Branched polymers on Bethe and Husimi lattices

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We study a branched polymer model defined on a lattice with coordination number q. We introduce q different site fugacities, corresponding to all possible incoming polymer bonds on a site. The model is solved exactly on the treelike Bethe and Husimi lattices. In particular, the interesting case of two nonzero fugacities is treated. The model presents qualitatively different phase diagrams when the coordination number of the lattice is changed. The system has in some cases one polymerized phase, but in other cases a second polymerized phase appears. The conditions for the existence of this second polymerized phase are established.

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I. INTRODUCTION

The study of linear polymers in solution modeled by self-avoiding walks (SAW) on a lattice has been the subject of active investigation for many years [1]. Just as linear polymers, randomly branched polymers have been described by different types of lattice animals [2,3], trails [4,5], silhouettes of dynamical trails [6], and chains with annealed crosslinks [7].

In the last few years, there has been considerable interest in new multicritical phenomena that occur in polymer systems. Recently, Orlandini et al. [8] studied the statistical mechanics of silhouettes of dynamical trails on the two-dimensional Sierpinski gasket by an exact real-space renormalization group method. In that model, two fugacities for sites with two or four incoming polymer bonds are introduced, but the model is not self-attracting, that is, no nearest-neighbor fugacity is considered. They reported that the model displays two multicritical points, the usual Θ point which marks the separation between swollen and denser polymers and a second multicritical point between two polymerized phases.

In this paper, we study a branched polymer model defined on a lattice with coordination number q that has silhouettes of dynamical trails as a particular case. The model consists of an annealed mixture of m-functional units ($1 \leq m \leq q$). We introduce q site fugacities corresponding to q different functional units, or equivalently, to the possible number of incoming polymer bonds on a site. The model is solved exactly on the treelike Bethe and Husimi lattices. In particular, the interesting case of two nonzero fugacities is treated; when they correspond to two and q incoming polymer bonds on a site, the model reduces to silhouettes of dynamical trails for $q = 4$, which approaches the two-dimensional square lattice. The model presents qualitatively different phase di-

agrams when the coordination number of the lattice and the number of permitted incoming bonds are changed. For some values of those parameters, a second polymerized phase appears. The conditions for the existence of two polymerized phases are established.

Another model for branched networks with similar characteristics is the model of polymers with annealed crosslinks, which turns out to be equivalent to the n-vector model of magnetism with two and four spin interactions, in the formal limit $n \to 0$ [7]. Since crosslinks cannot be defined unambiguously on the Bethe lattice, the model defined by Stilck and Wheeler [7] on that lattice is a particular case of our model. In this reference only one polymerized phase is reported for mean field and Bethe lattice calculations, but in the case of the Husimi lattice with coordination number 4 a second ordered (polymerized) phase appears.

This paper is organized as follows. After defining the model in Sec. II, the exact solution on the Bethe lattice for different cases is shown in Sec. III, with special emphasis on the case where the fugacity of sites with two incoming polymer bonds is nonzero; this case has the SAW problem as a particular limit. However, since there are no loops on the Bethe lattice, the solution presents some undesirable features. For the special case of silhouettes of trails, a better treelike approximation, with four site loops (squares), known as the Husimi tree, is used in Sec. IV, giving more satisfactory results. Final conclusions and discussions are presented in Sec. V.

II. DEFINITION OF THE MODEL

We consider a lattice model for branched polymers. In this model, polymer networks are defined with the following rules.

(i) Each site of the lattice is occupied by one monomer (an m-functional unit), which may be connected by polymer bonds with one or more nearest-neighbor monomers forming a polymer. Monomers bonded to only one

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monomer are polymer ends.

(ii) Every monomer bonded with two or more monomers must be connected through polymer bonds to a polymer end. Therefore networks without end sites are forbidden.

If the only relevant interaction present is the excluded volume effect between monomers, the model reduces to the usual lattice animal problem. We include a statistical weight K_n for each site with n incoming polymer bonds, with $1 \leq n \leq q$, where q is the coordination number of the lattice.

In the grand-canonical ensemble, the partition function for the system on an N-site lattice with coordination number q will be

$$\mathcal{Z}_N(\{K_n\}) = \sum_{\alpha_1=0}^{\infty} \cdots \sum_{\alpha_q=0}^{\infty} \prod_{n=1}^{q} K_n^{\alpha_n} \, \Gamma_N(\{\alpha_n\}), \quad (1)$$

where α_n is the number of sites with n incoming polymer bonds, and $\Gamma_N(\{\alpha_n\})$ is the number of configurations allowed by the above mentioned rules with fixed values of $\alpha_1, \ldots, \alpha_q$ ($\Gamma_N = 0$ if $\sum \alpha_n > N$).

