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## LETTER TO THE EDITOR

# Potts model formulation of branched polymers in a solvent

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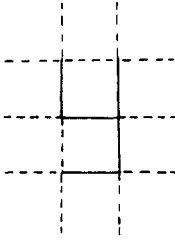
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**Abstract.** A Potts model formulation of the statistics of branched polymers or lattice animals in a solvent is given. The Migdal–Kadanoff renormalisation group is employed to study the critical behaviour or fractal dimension of the branched polymer. Four different critical behaviours are found, corresponding to random animal, collapse or  $\theta$  point, percolation and compact cluster. The  $\theta$  point behaviour is described by a tricritical point, while percolation corresponds to a higher-order critical point, where the effect of the solvent on the branched polymer is the same as the screening effect of the other clusters in percolation.

Linear polymers are made of bifunctional monomeric units, which are linked together to form long chains. If the monomer functionality is larger than or equal to 3, the resultant molecule is a branched polymer (Zimm and Stockmayer 1949). The statistics of dilute branched polymers in a good solvent can be suitably described by a single cluster made of sites (monomers) connected by nearest-neighbour bonds on a  $d$ -dimensional lattice (Lubensky and Isaacson 1979; see also Stauffer 1979, Stauffer *et al* 1982, Stanley *et al* 1982). A single isolated cluster is also called a lattice animal and corresponds to percolation in the very low density limit where the clusters can be treated as isolated. One important quantity is the radius of gyration (roughly the linear dimension of the cluster), which for a large number of monomers  $N_s$  behaves as  $R \sim N_s^\nu$ . This problem has recently received renewed attention for its intriguing connection with the Yang–Lee edge singularity in random fields as shown by the work of Parisi and Sourlas (1981). It has also been suggested that the lattice animal problem may be of relevance to the study of nucleation (Klein 1981, Heermann and Klein 1983). In this letter, I study the effect of a solvent on a branch polymer. A suitable lattice model for such a system is a single cluster made of  $N_s$  sites or monomers connected by  $N_b$  bonds where the sites interact via an effective nearest-neighbour interaction  $W = W_{SS} + W_{MM} - 2W_{SM}$ , where  $W_{SS}$  is the solvent–solvent interaction,  $W_{MM}$  the monomer–monomer interaction and  $W_{MS}$  the monomer–solvent interaction. Let us consider the most general case, in which both sites and bonds are independent variables and the sites are correlated. The generating function  $G_1$  for such a problem, which I call the site–bond correlated animal problem (SBCA), can be written as

$$G_1(\lambda_s, \lambda_b, K) = \sum_{N_s, N_b, N_{NN}} A(N_s, N_b, N_{NN}) \lambda_s^{N_s} \lambda_b^{N_b} \exp(KN_{NN}), \quad (1)$$

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**Figure 1.** Example of a lattice animal made of  $N_s = 6$  sites,  $N_b = 5$  bonds (bold lines),  $N_{NN} = 7$  nearest-neighbour pairs and  $N_t = 12$  perimeter bonds (broken lines).  $N_{NN} - N_b = N_u = 2$  is the number of NN pairs that are not bonded.

where  $\lambda_s$  and  $\lambda_b$  are respectively the site and bond activities,  $K = W/k_B T$  ( $k_B$  is the Boltzmann constant and  $T$  the temperature) and  $N_{NN}$  is the number of pairs of nearest-neighbour sites (figure 1). The quantity  $A(N_s, N_b, N_{NN})$  gives the number of distinct lattice animals with  $N_s$  sites,  $N_b$  bonds and  $N_{NN}$  pairs of NN monomers.

The special case

$$\lambda_s = 1, \quad K = 0, \quad (2a)$$

gives the random bond animal problem, while the random site animal problem is obtained by imposing

$$\lambda_b = e^{-K}, \quad K \rightarrow \infty. \quad (2b)$$

This latter result follows from the relation  $N_{NN} = N_b + N_u$  where  $N_u$  is the number of pairs of NN sites that are not bounded (figure 1), and from the restriction that configurations with  $N_u \neq 0$  are not allowed for random site animals.

