Branched polymer approach to the structure of lattice animals and percolation clusters

LETTER TO THE EDITOR

Branched polymer approach to the structure of lattice animals and percolation clusters

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Abstract. We treat the percolation problem as a solution of randomly branched chains, and argue that such chains are swollen by a three-body repulsion acting only within a connected cluster. This type of repulsion should not be subject to the screening effects which inhibit ordinary repulsions. The repulsion becomes relevant below six dimensions. We estimate its effect on the size of a cluster in analogy with Flory's argument for the swelling of linear chains. Above six dimensions the cluster size scales as mass to the $\frac{1}{4}$ power, as with isolated branched chains in high dimensions.

The purpose of this letter is to present a coherent picture of percolation and lattice animals from a polymer point of view. The field theory has been worked out in detail by Lubensky and Isaacson (1979). However, as for the self-avoiding chains, this is not always the most convenient language to answer all questions. de Gennes (1980) has pointed out that animals and percolation clusters can be regarded as properties of branched polymers and Daoud and Joanny (1981) have worked out some of the implications of applying a Flory self-consistent approach. This is the point of view we shall adopt. Our main purpose is to work out the implications and internal logic of this point of view and its relationship to other approaches. We believe the resulting picture is of sufficient interest to merit a detailed description.

Our starting point is the classical Stockmayer theory of gelation (Stockmayer 1943, 1944 and de Gennes 1979) and branched polymers (Zimm and Stockmayer 1949) which is valid on a Cayley tree (or for $d = \infty$). In polymer language this leads to (de Gennes 1980)

$$N \sim R^D; \qquad D \equiv 1/\nu_{bp} = 4, \tag{1}$$

where R is the radius of a branched polymer of mass N, D is the Hausdorff dimensionality. We write ν_{bp} to distinguish this 'polymer' index from the index ν for the connectivity length ξ_p discussed below. The same theory also predicts a gelation transition when the bond probability p exceeds a certain threshold p_c. For $p > p_c$ an infinite cluster is formed with a connectivity coherence length ξ_p and the classical index,

$$\xi_p \sim (p - p_c)^{-\nu}; \qquad \nu = \tfrac{1}{2}. \tag{2}$$

The fraction P_∞ of sites in the infinite cluster increases according to $P_\infty \sim (p - p_c)^\beta$ with $\beta = 1$.

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The lattice animal and percolation problems are essentially indistinguishable in this high-dimensional limit (Harris and Lubensky 1981). This can be seen directly by looking at the generating function for the cluster distribution in the spirit of the Kasteleyn–Fortuin (1969) expansion (Fortuin and Kasteleyn 1972). The probability of finding any specific connected structure as an animal is proportional to

$$P_a \propto p^c; \qquad p < 1, \tag{3}$$

where c is the number of connected internal bonds. For percolation one has an additional factor disconnecting the boundary

$$P_p \propto p^c (1-p)^b \tag{4}$$

where b is the number of disconnected boundary bonds. Now for any fractal object $(D < d)$ almost all sites are perimeter sites. This would seem to imply that b is proportional to c. In fact, for ensemble averages, $\langle b \rangle \propto \langle c \rangle$ strictly (up to an additive constant); however, for any given cluster, there is in general a correction to $b \propto c$. These corrections are due to self-contacts i.e. to disconnected bonds between sites belonging to the same cluster. The number P_2 of such contacts is

$$P_2(N) = N^2 r(N)^d \propto N^{2-d/D}. \tag{5}$$

If $D = 4$ the number of self-contacts becomes negligible for $d > 8$. One can then assume b proportional to c $(b = \alpha c)$ and equation (4) becomes

$$P_p \propto [p(1-p)^\alpha]^c; \qquad d > 8, \tag{6}$$

indistinguishable from the expression for animals (equation (3)) except for replacing p by $p(1-p)^\alpha$.

Below this dimensionality there are important differences, because the effect of interactions become important (Harris and Lubensky 1981). There are two types of interaction. First, as in the case of linear polymers, one has repulsive excluded volume effects; two monomers cannot occupy the same site. This corresponds to a repulsive monomer–monomer interaction with a leading term quadratic in the density. The interaction cannot distinguish between monomers belonging to different polymers. As a result it is screened at high densities (above c^* where polymers begin to overlap).

For linear polymers this result is well known. We know that self-avoiding chains in solution at concentrations $c \gg c^*$ are Gaussian (for $d > 2$) while the single isolated chain is not. Following de Gennes (1980) and Daoud and Joanny (1981), we argue that this effect dominates the difference between animals and percolation clusters. Excluded volume effects are dominant for animals but are screened by the high density in the percolation problem as they are for linear chains in solutions.