In this model K_1 is the activity of a polymer end (our definition is slightly different from the usual definition [9] where one-site polymers are possible). In terms of the analogy between polymer models and the $n \to 0$ limit of the magnetic n-vector model [1], the parameter K_1 is equivalent to an external magnetic field and therefore the phase diagrams will be calculated for $K_1 = 0$. Rule (ii) mentioned above implies, in this case, that the end points of a polymer network will be confined to the boundary of the lattice.

The statistical weight K_2 for linear chains is usually taken as a bond fugacity, instead of a site fugacity. Both treatments are equivalent, so we set all the statistical weights as site fugacities in order to write the partition function in a compact form.

III. SOLUTION ON THE BETHE LATTICE

In this section we solve the problem of equilibrium polymerization on the Bethe lattice, i.e., in the central region of a Cayley tree [10]. Like many treelike structures, the Cayley tree with coordination number q may be generated by attaching q subtrees to a central site; and every $(M+1)$-generation subtree may be constructed by connecting $(q-1)$ M-generation subtrees to a new root as indicated in Fig. 1. This property allows us to build

recursion relations for partial partition functions defined on subtrees, which are numbered according to the configuration of the root. This model may be solved on the Bethe lattice in a way which is similar to the one used for the self-attracting self-avoiding walk (SASAW) problem [11], so some details will be skipped.

If we label g_0 the partition function on a subtree with no polymer bond on the root, and g_1 when a polymer bond is present (Fig. 2), the resulting recursion relations are

$$g_0^{(M+1)} = \sum_{n=0}^{q-1} \binom{q-1}{n} K_n \left(g_0^{(M)} \right)^{q-1-n} \left(g_1^{(M)} \right)^n,$$
(2)

$$g_1^{(M+1)} = \sum_{n=1}^{q} \binom{q-1}{n-1} K_n \left(g_0^{(M)} \right)^{q-n} \left(g_1^{(M)} \right)^{n-1},$$
(3)

where, for the sake of convenience, we introduced K_0, which will be taken as unity for all calculations. Now, if we define the ratio

$$A^{(M)} = \frac{g_1^{(M)}}{g_0^{(M)}}, \quad (4)$$

we obtain only one recursion relation, namely,

$$A' = \frac{\displaystyle\sum_{n=1}^{q} \binom{q-1}{n-1} K_n A^{n-1}}{\displaystyle\sum_{n=0}^{q-1} \binom{q-1}{n} K_n A^n}, \quad (5)$$

where we have omitted the number of generations and denoted by A' the value of A considering one additional generation.

Connecting q subtrees to the central site we arrive at the (semi) grand partition function for the M-generation Cayley tree

$$\mathcal{Z}_M = \sum_{n=0}^{q} \binom{q}{n} K_n g_0^{q-n} g_1^n. \quad (6)$$

Taking the limit $M \to \infty$ this function gives the thermodynamic behavior of the model on the whole Cayley tree. Since we are interested in the solution on the Bethe lattice, we will use this partition function to define den-
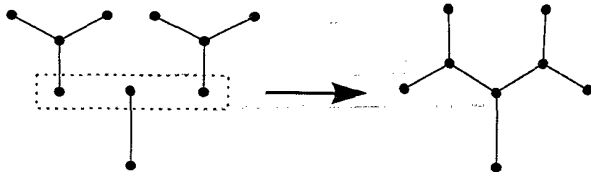

FIG. 1. Construction of a ($q = 3$, $M = 3$) subtree with $q = 3$ and $M = 3$ generations by attaching $q - 1 = 2$ subtrees with $q = 3$ and $M = 2$ generations.

FIG. 2. Root configurations associated with the two partial partition functions of subtrees on a Cayley tree with $q = 3$. Straight lines represent empty bonds and zigzag lines represent polymer bonds.

sities at the central site, such as the density of sites with i incoming polymer bonds

$$\rho_i = \frac{\binom{q}{i} K_i \, g_0^{q-i} \, g_1^i}{\mathcal{Z}} \, . \tag{7}$$

In the thermodynamic limit A tends to the fixed points of the recursion relation Eq. (5), defined by the equation $A' = A$; and densities may be expressed as functions of these fixed points as follows:

$$\rho_i = \frac{\binom{q}{i} K_i \, A^i}{\displaystyle\sum_{n=0}^{q} \binom{q}{n} K_n \, A^n} \, . \tag{8}$$

Among the fixed points of Eq. (5) only the stable ones represent thermodynamic phases. In regions of the phase space where more than one stable fixed point exist, it is necessary to apply the equal area rule for determining the phase diagram (a first order line is obtained).

In general, for the recursion relations $A'_i = A'_i(\{A_j\})$, $i, j = 1, \ldots, s$, the fixed point $\mathbf{A}^* \equiv (A_1^*, A_2^*, \ldots, A_s^*)$ is stable if the matrix $\mathcal{M}$, whose elements are

$$\mathcal{M}_{i,j} = \left. \frac{\partial A'_i}{\partial A_j} \right|_{\mathbf{A}^*} , \tag{9}$$

has all the eigenvalues with modulus less than one.