It is convenient to write the generating function  $G_1$  in the following way:

$$G_1(\lambda_s, \lambda_b, K) = G_2(H_1, H_2, p) \quad (3)$$

where

$$G_2(H_1, H_2, p) = \sum_{N_b, N_s, N_t} D(N_s, N_b, N_t) e^{-H_2 N_s} e^{-H_1 N_b} p^{N_b} (1-p)^{N_t} \quad (4)$$

where  $N_t$  is the number of perimeter bonds (figure 1),  $D(N_s, N_b, N_t)$  gives the number of distinct lattice animals with  $N_s$  sites,  $N_b$  bonds and  $N_t$  perimeter bonds and

$$e^{-H_1} = \lambda_b [e^{-K}/(1 - e^{-K})], \quad e^{-H_2} = \lambda_s e^{Kc}, \quad p = 1 - e^{-K}, \quad (5)$$

where  $c$  is the coordination number.

$G_2$  is the generating function for random bond percolation with bond probability  $p$ , and two ghost fields, one coupling to the bonds ( $H_1$ ) and the other coupling to the sites ( $H_2$ ). This generating function with two ghost fields was first introduced by Giri *et al* (1977) and Wu (1978). In the usual bond percolation problem  $H_1 = 0$ . It is crucial to note that in the SBCA generating function defined by (1) one is concerned with a single isolated cluster *in a solvent*. In the percolation problem defined through (4) one is concerned with a single cluster *in the presence of other clusters*, which are taken into account by imposing the absence of bonds along the *perimeter*. The equivalence given by (3)–(5) follows easily from the identity  $N_{NN} = cN_s - N_t - N_b$ , which can be proven for a regular lattice in  $d$  dimensions and can be verified in the example of figure 1.

In order to study the critical behaviour of the SBCA we make use of the Potts model formulation for the generalised percolation problem defined by (4). Consider the following  $s$ -state Potts model

$$-\frac{\mathcal{H}}{k_B T} = J \sum_{(ij)} \delta_{\sigma_i \sigma_j} + L \sum_{(ij)} \delta_{\sigma_i 1} \delta_{\sigma_j 1} + H \sum_i \delta_{\sigma_i 1} \quad (6)$$

where  $\sigma_i = 1, \dots, s$  are the Potts variables and the first two sums are over all pairs of NN sites. It has been shown by Giri *et al* (1977), Wu (1978) and Harris and Lubensky (1981a) that  $G_2(H_1, H_2, p) = d \ln Z / ds|_{s=1}$ , where  $G_2$  is given by (4) and  $Z = \sum_{\{\sigma_i\}} \exp(-\mathcal{H}/k_B T)$  is the partition function for the Potts model (6) and

$$H_2 = H, \quad e^{-H_1} = (e^J - 1)/(e^{J+L} - 1), \quad p = 1 - e^{-(J+L)}. \quad (7)$$

In view of (3)–(5), the Hamiltonian (6) also gives SBCA with the following relations obtained from (5) and (7):  $\lambda_b = e^J - 1$ ,  $\lambda_s = e^{-H-c(J+L)}$ ,  $K = J + L$ . In particular, from (2a) the random bond animal is obtained for  $H = 0$ ,  $L = -J$  and from (2b) the random site animal is given for  $L = -2J$ ,  $H = cJ - \ln \lambda_s$  ( $J \rightarrow \infty$ ). The Potts formulation for the special case of a random bond animal has also been proposed by Family and Coniglio (1980) and Harris and Lubensky (1981a, b).

In order to study the critical behaviour of the SBCA, I have applied the Migdal-Kadanoff RG to the Hamiltonian (6). Although I have carried out explicit calculations only for dimensionality  $d = 2$ , the results are qualitatively true also for  $d > 2$ . The details of the calculations are given later. There are four fixed points corresponding to four different critical behaviours.

