Vesicle model of linear- and branched-polymer θ collapses

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A perspective on the connections between linear and branched polymer θ collapses in two dimensions is provided by a vesicle model with vacancies. Percolation geometry plays simultaneously key roles in determining the multicritical properties of both problems. For branched polymers, besides two distinct θ lines, a transition between different collapsed regimes and several exponents are exactly obtained. Universality issues are also discussed.

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In the context of two-dimensional (2D) lattice statistics, multicritical phenomena of polymer models still pose many challenging and controversial problems, beyond the present range of control of powerful tools like conformal invariance [1]. The collapse transitions of both linear and branched polymers (BP's) are notable examples.

It was not until very recently that a full exact determination of the exponents of a model of θ collapse for linear polymers in 2D was achieved through the use of percolation vacancies as mediators of effective interactions [2,3]. In this formulation the θ point is obtained when the vacancies within which the polymer is constrained are at percolation threshold. In the light of present numerical evidence, this θ-point model most likely provides an appropriate description for a very extensive, if not exhaustive, class of 2D linear polymer collapses [4].

The situation is quite different for BP and lattice animal (LA) collapses [5]. In this context, until now, the most studied models were those in which collapse is induced by increasing a suitable cycle controlling fugacity, like strongly embedded site LA with nearest-neighbor (nn) attractive interactions between occupied sites. This model was studied by transfer matrix methods [6], and, most recently, θ-point exponents could be conjectured for it on the basis of a connection with planar vesicles and with the tricritical 0-state Potts model [7]. A more general formulation of the interacting LA problem, obtained by considering the limit for q approaching 1 of an anisotropic q-state Potts model, was already used in an attempt to identify the role played by percolation in the LA description [8,9]. This formulation, like that introduced below, involves three independent fugacities for a grand-canonical description of a single animal [9]. On the basis of the same model, the issue of universality of LA θ transitions was better focused in Ref. [7], where the possibility that LA could present two distinct branches of θ behavior, separated by the percolation critical point, was already envisaged. Two branches for the θ collapses of LA are also suggested by an analysis of numerical series results, which further give some indication, albeit not conclusive, of a possible transition between different collapsed regimes [10].

Quite remarkably, in both the linear and LA cases, the critical point of percolation turns out to be of key importance in the physics of θ collapse.

For linear polymers the percolation threshold coincides with the θ point since the statistics of a θ ring is the same as that of a critical cluster hull [2,3]. On the other hand, for interacting LA's of Refs. [9,10] one expects that, in particular conditions, the statistics coincides with that of critical percolation clusters. These conditions most likely single out a highly unstable point on the critical surface, possibly separating different domains of θ behavior.

In view of the central importance of percolation in this field, it is very tempting to search for models in which percolation geometry could simultaneously play roles appropriate to both cases. This issue is solved in the present paper by making contact with another area of current interest, namely vesicle statistics [11–14]. Our combined description of both linear and branched polymers and LA is indeed based on a planar vesicle model.

The main results of our analysis can be summarized as follows.

(i) We give evidence for the suspected existence of two distinct θ lines separated by a percolation critical point for LA described by three-parameter models. On the basis of exact results for vesicles and interacting linear polymers, we are able to determine the exponents on one line and to show that they coincide everywhere with the exponents conjectured for the cycle θ point in Ref. [7].

(ii) We prove the existence of a third transition line, also departing from the percolation point, and separating into two distinct regimes the compact phase. The crossover exponent on this line can be shown to be exactly equal to unity, and the critical regime on it is also compact ($\nu=\frac{1}{2}$) and, as far as the LA hull is concerned, coincides with the compact regime of a linear ring polymer beyond its θ threshold. This line and one of the θ lines in (i) are in fact tricritical in a strict sense, since, in a grand-canonical framework, the transition to compact behavior occurring in the region of parameters they limit together is a first order one, with droplet singularities.

(iii) We determine two relevant exponents at the highly unstable percolation point and, at least, give exact bounds for the third one.

Let us consider a self avoiding ring (SAR) on a hexagonal lattice. Hexagons act as annealed vacancies, occupied with probability p, and the SAR is constrained to step on occupied regions only. This is nothing but the linear polymer θ-point model of Ref. [2]. By letting an extra fugacity W control the area enclosed by the SAR, A, the generating function, becomes

$$G(K,p,W)=\sum_r K^{|r|}p^{H(r)}W^{A(r)} , \qquad (1)$$

where the sum is over rings r with perimeter $|r|$, $H(r)$ is the number of distinct hexagons touched by r, and a normalization per lattice site is implicitly understood. Equation (1) describes a disklike LA with a self-attracting ring perimeter, since, for $p<1$, in order to lower H, the ring has to revisit more than once (not consecutively) the same hexagons, creating what we call contacts.