An interesting particular case of the model is obtained when we assign the statistical weight to the polymer bond instead of assigning it to the different types of monomers; or equivalently when we set $K_i = K^{\frac{i}{2}}$ for $i \geq 2$ and $K_1 = 0$ (known in the literature as lattice animals). With this assignment, the recursion relation presents a fixed point associated with the nonpolymerized phase ($A^* = 0$), which is stable for $K \leq \frac{1}{q-1}$ and one or more fixed points corresponding to the polymerized phase ($A^* \neq 0$). Moreover, one of them tends stably (with eigenvalue less than unity) to zero when $K \to \left(\frac{1}{q-1} \right) +$. Therefore the transition between the nonpolymerized and the polymerized phase is of second order, showing the same critical behavior as SAW's.

With our definition, the case $K_1 \neq 0$; $K_i = 0$ for $i > 1$ corresponds to the dimmer problem. Equation (5) in this case reads

$$A' = \frac{K_1}{1 + (q-1)K_1 A} \, . \tag{10}$$

This result agrees with previous calculations for dimmers on the Bethe lattice [12].

From Eq. (5) it is clear that when $K_q \neq 0$ and $K_{q-1} = 0$ there exists a fixed point $A^* \to \infty$ which, according to Eq. (8), corresponds to a polymerized frozen phase ($\rho_{m=q} = 1$; $\rho_n = 0$ if $n < q$). To study the fixed point $A \to \infty$ we define the new variable $\alpha \equiv \frac{1}{A}$, satisfying the recursion relation

$$\alpha' = \frac{\displaystyle\sum_{n=0}^{q-1} \binom{q-1}{n} K_n \, \alpha^{q-1-n}}{\displaystyle\sum_{n=1}^{q} \binom{q-1}{n-1} K_n \, \alpha^{q-n}} \, . \tag{11}$$

The corresponding fixed point is $\alpha^* = 0$, whose stability is easier to analyze.

It is of particular interest to consider two nonzero fugacities, making all the others equal to zero. This choice of the parameters may be interpreted as follows: we have two kinds of monomers with different fugacities that could be linked to m and n neighbors, respectively.

Analyzing the recursion relations for A and α [Eqs. (5) and (11)] and the eigenvalues of their fixed points we found different features according to the values of q, m, and n (with $q \geq m > n \geq 2$). They may be grouped in the following way.

$m < q$. There is no fixed point $\alpha^* = 0$, therefore the polymerized frozen phase is not present, but for some values of q, m, and n a second ordered phase (not frozen) appears. When two polymerized phases are present we will refer to the lower density of type-K_m monomers (lower ρ_m) as polymerized 1 and to the other as polymerized 2. Note that the polymerized 2 phase for $q = m$ is a frozen phase.

(1) $n = 2$. The stability line of the nonpolymerized phase is $K_2 = \frac{1}{q-1}$ and on this line a fixed point $A^* \neq 0$ vanishes, allowing a second order transition between the nonpolymerized and the polymerized 1 phases.

(2) $n > 2$. The transition to the nonpolymerized phase is always of first order, because the eigenvalue λ_{NP} corresponding to the fixed point $A^* = 0$ is equal to zero for all K_m and K_n.

$m = q$. (1) $n = q - 1$. The fixed point associated with the frozen phase ($\alpha^* = 0$) does not exist. If $q > 3$ we have $\lambda_{NP} = 0$, giving a first order transition. For $q = 3$, when $K_3 = 0$ we recover the SAW model that has a second order transition, but for any other value of K_3 the transition is of first order. Therefore, there is a critical point for $K_3 = 0$.

(2) $n < q - 1$. In this case (which excludes $q = 3$) the fixed point $\alpha^* = 0$ corresponding to the frozen phase appears. The transition to the nonpolymerized phase is always of first order ($\lambda_{NP} = 0$), except when $n = 2$, where for small K_q we have a SAW behavior.

For $n < q - 2$ the eigenvalue $\lambda_{P2} = \frac{\partial \alpha'}{\partial \alpha} \mid_{\alpha=0}$ is zero for all K_n and K_m; as a result, the transition to the frozen phase will always be of first order.

For $n = q - 2$ the eigenvalue λ_{P2} is not constant. Therefore the polymerized 2 phase is stable only in some regions of the phase space, and the phase diagram may have different multicritical behavior depending on the stability of the other phases.

We have analyzed, in a general way, the model restricted to only two parameters. We found a variety of situations that led to many different phase diagrams depending on the values of q, m, and n. In the following subsection we will study particular cases for $n = 2$, which are of interest because they model the polymeriza-

tion problem with linear and branched polymerized behaviors. Then we will analyze two particular cases with $n \neq 2$.

A. Linear-branched behavior

First, we will consider the problem for any value of q and m, and then we will analyze some particular values to illustrate the different situations.

