $\nu = \nu_0^S = 3/(d+2)$, the Flory exponent in this (SAW) limit.

(*b*) For SAWs on a pure lattice at the θ-point, the appropriate bound was suggested to be [7] $N^{1/d} \leqslant R \leqslant N^{\nu_0^S}$. In this limit $\alpha = 2d$ ensures the proper three-body term in the free energy $F(R)$. Again $\delta = 2$ here gives the elastic term in $F(R)$.

One then gets [7] $\nu = \nu_0^\theta = (d+5)/[(d+2)(d+1)]$. For $d = 2$, the $F(R)$ obtained here (and also the ν_0^θ value) is the same as that obtained from various screening considerations [7]. This gives $\nu_0^\theta \simeq 0.58$ in $d = 2$ and ν_0^θ becomes equal to $\frac{1}{2}$ at $d = d_c \simeq 2.4$, so that the three-body repulsive term vanishes (becomes independent of N) and $\nu_0^\theta = \frac{1}{2}$ for $d \geqslant d_c \simeq 2.4$. This approximation therefore suggests that the upper critical dimensionality is less than three (of course $\nu_0^\theta = \frac{1}{2}$ in $d = 3$).

(*c*) For SAWs on the percolation clusters, $N^{1/d_B} \leqslant R \leqslant N^{1/d_{min}}$ where d_B and d_{min} denote the percolation backbone dimension and the shortest chemical path dimension respectively [10]. κ $(\equiv \delta/\alpha)$ should incorporate here the spectral (random walk) dimension of the percolation cluster for the elastic energy term [7], such that [7, 12]

$$\nu = \nu^S = (d_{min} + \kappa d_B)/d_B d_{min}(1 + \kappa) \tag{A3}$$

where $\kappa = d_W d_{min}/d_B(d_W - d_{min})$.

Here, d_W denotes the random walk dimension on the percolation cluster. This same expression was obtained earlier by Aharony and Harris [4] in a different way. This gives $\nu^S \simeq 0.77$, 0.66 and $\frac{1}{2}$ in $d = 2$, $d = 3$ and $d \geqslant 6$ respectively.

(*d*) For SAWs at the θ-point on the percolation cluster the appropriate bound is assumed to be [7] $N^{1/d_B} \leqslant R \leqslant N^{\nu^S}$. The value of κ here corresponding to the three-body interaction then gives [7, 12]

$$\nu = \nu^\theta = (1 + \kappa d_B \nu^S)/d_B(1 + \kappa) \tag{A4}$$

where $\kappa = d_W d_{min}/2d_B(d_W - d_{min})$.

This gives $\nu^\theta \simeq 0.68$, 0.61 and $\frac{1}{2}$ in $d = 2$, $d = 3$ and $d \geqslant 6$ respectively. Note that the upper critical dimensionality for the θ-point on the percolation cluster here also shifts to $d_c = 6$.

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