Quantities like the grand-canonical average radius

$$R(K,p,W)=\sum_r K^{|r|}p^{H(r)}W^{A(r)}R(r)/G , \qquad (2)$$

where $R(r)$ represents the gyration radius of r, are expected to become singular for (K,p,W) approaching transition surfaces. So, if a surface is second order and can be parametrized as $K=K_c(p,W)$, we expect, for $K\to K_c$,

$$R(K,p,W)\sim(K_c-K)^{-\nu} , \qquad (3)$$

where ν is a suitable exponent, possibly depending on W and p.

If we consider the center of each hexagon enclosed by r in Eq. (1) as a LA site on the dual, triangular lattice, G can be rewritten as the generating function of a strongly embedded LA without holes, with site fugacity $\lambda=K^6W$, nearest neighbor Boltzmann factor $\mu=K^{-2}$ for each pair of nn sites, and a factor due to interactions on the perimeter, $p^{H(r)}$. This follows from the obvious relation $6A(r)=|r|+I(r)$, where $I(r)$ represents the number of pairs of nearest-neighbor (nn) hexagons enclosed by r.

For $p=1$ the model reduces to the planar vesicle studied extensively in Refs. [13,14].

The interactions tuned by p have the effect of inducing collapse of the perimeter on itself. Lower p's favor contact rich configurations in which the animal's perimeter bends on itself several times, creating deep invaginations through which the exterior penetrates the vesicle's structure. Physically, p, combined with K, should produce effects similar to those of solvent and contact fugacities in the generalized interacting LA model of Refs. [9,10]. Indeed, decreasing K, and thus lowering $|r|$, contrasts the tendency to create contact rich configurations by reducing p. The model can display compact configurations which are either rich or poor in contacts. The latter ones are those in which r has a disklike shape, without reentrancies.

Even if contacts are realized here in a peculiar way, in the spirit of previous studies of the linear polymer θ-point [2], we will assume that model (1) is representative of a wider class of 2D LA problems described by three-parameter models [7,9,10]. The different transition surfaces and the various multicritical lines and points we find are qualitatively sketched in Fig. 1.

We prove below that the plane $W=1$ contains a region of droplet singularities for model (1). Thus any renormalization group (RG) description of this model should leave this plane invariant under transformation, and we expect that the flow in this plane is the same as that applying to the linear polymer θ-point model of Refs. [2,3].

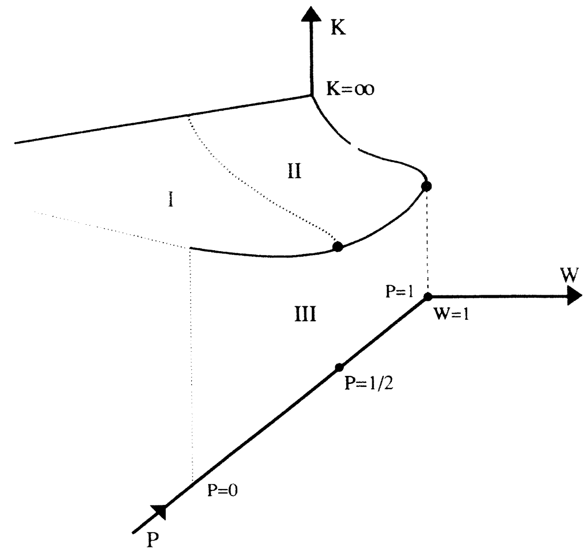

FIG. 1. Sketch of surfaces of critical and first order singularities in (K,p,W) space. Region III corresponds to a first order transition to contact poor compact regime. In regions I and II the critical regimes are contact rich compact, and swollen BP, respectively.