When only K_2 and K_m are different from zero, Eq. (5) reads

$$A' = \frac{(q-1)K_2 A + \binom{q-1}{m-1} K_m A^{m-1}}{1 + \frac{(q-1)(q-2)}{2} K_2 A^2 + \binom{q-1}{m} K_m A^m} . \quad (12)$$

According to Eq. (12) the eigenvalue from the nonpolymerized phase is

$$\lambda_{\mathrm{NP}} = (q-1)K_2 , \quad (13)$$

therefore the nonpolymerized phase is stable for

$$K_2 \leq \frac{1}{q-1} . \quad (14)$$

This result is in perfect agreement with the SAW problem, i.e., in the limit $K_m \to 0$. So, the stability line of the nonpolymerized phase is

$$K_2(K_m) = \frac{1}{q-1} . \quad (15)$$

Now we will analyze the fixed points associated with the polymerized or polymerized 1 phase (the name depends on the existence of a second ordered phase), looking for a stable one that tends to zero when $(q-1)K_2 \to 1+$. When such a fixed point exists, we will have a second order transition (for K_m sufficiently small).

The polymerized fixed point is a positive root of the polynomial

$$P(A) = \binom{q-1}{m} K_m A^m - \binom{q-1}{m-1} K_m A^{m-2}$$
$$+ \frac{(q-1)(q-2)}{2} K_2 A^2 + 1 - (q-1)K_2. \quad (16)$$

It is clear that there is always a root that tends to zero when $(q-1)K_2 \to 1+$. We will study the sign and the stability of this root to determine the region where a second order transition could occur, i.e., where $\lim_{(q-1)K_2 \to 1+} A^* = 0$ and $\lambda \leq 1$ (λ is the corresponding eigenvalue). For this purpose we define $\epsilon \equiv (q-1)K_2 - 1$, so we are interested in the case $\epsilon \to 0+$.

We will analyze the polynomial for $A \ll 1$; we find three different typical patterns of behavior for $m = 3$; $m = 4$; and $m \geq 5$.

For $m = 3$, the relevant terms of the polynomial and the eigenvalue for $A \ll 1$ and $\epsilon \ll 1$ are

$$P(A) \approx -\frac{(q-2)(q-3)}{2} K_3 A - \epsilon, \quad (17)$$

$$\lambda \approx 1 + \frac{(q-2)(q-3)}{2} K_3 A. \quad (18)$$

It is clear that for $\epsilon > 0$ the root is negative for any $K_3 > 0$. So, in this case we will always have a first order transition (except for $K_3 = 0$ that corresponds to the SAW problem). Besides, we can see that for $\epsilon < 0$ there is a positive root that tends to zero, but it is unstable according to Eq. (18).

For $m = 4$, neglecting terms of order greater than A^3 and ϵA^2, we have

$$P(A) \approx \frac{(q-2)}{2} \left[1 - \frac{(q-1)(q-3)}{3} K_4 \right] A^2 - \epsilon, \quad (19)$$

$$\lambda \approx 1 - (q-2) \left[1 - \frac{(q-1)(q-3)}{3} K_4 \right] A^2. \quad (20)$$

Therefore, if

$$K_4 \leq \frac{3}{(q-1)(q-3)} \quad (21)$$

there is a positive root that goes continuously to zero when $(q-1)K_2 \to 1+$, and the associated eigenvalue tends to $1-$. In other words, we have a stable polymerized 1 fixed point that tends to the nonpolymerized fixed point. This means that the line $K_2 = \frac{1}{q-1}$, $K_4 \leq \frac{3}{(q-1)(q-3)}$ is a second order transition line, and the point

$$K_2 = \frac{1}{q-1}, \quad K_4 = \frac{3}{(q-1)(q-3)} \quad (22)$$

will be a tricritical point if $q > 4$. The case $q = 4$ must be studied separately.

Finally, for $m \geq 5$, repeating the above procedure we obtain

$$P(A) \approx \frac{(q-2)}{2} A^2 - \epsilon, \quad (23)$$

$$\lambda \approx 1 - (q-2) A^2. \quad (24)$$

These equations show that for all K_m there is a stable polymerized 1 fixed point that goes to zero when $(q-1)K_2 \to 1+$. In this case the line $K_2 = \frac{1}{q-1}$ will be a second order transition line that will end in a critical end point, since a second ordered phase appears.

The transition polymerized 1–polymerized 2 is always of first order. This transition line may end on a critical point or simply continue to infinity depending on the values of q and m. We found that the critical point only exists if $(8 - m)q - 16 > 0$. Clearly, for $q > m \geq 8$ the transition line goes to infinity.

The coordinates of the critical point (when it exists) are

$$K_{2\mathrm{CP}} = \frac{2m(q-m)}{(q-1)\left[(8-m)q - 16\right](m-2)}, \quad (25)$$

$$K_{m_{CP}} = \frac{(q-2)(m-4)^2}{\binom{q-1}{m} \left(\frac{m-4}{q-m}\right)^{\frac{m}{2}} [(8-m)q - 16](m-2)}.$$
(26)

Some particular values of q and m that show qualitatively different phases diagrams follow.

