Percolation, the Special Θ' Point, and the Θ-Θ' Universality Puzzle

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(Received 22 July 1991)

Results for $d=2$ percolation allow one to determine exactly the critical exponents for a polymer undergoing the special surface transition, while its bulk is at the Θ' point. $\gamma_1=\frac{8}{7}$ and $\phi_s=\frac{8}{21}$ are the entropic and the crossover surface exponents, respectively. On the other hand, exact enumerations analysis leads to conjecture $\gamma_1=\frac{4}{7}$ at an ordinary Θ' point. This strongly supports universality of Θ and Θ' points. Similar exact results are obtained for a multicritical walk in the presence of correlated percolation vacancies.

PACS numbers: 05.70.Jk, 36.20.Ey, 64.60.Ak, 64.60.Kw

Adsorption on a substrate and collapse of a polymer are processes of much fundamental and applicative interest [1-3], especially when they can compete and occur simultaneously. A system which attracted particular attention in the recent literature consists of a linear polymer in dilute solution, with effective attractive interactions between monomers and between each monomer and a solid wall limiting the solvent. Models for such a system can be formulated, e.g., in the framework of lattice self-avoiding walks (SAW) [4-6], and their properties are expected to be relevant for a variety of problems, ranging from polymer physics to membrane biophysics [7].

In the context of statistical mechanics, polymer adsorption can be seen as a problem in surface critical phenomena [3], and is by now relatively well understood, when occurring alone. Adsorption is a multicritical phenomenon and corresponds to the special transition of magnetic systems with a boundary surface [3]. In bulk dimension $d=2$ ($d=1$ dimensional boundary), the critical exponents are even known exactly [8].

The situation is less clear as far as the coil-globule transition of a polymer in the bulk is concerned. A SAW with an attractive interaction for each pair of nearest-neighbor (NN) not consecutively visited sites shows a critical Θ temperature above which it behaves as a polymer in good solvent [fractal dimension $D\simeq(d+2)/3$], and below which it becomes a compact globule ($D=d$) [9]. The Θ point separating these two regimes is again multicritical. In $d=2$ the Θ point still constitutes a big theoretical challenge, in spite of the intensive studies recently devoted to it. These studies were strongly stimulated by introduction of the so-called Θ'-point model [10,11]. For this model, described below in a generalized form, bulk and ordinary surface exponents were either exactly computed or conjectured on the basis of Coulomb gas and conformal invariance methods [11]. Results for the Θ' point soon raised the problem of the universality of Θ-point behavior. Indeed, at variance with bulk critical indices, surface exponents estimated on the basis of numerical investigations on different Θ-point models [5,12, 13] turned out to be in open disagreement with those predicted in Ref. [11].

Below we keep the distinction between Θ'- and Θ-point models. The former has the peculiarity that interactions are caused by annealed percolation vacancies.

When combined in the same model, adsorption and collapse are expected to give rise to a higher-order multicritical point (special Θ point) as discussed in many recent works [4-6]. However, also in $d=2$, the critical exponents associated with this point remained a puzzle so far, even after the use of sophisticated transfer-matrix methods [14].

In this Letter we generalize the Θ' model to describe both polymer collapse and adsorption. This leads to exact predictions for the special Θ'-point critical behavior based on the connection between our model and bulk and surface percolation geometry. As a further bonus we clarify the long-standing puzzle concerning Θ and Θ' universality. Indeed, we explain discrepancies between previous predictions and results on surface magnetic exponents in terms of the basic distinction between ordinary and special surface critical behavior [3].

Consider a semi-infinite hexagonal lattice as sketched in Fig. 1. Hexagons are present or absent with probabilities p and $1-p$, respectively. This defines a site percolation problem on the dual, triangular lattice. A SAW is then assumed to take place on the hexagonal lattice, subject to the condition of not stepping on edges belonging to occupied hexagons. If only bulk properties are considered, this is the model of the Θ' point proposed in Ref. [10]. However, introduction of semi-infinite geometry allows one to get further insight into it and to establish a new connection with the special Θ'-point physics, by properly choosing the boundary conditions on the surface.

The generating function of the problem is given by

$$G(K,p)=\sum_C P(C) \sum_{W \text{ compatible with } C} K^{|W|}, \qquad (1)$$

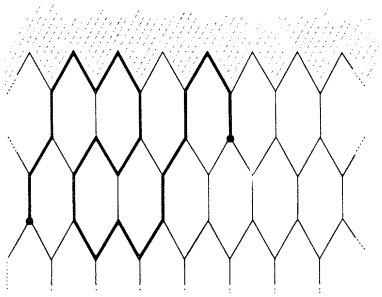

FIG. 1. Walk of $N=22$ steps with $N_s=6$, $N_t=4$, $N_2=4$, and $N_3=0$.