We know that for $W=1$ there exists a θ point at $p=\frac{1}{2}$, with $K_c(\frac{1}{2},1)=1$, separating the critical line $K=K_c(p,1)$ into a swollen SAR branch ($p>\frac{1}{2}$), with $\nu=\frac{3}{4}$, and a compact one ($p<\frac{1}{2}$), with $\nu=\frac{1}{2}$ [2]. At the θ point the SAR has the same statistics as a percolation hull, and $\nu=\frac{4}{7}$. Indeed $p=\frac{1}{2}$ is the percolation threshold for hexagons, and clearly this point also plays the role of the percolation point for our LA. On the $W=1$ plane this point is twice unstable, and its exponents must be $y_1=\nu^{-1}=\frac{7}{4}$ and $y_2=\frac{3}{4}$, the percolation correlation length index [2].

On the $p=1$ plane it is by now well established that, for $W<1$, the vesicle behaves as a swollen BP, as thin ramified configurations dominate asymptotically [13,14]. The crossover from the $W=1$ compact ring, to BP behavior, controlled by an attractive fixed point at $W=0$, is described by an exponent $\phi=y\nu=\frac{3}{2}$. y is the dimension of a relevant scaling field proportional to $(1-W)$, whose existence can be established for any fixed point on the $W=1$ critical line, as shown below. The value $y=2$ is consistent with the compactness of the region enclosed by r. This follows from the fact that $\partial\ln G/\partial\ln W=\langle A\rangle$, and that W is directly coupled to the above field. Thus scaling gives $\langle A\rangle(K,p,1)\propto(K_c-K)^{-\phi}$, indicating that y is the fractal dimension of the enclosed region.

For model (1), $\phi=\frac{3}{2}$ must hold on the whole line $K=K_c(p,1)$ for $\frac{1}{2}<p\le 1$ on the $W=1$ plane, since a swollen SAR has a compact interior, with fractal dimension $y=2$, and $\nu=\frac{3}{4}$ [15]. For $p<\frac{1}{2}$ the SAR is collapsed ($\nu=\frac{1}{2}$) and the interior is still dense ($y=2$) [16], so $\phi=1$ has to be expected on this branch. Of course, the interior is still compact but, unlike in the $p>\frac{1}{2}$ case, many contacts can be present.

For $p=\frac{1}{2}$ and $W=1$, the existence of the above mentioned scaling field should imply $y_3=2$ for the exponent controlling crossover to the deflated regime. However, the scaling argument, which reveals consistent for both the $p>\frac{1}{2}$ and $p<\frac{1}{2}$ regimes, could fail, in principle, in case a zero amplitude should apply to the leading singular behavior of $\langle A \rangle$. This cannot be excluded in the absence of independent information [17]. On the other hand, we know the fractal dimension ($\frac{91}{48}$) of a percolation cluster exactly [18]. Since the area enclosed by a percolation hull cannot be less than the area of a percolation cluster, in which internal holes are excluded, the dimension we are seeking must satisfy

$$\tfrac{91}{48} \le y_3 \le 2 \ . \tag{4}$$

Indeed, the dimension can also not exceed that of the lattice.

We now elucidate the multicritical nature of the line $K=K_c(p,1)$, $W=1$. As anticipated, the whole region $K<K_c(p,1)$, $0\le p\le 1$, on the $W=1$ plane, is a surface of droplet singularities [13]. G is clearly finite on this surface, while it is not hard to prove that $G=\infty$ as soon as $W>1$. Indeed, for nonzero values of the other parameters, configurations with maximal area at given perimeter dominate asymptotically and let the sum in Eq. (1) blow up to infinity. Keeping only one term corresponding to such a configuration for each $|r|$ in Eq. (1), the resulting sum clearly becomes a lower bound for G. On the other hand, as soon as $W>1$, since, for large $|r|$, $H(r)$ is at most $O(|r|)$, and $A(r)$ is $O(|r|^2)$, this bound diverges to infinity for any $K,p>0$. This transition, of first order, signals a sudden jump from finite ring to infinite compact disk with the solvent fully expelled to the exterior of the structure and without contacts. The whole transition line $W=1$, $K=K_c(p,1)$, with $\frac{1}{2}<p\le 1$, corresponds to the same strongly embedded site LA collapse described in Ref. [7] ($\nu_\theta=\frac{1}{2},\phi_\theta=\frac{2}{3}$ [19]) on the basis of a model equivalent to ours restricted to the $p=1$ plane.