The second type of interaction is peculiar to the branched polymer problem and is more subtle. In a branched object, one obviously needs a three-body term to generate the branch points. This is clear in the Stockmayer (1943, 1944) approach. In the field-theory approach this is done by the cubic (ϕ^3) term in the free energy functional. The effect on the density ρ is attractive. The most obvious effect is to generate explicit three-body correlations in the branched clusters. These attractive effects are included when one starts from a 'free' branched polymer $(D = 4)$. When there are geometrical constraints (i.e. for finite d) the branching is no longer free. If one maps the Stockmayer construction, generated on a tree, onto a finite-dimensional lattice, allowing multiple occupancy, one finds new, fortuitous branching points which were not generated by the original construction. (A simple ϕ^3 attraction would give an extra statistical weight

for each of these fortuitous contacts, thus distorting the original ensemble. To compensate for this unwanted attraction and restore the original ensemble, an extra three-point *repulsion* is necessary (Lubensky and Isaacson 1979) in a finite-dimensional space.) The extra repulsion produces a three-body interaction proportional to ρ^3.

From this discussion, it is not clear how this effect can be distinguished from the ordinary excluded volume effects. The essential point is that the geometrical inhibitions of the branching process imply an interaction only between monomers belonging to the same connected cluster. This repulsion is different from excluded volume effects, which cannot distinguish between monomers belong to different clusters. In a solution which screens the excluded volume repulsions, one is still left with a correlated repulsion between monomers belonging to the same cluster which has a leading three-body term. The result is an important difference between percolation and solutions of linear chains. For the latter, one only has excluded volume interactions which are *screened*. Thus the chains in solution are free (i.e. Gaussian) at least for $d > 2$. For the branched chains there remains an *unscreened* 'branching' three-body repulsion.

To estimate the effect of these interactions on chain dimensions we consider first a single branched polymer. There is no screening. The dominant interaction is therefore the excluded volume two-body repulsion which becomes relevant below $d = 8$ (equation (5)). A Flory estimate for the free energy gives

$$F_a = R^2/N^{1/2} + N^2/R^d. \tag{7}$$

Minimising F_a gives (Issacson and Lubensky 1981)

$$\nu_a = 5/2(d+2). \tag{8}$$

For percolation, the excluded volume effects are screened. But each cluster still has the internal 'branching' repulsion and therefore:

$$F_p = R^2/N^{1/2} + N^3/R^{2d}. \tag{9}$$

This gives

$$\nu_{bp} = 7/4(d+1). \tag{10}$$

The upper critical dimensionality is $d = 6$. Thus percolation clusters are ideal ($\nu_{bp} = \frac{1}{4}$) above $d = 6$ in the same way that isolated linear chains are Gaussian above $d = 4$. The upper critical dimensionality in solution is six (rather than four) because of the unscreened 'branching' repulsion.

A curious feature of these Flory expressions was noted by Daoud (1982). For isolated linear chains the Flory expressions have a lower critical dimensionality $d_l = 1$. That is, for $d = 1$ the Hausdorff dimension D becomes equal to the dimension of space d. This reflects the fact that the intrinsic dimensionality of a linear chain is one, so that non-intersecting chains cannot be embedded in a space of lower d. For solutions one is left with a rather unsatisfactory situation because screening of the excluded volume repulsions breaks down at $d = 2$.

For branched chains both equations (8) and (10) give (Daoud 1982),

$$d_l\nu = 1; \qquad d_l = \tfrac{4}{3}. \tag{11}$$

Indeed, $d_l = \frac{4}{3}$ even for a general n-body repulsion†, unlike linear chains where $d_l = 1$ generally (Daoud 1982).

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† If one replaces the interaction term in (9) by an n-body repulsion ($N^n/R^{(n-1)d}$) one finds $\nu_{bp}^{(n)} = (2n+1)/2[(n-1)d+2]$ and (11) still holds.

However, there is no obvious topological interpretation of the value $\frac{4}{3}$, in contrast to the linear chain case. Branched chains are complex objects and, in contrast to linear chains, have no obvious intrinsic dimensionality. Still one can define an embedding dimension d_e as the lowest dimension of a cartesian space into which a non-intersecting cluster can be packed by rotating bonds. An obvious, but trivial, upper bound on d_e is given by the Hausdorff dimension D. A lower bound is the fracton dimension $\tilde{D}$ defined recently (Alexander and Orbach 1982), which determines the diffusion volume explored by a random walk and the state counting in the relevant Hilbert space. A random walk confined to an embedded object cannot explore more sites than are available in the embedding space. Empirically it was found (Alexander and Orbach 1982) that the fracton dimension for percolation clusters has the universal value $\frac{4}{3}$ for percolation clusters generated in two and higher dimensions. Recent computer experiments (Pandey and Stauffer 1983 and Havlin and Ben Avraham 1983) have tended to enhance the confidence in this finding. The meaning of this universality has been discussed (Rammal and Toulouse 1983, Alexander 1983, Leyvraz and Stanley 1983) but is not really understood. The independent result (11) suggests that $\frac{4}{3}$ is in some sense the intrinsic dimensionality of branched clusters and therefore determines both the fracton dimension $\tilde{D}$ and the embedding dimension d_e.