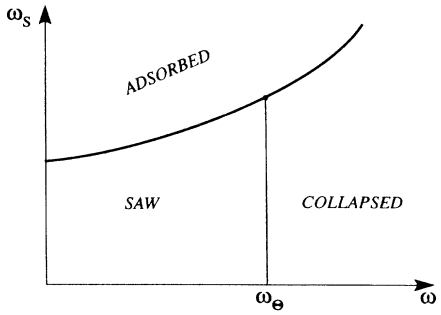

FIG. 2. Critical regime (schematic) for a walk described by Eq. (4). The curved line corresponds to the special regimes. The vertical segment corresponds to ordinary Θ behavior and terminates at the special Θ point.

with C denoting percolative configurations with probability P, and W a walk of $|W|$ steps. K is a step fugacity. Performing the annealed sum over C in Eq. (1), a walk with N steps touching H distinct hexagons contributes with a grand-canonical weight $K^N(1-p)^H$.

For a walk which does not touch or step on the boundary, one has

$$H=N+1-N_2-2N_3\,, \tag{2}$$

where N_2 (N_3) is the number of hexagons visited 2 (3) times by nonconsecutive steps of the walk. When steps are made on the surface, H has to be modified, and its expression depends on the boundary conditions we impose. It is natural to assume that, since there are no hexagons across the boundary, there is no further restriction for steps on it, in addition to the usual one, referring to occupations of hexagons within the semi-infinite region. It can be shown that, in this case,

$$H=N+1-N_2-2N_3-(N_s+N_t)/2\,, \tag{3}$$

where N_s (N_t) is the number of steps at (towards) the surface (Fig. 1) [15]. Thus, the effect of annealed vacancies is to introduce attractive self-interactions ($1-p<1$) for the walk [Eq. (2)], and attractive interactions between the surface and the walk, as well, when they are coming into contact [Eq. (3)].

Equations (2) and (3) indicate that our model has the same ingredients as a more standard model (Θ-point model) of the special Θ transition in $d=2$. In that context one usually [5] considers a SAW with origin on the surface, described by a generating function of the form

$$G(K,\omega,\omega_s)=\sum_W K^{|W|}e^{\omega N_t(W)}e^{\omega_s N_s(W)}\,, \tag{4}$$

where ω and ω_s are reduced attraction energies, while N_t and N_s represent the number of self-interactions and the number of steps on the surface, respectively. N_t is the number of NN visited sites.

Our Θ' model should display the same universal features as the Θ-model (4). The expected phase diagram for model (4) is reported in Fig. 2. Equations (2) and (3) and the weight $K^N(1-p)^H$ tell us that in the Θ' model N_2+2N_3 and $(N_s+N_t)/2$ are replacing N_t and N_s in (4), respectively. Furthermore, our parametrization of (1) implies that, as a function of p, we move along a line $e^{\omega}=e^{\omega_s}=(1-p)^{-1}$ on the plane corresponding to that of Fig. 2.

The point $p=\frac{1}{2}$ of our Θ' model *must* exactly correspond to the special Θ' point in Fig. 2. Indeed, a given percolative configuration C can be identified by giving the contours (hulls) of occupied clusters. On our hexagonal lattice these hulls are self-avoiding and mutually avoiding rings (SAR) which can possibly touch the surface. Thus, a SAR obeying our prescriptions is geometrically indistinguishable from each individual hull specifying C. If N_a and N_p hexagons are, respectively, absent and present in C, the weight for each N-step ring is just $K^N P(C)=K^N(1-p)^{N_a}P^{N_p}$. So, for $K=1$ and $p=\frac{1}{2}$, there is also an identity in statistical weight between the SAR and each hull. On the other hand, $p=\frac{1}{2}$ is the threshold of triangular site percolation. So, at $p=\frac{1}{2}$ and $K=1$, our SAR must be critical and have the same geometrical properties as the percolation hull. In these conditions the SAR has thus the fractal dimension $D=1/\nu=7/4$ of the hull [16] and its grand-canonical radius of gyration grows like $\Delta K^{-1/D}=\Delta K^{-4/7}$ for $\Delta K=1-K$ approaching zero [11].