1. $q = m = 4$ case

First, we will study the polymerized 1 phase. In this case the polynomial from Eq. (16) takes the form

$$P(A) = [(q-1)K_2 - K_4] A^2 + 1 - (q-1)K_2 . \quad (27)$$

This polynomial has only one positive real root,

$$A_{P1}^* = \sqrt{\frac{(q-1)K_2 - 1}{(q-1)K_2 - K_4}} , \quad (28)$$

that is well defined if $(q-1)K_2 \geq 1$ and $(q-1)K_2 > K_4$, or if $(q-1)K_2 \leq 1$ and $(q-1)K_2 < K_4$. The eigenvalue associated with this fixed point may be written in the forms

$$\lambda_{P1} = -1 + \frac{2(1 + K_4 A^2)}{1 + (q-1)K_2 A^2} \quad (29)$$

or

$$\lambda_{P1} = 1 - \frac{2[(q-1)K_2 - K_4] A^2}{1 + (q-1)K_2 A^2} , \quad (30)$$

where we have used $P(A) = 0$.

From these equations it is clear that $|\lambda_{P1}| \leq 1$ only if $(q-1)K_2 \geq K_4$. Consequently, we have a stable polymerized 1 fixed point in the region where $(q-1)K_2 \geq 1$ and $(q-1)K_2 \geq K_4$.

To study the stability of the polymerized 2 phase we note that Eq. (11) in this case reads

$$\alpha' = \alpha \frac{(q-1)K_2 + \alpha^2}{K_4 + (q-1)K_2 \alpha^2} . \quad (31)$$

Clearly, there exists a fixed point $\alpha^* = 0$. Differentiating Eq. (31) with respect to α and evaluating in $\alpha = 0$ we obtain

$$\lambda_{P2} = \frac{(q-1)K_2}{K_4} . \quad (32)$$

So, we see that this phase is stable in the region where $K_4 \geq (q-1)K_2$, and the stability line is

$$K_{4_{P2}}(K_2) = (q-1)K_2 . \quad (33)$$

Note that it coincides with the stability line of the polymerized 1 phase (for $K_4 \geq 1$). Hence the polymerized 1–polymerized 2 transition is always of second order.

For $(q-1)K_2 < 1$ there is a region where the nonpolymerized and the polymerized 2 phases are both stable. Consequently, there will be a first order line that we determine by the equal areas rule:

$$K_4(K_2) = 1 . \quad (34)$$

The $(K_2 = \frac{1}{q-1}; K_4 = 1)$ point where two second order lines converge and continue as a first order line that is not tangent to any of them is a bicritical point. The corresponding phase diagram is shown in Fig. 3.

2. $q = m = 3$ case

The phase diagram for this case (Fig. 4) shows the features predicted when we analyzed the problem for arbitrary q and m. There is no frozen phase, and the nonpolymerized-polymerized transition is of first order for all $K_3 > 0$, showing a critical point at $K_3 = 0$. Here the equation of the equal area rule was solved numerically and the stability line of the polymerized phase was found analytically:

$$K_{2_{NP}}(K_3) = \frac{1}{q-1} , \quad (35)$$

$$K_{3_P}(K_2) = \sqrt{2(q-1)K_2 [1 - (q-1)K_2]} . \quad (36)$$

3. $q = 6; m = 4$ case

For these values of q and m, only one polymerized phase exists and the phase diagram presents a tricritical point with coordinates given by Eq. (22). In analogy with the other studied cases, the stability lines are obtained analytically. They are
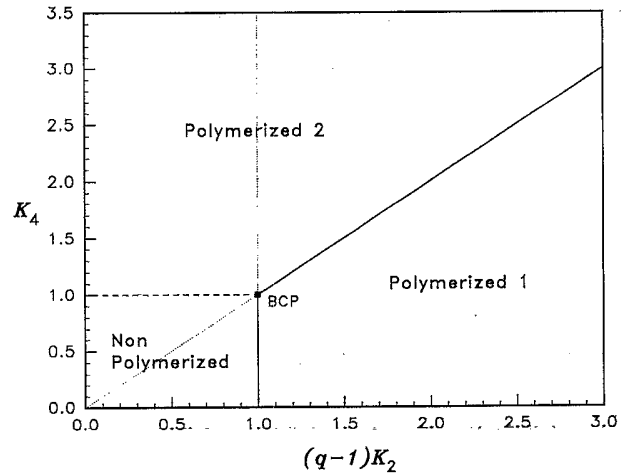
$$K_{2_{NP}}(K_4) = \frac{1}{q-1} , \quad (37)$$