(1) *Random animal fixed point.* This gives rise to a critical surface in the parameter space  $\lambda_s$ ,  $\lambda_b$ ,  $K$  where the critical behaviour is the same as for the random animal problem.

(2)  *$\theta$  fixed point.* This describes a line of tricritical points where the branched polymer exhibits a collapse in analogy with the globule-coil collapse in a linear polymer in a poor solvent.

(3) *Percolation fixed point.* This is the most unstable fixed point, where the branched polymer exhibits a further collapse. This higher-order critical point is realised for the special values of  $\lambda_s$ ,  $\lambda_b$ ,  $K$ , which corresponds via (5) to  $H_1 = H_2 = 0$ ,  $p = p_c$  (random-bond percolation threshold). Therefore for such values of the parameters, the fractal dimensionality of the single isolated cluster in the animal problem is the same as that of the percolating cluster in the percolation problem. Physically this means that the effect of the solvent on the single isolated cluster in the animal problem is equivalent to the screening effect of all the other clusters in the percolation problem, as clearly shown from (3)–(5). This percolation behaviour is a new prediction for dilute branched polymers in a solvent. There is no analogue for dilute linear polymers.

(4) *Compact fixed point.* This corresponds to a further shrinking of the branched polymer with fractal dimensionality equal to  $d$ .

Each one of the above four critical behaviours is characterised by a critical exponent  $\nu_i$  ( $i = 1, 2, 3, 4$ ) related to the radius of gyration by  $R \sim N_s^{\nu_i}$ . Using numerical data and the Flory theory, we have  $\nu_1 < \nu_2 < \nu_3 < \nu_4 = 1/d$ . The branched polymer always shrinks as additional attractive interactions are introduced. More specifically, the Flory theory (Isaacson and Lubensky 1980, de Gennes 1980, Daoud and Joanny 1981) gives  $\nu_1 = 5/[2(d+2)]$ ,  $\nu_2 = 7/(4d+4)$ ,  $\nu_3 = 2/(d+2)$ . Although it may be difficult to measure precisely these critical exponents experimentally, nevertheless it should be possible to observe crossover from one regime to the other, using the same

techniques as for a dilute linear polymer system (Swislow *et al* 1980) or using computer 'experiments' (Redner 1979).

Harris and Lubensky (1981b), in their study of the animal problem in which they used the  $\epsilon$  expansion, also found the same structure of fixed points. But due to the complexity of the field theoretical formulation, the physical interpretation of the percolation fixed point was not clear. In a different approach Family and Coniglio (1980) studied the lattice animal problem in the presence of other clusters. For a special value of the parameters they also found a percolation fixed point. This is physically different from the case which I have introduced which applies to a single *isolated* cluster in the presence of a *solvent*.

In the generating function (1) it is possible to express the number of sites  $N_s$  in terms of number of independent loops  $N_L$  and number of bonds  $N_b$  via Euler's law:  $N_s = 1 + N_b - N_L$ . This allows us to study the SBCA as a function of the chemical potential of loops instead of  $\lambda_s$ . Since the random animal behaviour is characterised by only one relevant eigenvalue, the changing of the number of loops does not change the critical exponent, in agreement with the  $\epsilon$ -expansion result (Lubensky and Isaacson 1979). This is not true for the percolation point, which is characterised by three eigenvalues. Therefore any change of the parameters including the chemical potential for loops will always move away from the percolation fixed point under successive renormalisation.

The SBCA problem is analogous with another model, one that was originally developed to study solvent effects in the sol-gel transition (Coniglio *et al* 1979, 1982); subsequently it provided a satisfactory definition of a droplet that was used to describe the phase transition in the Ising model (Coniglio and Klein (1980), see also the recent review by Kertész *et al* (1983) and references therein). This is the site-bond correlated percolation problem where the clusters are made of sites connected by bonds. The sites are correlated according to the lattice-gas Hamiltonian while the bonds are random. The critical behaviour of the clusters is generally the same as in random percolation, except for a special value of the parameters where crossover to Ising critical behaviour is found.