Most important here is that the fractal dimension D_s of the intersection of the critical percolation hull with a boundary is by now known exactly [17]. Thus one can, e.g., consider the SAR statistics in the case that it touches one point of the boundary ($N_s\geq 2$). Such statistics is identical to that of occupied cluster external hulls passing through the same point. So, on the basis of the above identification, indicating by $\langle N_s\rangle$ the grand-canonical average number of steps of the ring on the surface, and taking into account that $\Delta K^{-1/D}$ is the correlation length, we expect

$$\langle N_s\rangle\sim\Delta K^{-D_s/D}=\Delta K^{4D_s/7}\,, \tag{5}$$

with $D_s=\frac{2}{3}$ [17], for $\Delta K\to 0^+$. Moreover, this behavior

should hold for a quantity like $\langle N_s+N_t\rangle$ as well, because clearly, for SAR, $N_s+2\leq N_t+N_s\leq 2N_s$, if $N_s>0$.

Insight into the entropic (magnetic) exponents of our Θ' model can be obtained by realizing that at $K=1$, $p=\frac{1}{2}$ this is exactly equivalent to the $O(n=1)$ loop gas in the low-temperature phase, which can be solved by Coulomb gas techniques [11]. In fact, this loop gas exactly corresponds to the zero-temperature Ising model. As a consequence of this being ordered, the bulk and surface correlation exponents, η and η_s, respectively, both have to be zero [11]. This further implies that $\gamma=\gamma_1=\frac{8}{7}$, γ and γ_1 being, respectively, the bulk and surface magnetic exponents of our walk at $p=\frac{1}{2}$ [$\gamma=\nu(2-\eta)$, $\gamma_1=\nu(2-\eta/2-\eta_s/2)$].

Notice that the same value of γ_1 was conjectured for the Θ'-point model in Ref. [11]. However, as we show below, the interpretation given there to γ_1 was different from ours, because it was not seen as a special exponent. The critical point of our model at $p=\frac{1}{2}$ must clearly coincide with some point in the plane corresponding to that of Fig. 2. First of all, we can exclude its location in the whole region above the adsorption line. Indeed, there one should trivially have $D_s=1$, corresponding to a polymer adsorbed on the boundary [3]. Once one excluded the adsorbed region, only surface critical behavior consistent with Θ' bulk exponents is possible. This means that the point has to fall in the vertical segment representing the locus of Θ' ordinary and special critical points [18].

The divergence (5) obtained above for $\langle N_s\rangle$, and for $\langle N_s+N_t\rangle$, also allows us to exclude ordinary critical behavior. Indeed, a general theorem, and conformal invariance, imply a scaling dimension $y_s=-1$ for a coupling like ω_s in model (4) at an ordinary transition [19], because the conjugate operator has nonzero average at the boundary. As shown below, $y_s=-1$ would imply that $\langle N_s\rangle$ does not diverge, in contradiction with Eq. (5). On the contrary, we can conclude that $y_s=D_s=\frac{2}{3}$ is the correct scaling dimension of a parameter like ω_s at our critical point. Indeed, let us indicate by

$$f_s=\ln G=f_s(K,\omega,\omega_s) \tag{6}$$

the surface free energy of a walk whose G is of the form (4), but now appropriate to the Θ'-point model. We clearly have

$$\langle N_s\rangle\sim\langle N_s+N_t\rangle\propto\frac{\partial f_s}{\partial\omega_s}\,. \tag{7}$$

According to whether the point we consider belongs to the special or to the ordinary critical regime, we will have that, in terms of deviations of ω_s, ω, and K from the appropriate values, the scaling of $\langle N_s\rangle$ can be written as

$$\langle N_s\rangle(\Delta K,\Delta\omega,\Delta\omega_s)=l^{y_s}\langle N_s\rangle(l^{y}\Delta K,l^{y_\Theta}\Delta\omega,l^{y_s}\Delta\omega_s)\,, \tag{8}$$

where we already know $y=\frac{7}{4}$ and $y_\Theta=\frac{3}{4}$, the bulk crossover exponent of the Θ' point [11,20]. Now, if $y_s=-1$, like at an ordinary transition, $\langle N_s\rangle$ cannot diverge for $\Delta K\to 0$. We know, however, that this is the case from Eq. (5), which is clearly compatible with (8) if and only if $y_s=D_s=\frac{2}{3}$.

Thus our model, for $p=\frac{1}{2}$, is at the special Θ' point, with $y_s=\frac{2}{3}$. At such a point the surface crossover exponent is defined by $\langle N_s\rangle\sim\Delta K^{-\phi_s}$ [3], which here implies $\phi_s=D_s/D=8/21$. For directed polymers one has $\phi_s=\frac{1}{3}$ [14].

The $p=\frac{1}{2}$ critical point of the Θ' model with boundary coincides with the special Θ' point on the (ω,ω_s) plane, and we expect the relative exponents to be universal and independent of the specific details of our Θ' model.