FIG. 3. K_4 against $(q-1)K_2$ phase diagram for the Bethe lattice with coordination number $q = 4$. The full lines represent second order transitions and the dashed line locates the first order transitions. The stability (spinodals) curves are also shown (dotted lines). The critical lines end in a bicritical point (BCP).
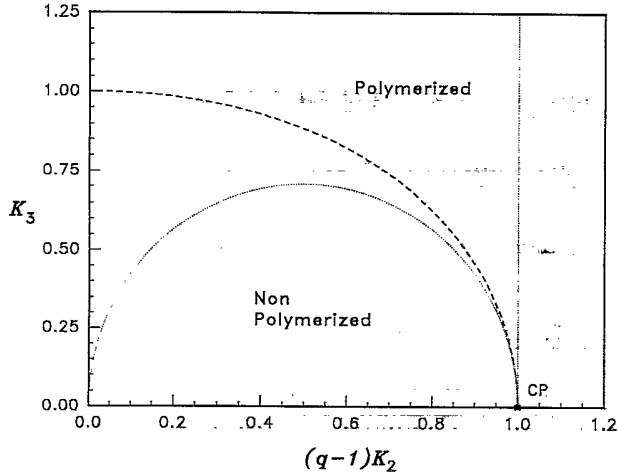
FIG. 4. K_3 against $(q-1)K_2$ phase diagram for a $q = 3$ Bethe lattice, showing the first order curve (dashed line) and the spinodal lines (dotted lines), as well as the critical point (CP) corresponding to the SAW limit $K_3 = 0$.

$$K_{4P}(K_2) = \frac{(q-1)K_2 + 1}{10}$$
$$\times \left(1 + \sqrt{1 - \frac{4(q-1)^2 K_2^2}{[(q-1)K_2 + 1]^2}}\right). \quad (38)$$

This case is equivalent to the problem studied in Ref. [7].

4. q = 6; m = 5 case

Two polymerized phases are present. The stability line of the nonpolymerized phase is

$$K_{2\mathrm{NP}}(K_6) = \frac{1}{q-1} . \quad (39)$$

As shown in Fig. 5, the phase diagram presents a critical endpoint, and the first order polymerized 1–polymerized 2 transition line ends on a critical point whose coordinates are [see Eq. (25) and Eq. (26)]:

$$K_{2\mathrm{CP}} = \frac{1}{3}, \quad K_{5\mathrm{CP}} = \frac{2}{3} . \quad (40)$$

The first order line and the stability lines of the polymerized phases were obtained numerically.

5. q = 6; m = 6 case

A second ordered phase appears, but in this case, as $q = m$ it is a frozen phase.

The polymerized 2 phase is stable for all K_2 and K_6 (in general, for $m = q \geq 5$ the polymerized 2 phase is stable for all K_q and K_2). The stability lines of the other phases are

$$K_{2\mathrm{NP}}(K_6) = \frac{1}{q-1} , \quad (41)$$

$$K_{6P1}(K_2) = \frac{(q-1)^2 K_2^2}{(q-1)K_2 - 1}. \quad (42)$$

As shown in Fig. 6, the phase diagram presents a critical end point with coordinates

$$K_{2\mathrm{CEP}} = \frac{1}{q-1}, \quad K_{6\mathrm{CEP}} = 1 , \quad (43)$$

because the second order line ends in a first order one. The first order line was obtained numerically.
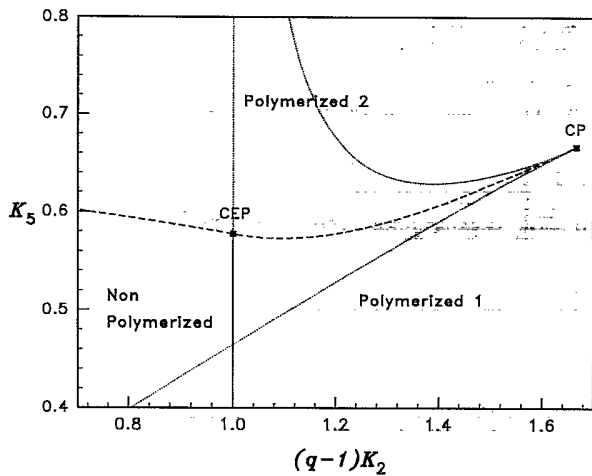

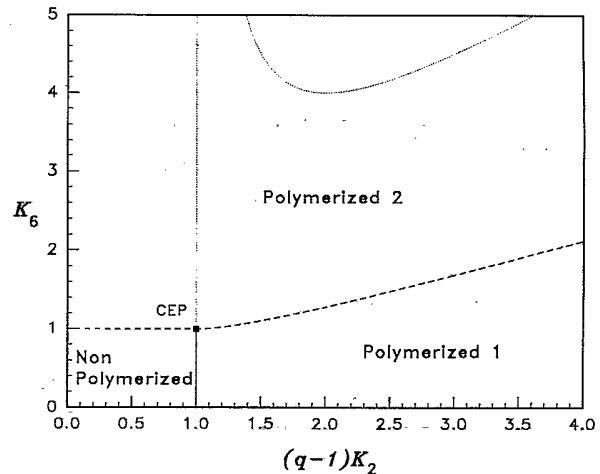
FIG. 5. K_5 against K_2 phase diagram for the $q = 6$ Bethe lattice, showing the second order line (full line), the first order curve (dashed line), and the spinodal lines (dotted lines). The critical line ends in a critical end point (CEP) and the first order line ends in a critical point (CP).