For critical regimes at $W<1$, one can prove that, for any nonzero p, $K_c(p,W)\propto W^{-1/4}$, for $W\to 0$, with proportionality constant depending on p. This follows from generalizing inequalities already established for the $p=1$ case [14], and based on the relation $A(r)=|r|/4+N_i(r)/2-\frac{1}{2}$, where N_i is the number of hexagonal lattice sites enclosed by r. G can be obtained as the order n contribution to the partition function of an $O(n)$ spin model when n approaches zero. In a given hexagon percolative configuration C, to be weighted with its probability in an annealed way, the Hamiltonian has the form

$$-\beta H(\mathbf{s},\sigma)_C = K\sum_{\langle i,j\rangle_C} \mathbf{s}_i\cdot\mathbf{s}_j\sigma_{ij} + \operatorname{arctanh}(W)\sum_{\text{pl.}}\prod_{kl\in\text{pl.}}\sigma_{kl} \ , \tag{5}$$

where the first sum is over nn edges separating hexagons which are occupied in C, and the second is over all hexagonal plaquettes and gives an Ising gauge action, with $\sigma=\pm 1$ associated to each hexagonal edge. $\mathbf{s}$ are n-component spins satisfying $\mathbf{s}^2=n$. Since, in view of the structure of Eq. (5), neither p nor K can affect a possible renormalization of W to leading n order, one expects W to renormalize trivially under a 2D decimation, i.e., $W'=W^{b^2}$, for rescaling b. This implies that criticality, for $W<1$, is always controlled by fixed points at $W=0$. For W approaching zero, the dominant configurations are those in which $N_i=0$, and each hexagon enclosed by r contributes to H. For p close to unity the statistics is that of a ramified structure with thin branches and swollen BP critical behavior. Upon decreasing p, configurations with many external contacts are favored and the branches tend to collapse on each other to form a compact structure, very much like in a standard model of a self-attracting bond BP. It is thus reasonable to expect a θ-collapse transition when moving along the intersection of the critical surface with the $W=0$ plane. The above RG argument and conjectures for similar LA models [7,10] suggest a whole θ line joining this collapse transition point at $W=0$ with the percolation point at $W=1$ (Fig. 1). We thus expect that the critical sheet at $0\le W\le 1$ is split in two domains by this line. A determination of ν and ϕ on this θ line is not possible with the methods used here, and should be attempted numerically [20].

This completes our scenario, leading to the identification of a second region of compact behavior, corresponding to the low-p portion of the $W\le 1$ critical sheet. Unlike the previous one, this compact regime is rich in contacts and solvent inclusions, as also suggested by the analysis of the low-p region on the $W=0$ plane.

The line of separation between the two compact regimes $[W=1, K=K_c(p,1), 0<p<\frac{1}{2}]$, coincides with the compact SAR critical line on the $W=1$ plane. Thus, like swollen SAR's mark the separation of the contact poor dense BP phase from the swollen BP regime, collapsed SAR's constitute the border between contact rich and contact poor compact regimes.

Finally we point out that the existence of a scaling field with $y=2$ for fixed points at $W=1$ immediately follows from the above simple transformation of W under decimation.

The above connections between linear polymer and LA properties follow from the fact that the model identifies the LA hull with a SAR. Studies of properly defined LA hulls in other models could allow interesting comparisons.

Up to now, the role of percolation in LA statistics was always discussed with reference to the bond case [7,9,10]. Here the choice of site percolation is of key importance in the whole approach.

The ideas inspiring our models can also be generalized, to the same extent, to discuss 3D LA properties in connection with vesicle statistics and percolation.

To establish how universal are the properties of model (1) remains an open issue. In particular, the restriction to LA with trivial homology could be limiting in this respect. Indeed, it has recently been shown that LA like ours at $p=1$ present some differences in thermodynamic properties in case holes are permitted [21]. On the other hand, the results of Ref. [7] clearly suggest that, at least at the θ transition to contact poor compact regime, holes should not matter for universal properties like exponents. Thus conjecturing universality is not too daring. In any case, our model is physically sound on its own, and the fact that many properties have been exactly established for it gives a solid reference point for the general study of universalities in LA collapses.

One of the most important results here is the existence and exact characterization of a transition between different collapsed regimes. This phenomenon is certainly worth investigating in other more standard models and, possibly, experiments [22].

A particularly lucky circumstance here is that we are also able to determine the relevant indices y_i at the percolation multicritical point. The values we find for y_1 and y_2, and the bounds on y_3, are fully consistent with 2D percolation in the framework of conformal invariance [1]. Tests of their universality will be extremely interesting, albeit very challenging.

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