Following through the analogy between percolation and semi-dilute solutions leads to a rather rich picture. We can generalise slightly the standard percolation model, which corresponds to a melt, and consider a 'semi-dilute' situation with monomer concentration c. At short distances a given branched polymer sees only itself and therefore has animal indices, equation (8). The crossover determines a de Gennes 'blob' size

$$\xi_b^{(1/\nu_a - d)} = c; \qquad \xi_b \propto c^{-5/(3d-4)}. \tag{12}$$

For $8 \geq d \geq 6$ one then has an ideal branched chain of blobs with $\nu_{bp} = \frac{1}{4}$. The size of the clusters depends on c

$$P(N) \propto c^{-x} N^{1/4} \tag{13}$$

where, using (8) and (12)

$$x = (8 - d)/2(3d - 4), \qquad 8 \geq d \geq 6. \tag{14}$$

The generalisation to $d < 6$ is straightforward.

For $d > 6$ we predict $D = 4$, in contrast to the scaling prediction $D = d - \beta/\nu$ of Kapitulnik *et al* (1983). This discrepancy may be traced to the breakdown of hyperscaling above the upper critical dimension (Aharony *et al* 1983). The same type of breakdown occurs at an ordinary phase transition of, e.g., an Ising ferromagnet. For $d > 4$, the spin density correlation function $\langle s(0)s(r)\rangle \equiv M^2(r)$ decreases at large distance to the square of the magnetisation M^2. At $T \neq T_c$, $M^2(r)$ goes as r^{2-d} at short distances, and at large distances the difference $M^2(r) - M^2$ decays exponentially with a characteristic decay length $\xi \sim |T - T_c|^{-1/2}$. This ξ is independent of—and much larger than—the distance $r_1 \sim |T - T_c|^{-1/(d-2)}$ at which the extension of the short-distance behaviour of $M^2(r)$ would cross M^2. Thus over most of the correlation volume the $M^2(r)$ is nearly constant. It is this fact which makes mean-field theory applicable in high dimensions.

The breakdown of hyperscaling occurs similarly in percolation, and the various lengths in the problem have an appealing interpretation in terms of the geometry of the infinite cluster. The infinite cluster has an average density $P(p)$ which increases

linearly in $p - p_c$, so that $\beta = 1$ (cf equation (2)). The structure near a monomer of this cluster is that of an ideal randomly-branched polymer, with $D = 4$. Thus the density $\rho(r)$ of infinite cluster averaged over a distance r around such a monomer is given by $\rho(r) \sim r^{4-d}$, for r sufficiently small. For large r, $\rho(r)$ approaches its asymptotic limit $P(p)$. This crossover of density occurs at a distance $r \simeq \xi_d$ given by $\xi_d^{4-d} \simeq P(p) \sim (p - p_c)$. The decay of $\rho(r)$ to $P(p)$ is not governed by this length scale, but by a much longer one. To see this, we consider the density $\rho'(r)$ which is connected to the origin *within* distance r. This density is also that of a randomly branched polymer, and thus it falls off as r^{4-d}. But this density need not become constant beyond $r \simeq \xi_d$, since the density $P(p)$ of monomers on the infinite cluster need not be connected to the origin within the distance r. Beyond some distance ξ_p the monomers of ρ' intersect the 'backbone' of the infinite cluster—i.e. those monomers connected to infinity by two disjoint paths. The probability that a monomer on the infinite cluster is connected to infinity by a second path is $P(p)$; thus the density of backbone points is of order $P(p)^2$ for $d \geqslant 6$. At the distance $r \simeq \xi_p$ the ρ' monomers intersect the backbone with a probability of order 1:

$$P(p)^2 \xi_p^4 \simeq 1.$$

Thus ξ_p scales as $(p - p_c)^{-1/2}$ as expected for the correlation length for percolation. At scales of the order of ξ_p, many parts of the infinite cluster interpenetrate but do not touch. The number of interpenetrating parts is of order $\rho(\xi_d)/\rho'(\xi_d) \sim (p - p_c)^{(d-6)/(2d-8)}$. A third length of interest is the distance between tri-connected 'nodes' of the structure. These are the points connected to infinity by three disjoint paths, and their density is thus $P(p)^3$. The average distance between them is thus $\xi_s \sim (p - p_c)^{-3/d}$. But the typical distance between two chemically adjacent nodes is of order ξ_p. The three lengths ξ_d, ξ_p and ξ_s all scale as $(p - p_c)^{-1/2}$ as d approaches six from above. They all have the same scaling exponent below six dimensions as hyperscaling sets in.

The three-length-scale picture for the infinite cluster also emerges in a semi-dilute solution of linear chains at concentration c above four dimensions. Here the chains have Hausdorff dimension $D = 2$, and the relevant contacts are between two monomers rather than between three. The smallest length is the blob size $\sim c^{1/(2-d)}$, corresponding to 'density' length ξ_d. The density of contact points of different chains is c^2 and thus these points are spaced at a distance $\xi_s \sim c^{-2/d}$. Finally, the distance ξ_p between (interchain) contacts on a given chain obeys $c\xi_p^2 \cong 1$, so that $\xi_p \sim c^{-1/2}$. This is the familiar Edwards length (Edwards 1965).

The argument of Kapitulnik *et al* (1983) giving $D = d - \beta/\nu$ relies on the proportionality of ξ_d, ξ_s and ξ_p. Thus it is clear that the argument does not apply above the upper critical dimension.

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