FIG. 6. K_6 against $(q-1)K_2$ phase diagram for a $q = 6$ Bethe lattice, showing the second order line (full line), the first order curve (dashed line), and the spinodal lines (dotted lines). The critical line ends in a critical end point (CEP).

B. Branched-branched behavior

In this subsection we treat $K_n, K_m \neq 0$ cases, with $q \geq m > n > 2$. We note that with these conditions the system does not have the SAW limit, therefore, even for $K_m = 0$, the polymers have a branched regime. Besides, the transition to the nonpolymerized phase is always of first order.

In general, the possible phase diagrams for these cases are qualitatively the same as those obtained for $n = 2$, except that the transition to the nonpolymerized phase is always of first order. Consequently in some cases a triple point appears.

Another difference is that for the existence of a second ordered phase when $q > m$ we have found only a necessary (but not sufficient) condition: m must be greater than $n + 2$ ($m > n + 2$) for having a second polymerized phase. Therefore we consider here two particular cases that lead to qualitatively different phase diagrams.

The case we first study here is $q = m = 6$, $n = 4$, for which the recursion relation [Eq. (5)] reads

$$A' = \frac{10K_4 A^3 + K_6 A^5}{1 + 5K_4 A^4} . \tag{44}$$

We note the existence of a nonpolymerized fixed point ($A^* = 0$) and it is straightforward to show that this phase is always stable. So, the transition to this phase will be of first order.

Working as we did in the last subsection, we find two nontrivial fixed points corresponding to two ordered phases, a polymerized 1 and a polymerized 2 phase. The latter is frozen phase ($\rho_6 = 1$, $\rho_4 = 0$).

The stability lines of these two fixed points are coincident. Consequently the transition between these phases is always of second order, and the transition line will end in a critical end point on the nonpolymerized-polymerized first order line. The expression for the second order polymerized 1– polymerized 2 curve is
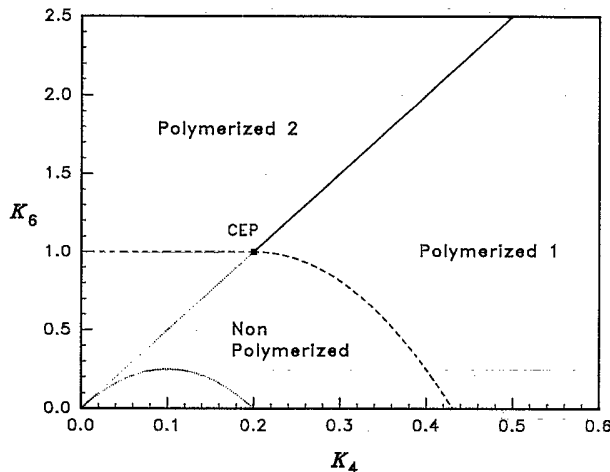

FIG. 7. K_6 against K_4 phase diagram for the $q = 6$ Bethe lattice, showing the second order line (full line), the first order curve (broken line), and the spinodal lines (dotted lines). The critical line ends in a critical end point (CEP).
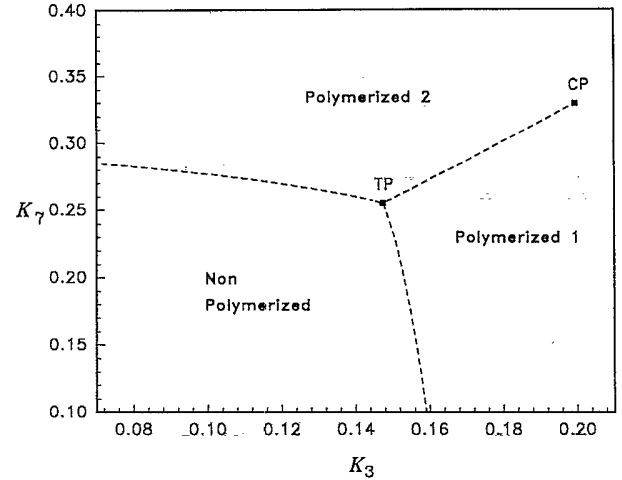

FIG. 8. K_7 against K_3 phase diagram for the $q = 9$ Bethe lattice, showing three first order lines (dashed line) joined in a triple point (TP). The polymerized 1–polymerized 2 first order line ends in a critical point (CP).

$$K_6(K_4) = 5K_4 . \tag{45}$$

We should add that for $K_6 < 5K_4(1 - 5K_4)$ there is no polymerized 1 fixed point.