In order to verify our predictions, and further clarify the role of boundary conditions in our model, we performed exact enumerations for walks of up to 34 steps with origin on the surface. We studied, in particular, the γ_1 exponent, describing the quantity

$$C_N=\sum_H C_N(H)(1-p)^H\underset{N\to\infty}{\sim}N^{\gamma_1-1}K_{\Theta'}^{-N}\,, \tag{9}$$

with $p=\frac{1}{2}$ and $C_N(H)$ representing the number of N-step walks touching H hexagons. Our estimate, obtained by differential approximants [21] at $K=1$, was $\gamma_1=1.11\pm0.04$, in very good agreement with the predicted value.

We also studied the scaling behavior of $\langle N_s\rangle$, getting an estimate $\phi_s=0.41\pm0.03$, again consistent with $\phi_s=\frac{8}{21}$.

Our work also explains why previous studies of the Θ-point models failed to show $\gamma_1=\frac{8}{7}$, and led to the most likely wrong belief that the Θ and Θ' points could belong to different classes. So far, all investigations of the Θ-point γ_1 exponent, both for SAW and for trails, gave values compatible with $\gamma_1=\frac{4}{7}$ [5,12,13], a value corresponding to $\eta_s=2$ and consistent with conformal invariance. In these studies, however, one was looking for ordinary critical behavior, and no interactions with the surface were included in the models. Thus $\gamma_1=\frac{4}{7}$ should qualify as the correct ordinary surface exponent at the Θ point, while $\gamma_1=\frac{8}{7}$ as the special one, if universality holds.

Using our exact enumeration we also studied the ordinary surface behavior at the Θ' point by putting H equal to expression (2) for the walks in Eq. (9). In the correspondence with model (4), this boundary condition is equivalent to putting $\omega_s=0$. With this modified H in Eq. (9) we obtained from our exact enumeration $\gamma_1=0.57\pm0.02$, in very good agreement with the conjecture $\gamma_1=\frac{4}{7}$, and with previous results for Θ-point models [5,12]. This clearly supports our conclusion that $\gamma_1=\frac{8}{7}$ and $\gamma_1=\frac{4}{7}$ are the correct exponents at special and ordinary Θ' criticality, respectively. On the other hand, since only ordinary criticality was studied so far for other Θ-point models, it is natural to expect $\gamma_1=\frac{8}{7}$ also for the special Θ point.

The new ideas and methods presented above for the study of the special Θ' point can easily be generalized to a

model on a hexagonal lattice with correlated percolation vacancies [22]. In this model an Ising variable σ specifies the occupation status of each hexagon and the σ's interact through a NN interaction, L. At the critical triangular coupling, $L_c = 0.274\ldots$, a walk through vacancies has a multicritical behavior, for which the bulk exponents are $\nu = \frac{8}{11}$ (the reciprocal of the fractal dimension of Ising cluster hulls at criticality [23]) and $\eta = \frac{1}{4}$, consistent with a $c = \frac{1}{2}$ central charge [22].

Following the same line of reasoning as above, one concludes that the walk with open Ising boundary at L_c must be at a special point, with $y_s = \frac{5}{6}$ ($\phi_s = y_s \nu = \frac{20}{33}$), the fractal dimension of Ising clusters at a boundary [23]. Following the methods of Ref. [22], we estimated this exponent by extensive Monte Carlo enumeration as $\phi_s = 0.62 \pm 0.03$. The special character of the point $L = L_c$ has been also revealed by the fact that there one finds $\gamma_1 = 0.99 \pm 0.04$, consistent with $\gamma_1 = 1$, in contrast with an ordinary value $\gamma_1 = 0.85 \pm 0.04$. This ordinary γ_1 could, e.g., be consistent with $\eta_s = \frac{35}{24}$ and $\gamma_1 = \frac{5}{6}$, both values being compatible with a $c = \frac{1}{2}$ conformal theory.

Summarizing, we were able to determine exactly the critical behavior of a polymer at the special Θ' point in $d = 2$ on the basis of the geometrical properties of percolation at ordinary criticality.

Our results show that the surface magnetic exponents previously conjectured for the Θ' point do not pertain to the ordinary, but to the special regime, thus solving the long-standing puzzle of universality of Θ and Θ' points.

Similar results can be obtained for a recently proposed walk model with correlated Ising vacancies.

Note added.—Most recently, the value $\delta_1 = \frac{4}{7}$ for the ordinary Θ' point has been derived exactly on the basis of Coulomb gas methods [24].

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