The site-bond correlated percolation is also obtained from the Potts model (6) in the limit  $s \rightarrow 2$  instead of the  $s \rightarrow 1$  limit as for the SBCA. This is the reason why for the special values of the parameters corresponding to  $H = L = 0$  in one problem one finds Ising behaviour ( $s \rightarrow 2$ ) while in the other case one finds percolation behaviour ( $s \rightarrow 1$ ). It is also interesting to note that in view of the mapping of the Potts Hamiltonian (1) into the lattice-gas Potts model (Coniglio and Klein 1980), the critical behaviour of the SBCA problem as well as the site-bond correlated percolation problem has the same general structure found in the lattice-gas Potts model by Nienhuis *et al* (1979), namely a critical  $s$ -Potts, a tricritical  $s$ -Potts and an  $(s + 1)$ -Potts higher-order critical point.

The Migdal-Kadanoff RG applied to Hamiltonian (6), where the one-site interaction has been treated on the same footing as the two-site interaction  $(H/c)_{(ij)}(\delta_{\sigma_{i1}} + \delta_{\sigma_{j1}})$ , leads to the following recursion relations in the limit  $s \rightarrow 1$ :

$$\begin{aligned}x' &= (\tilde{x}^2 + \tilde{z}^2 - 1)/(2\tilde{x} + \tilde{z}^2 - 2), & w' &= \tilde{x}^2 \tilde{w}^2 / (\tilde{x}^2 + \tilde{z}^2 - 1), \\z' &= \tilde{z}(\tilde{x}\tilde{w} + \tilde{x} - 1)/(2\tilde{x} + \tilde{z}^2 - 2),\end{aligned}$$

where  $\tilde{x} = \exp[b^{(d-1)}J]$ ,  $\tilde{w} = \exp[b^{(d-1)}(L + 2H/c)]$ ,  $\tilde{z} = \exp[b^{(d-1)}H/c]$  and  $x' = \exp(J)$ ,  $w' = \exp[L' + (2/c)H']$ ,  $z' = \exp(H'/c)$ ,  $b$  is the scaling length factor. The

fixed point structure does not depend on  $d$  and has been analysed before. In particular, for  $b = 2$  and  $d = 2$  I find the following non-trivial fixed points:

- (1) *random animal fixed point*:  $x^* = \infty$ ,  $z^* = 2$ ,  $w^* = 0$ ,  $y_1^{-1} = \nu_1 = 1$ ;
- (2)  *$\theta$  fixed point*:  $x^* = 11.77$ ,  $z^* = 6.20$ ,  $w^* = 1.03$ ,  $y_2^{-1} = \nu_2 = 0.51$  and another relevant eigenvalue exponent  $\bar{y}_2^{-1} = 1.41$ ;
- (3) *percolation fixed point*:  $x^* = 1.61$ ,  $w^* = 1$ ,  $z^* = 1$  with  $y_3^{-1} = \nu_3 = 0.53$  with two more relevant eigenvalue exponents  $\bar{y}_3^{-1} = 1.63$  and  $\bar{y}_3^{-1} = 1.46$ ;
- (4) *compact fixed point*:  $w = 1$ ,  $z = 1$ ,  $x = \infty$  with  $y_4^{-1} = 0.5$ .

Note that in the Migdal–Kadanoff approximation  $\nu_2 < \nu_3$  as opposed to the general trend found from Flory's theory.

In conclusion, I have introduced a model for a branched polymer in a solvent. Besides the three critical behaviours expected in analogy with a linear chain in a poor solvent (random,  $\theta$ -collapse, compact), a percolation critical behaviour is found for special values of the parameters. These behaviours could be studied experimentally using, for example, the same technique employed by Swislow *et al* (1980) in the study of dilute linear polymers in a poor solvent and by computer experiments.

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