The first order line was calculated numerically, by the equal areas rule. The resulting phase diagram is shown in Fig. 7.

A particular case with $q > m$ that shows a second ordered phase and a triple point is $q = 9$, $m = 7$, and $n = 3$. For this case the first order lines and the stability lines were calculated numerically. The corresponding phase diagram is shown in Fig. 8. Note the appearance of a triple point that was not present in the phase diagrams obtained for $n = 2$.

The undesirable feature of having for $q = m$ a frozen second ordered phase, and the fact that the stability of the nonpolymerized phase is independent of K_m for all cases, suggest the study of our model on the Husimi lattice. As will be shown, the inclusion of closed loops (only elementary squares) entails the disappearance of those nonphysical properties.

IV. SOLUTION ON THE HUSIMI LATTICE

In the present section we will study the polymerization problem on the Husimi lattice, i.e., on the central region of the Husimi tree. We will consider the most relevant case, namely, the one which approaches the two-dimensional square lattice and models silhouettes of trails, that for our model is the particular case $q = m = 4$, $n = 2$.

The Husimi tree [13] is constructed in the same way as the Cayley tree, except that the basic elements are squares instead of lines. For this reason, we only have elementary closed loops (elementary squares).

The procedure is the same as in the Bethe lattice. First, we obtain recursion relations for the partial parti-

tion functions. Then, we define new variables in terms of which we will express the densities, and for those variables we find recursion relations. The stable fixed points of those relations will determine the different phases. Finally, we study the stability regions of the fixed points, and make the equal areas construction in order to find the first order transition line (in regions where there are more than one stable fixed point).

The different types of roots associated with the corresponding partial partition functions are shown in Fig. 9. To avoid counting prohibited configurations like isolated clusters, it is necessary to distinguish whether the polymer that occupies the two lower sides of the root square contacts the external surface or not. This explains the existence of g_2 and g_3, because the only difference between them is that the polymer that crosses the root g_2 reaches the external surface, and that of g_3 does not.

For the partial partition functions associated with those roots, the recursion relations are

$$g_0' = (g_0 + K_2 g_2)^3 + 2K_2^2 g_1^2 (g_0 + K_2 g_2)$$
$$+ K_2^2 g_1^2 [K_2 g_0 + K_4 (g_2 + g_3)], \qquad (46)$$

$$g_1' = 2K_2 g_1 (g_0 + K_2 g_2)^2 + 2K_2 g_1 (g_0 + K_2 g_2)$$
$$\times [K_2 g_0 + K_4 (g_2 + g_3)]$$
$$+ 2K_2 g_1 [K_2 g_0 + K_4 (g_2 + g_3)]^2 + 2K_2^3 g_1^3, \qquad (47)$$

$$g_2' = K_2^2 g_1^2 (g_0 + K_2 g_2) + 2K_2^2 g_1^2 [K_2 g_0 + K_4 (g_2 + g_3)]$$
$$+ \left\{ [K_2 g_0 + K_4 (g_2 + g_3)]^3 - (K_2 g_0 + K_4 g_3)^3 \right\}, \qquad (48)$$

$$g_3' = (K_2 g_0 + K_4 g_3)^3 . \qquad (49)$$

Defining

$$A = \frac{g_1}{g_0}, \quad B = \frac{g_2}{g_0}, \quad C = \frac{g_3}{g_0}, \qquad (50)$$

we obtain the new relations

$$A' = \frac{2K_2 A}{D} \left\{ (1 + K_2 B)^2 + (1 + K_2 B)[K_2 + K_4 (B + C] \right.$$
$$\left. + K_2^2 A^2 + [K_2 + K_4 (B + C)]^2 \right\}, \qquad (51)$$

$$B' = \frac{1}{D} \left\{ K_2^2 A^2 [1 + 2K_2 + K_2 B + 2K_4 (B + C)] \right.$$
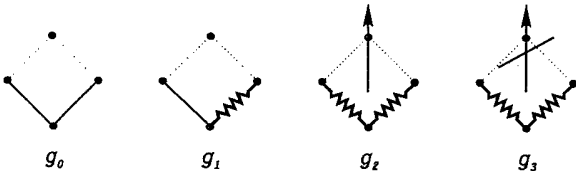$$\left. + [K_2 + K_4 (B + C)]^3 - (K_2 + K_4 C)^3 \right\}, \qquad (52)$$

FIG. 9. Root configurations associated with the three partial partition functions of subtrees on a Husimi tree with $q = 4$. Straight lines represent empty bonds, zigzag lines represent polymer bonds, and dotted lines may be occupied by a polymer bond or not. The arrow means that the polymer network is connected to the boundary and the crossed arrow means that the polymer does not reach the boundary.

$$C' = \frac{(K_2 + K_4 C)^3}{D}, \qquad (53)$$

where we defined

$$D = (1 + K_2 B)^3 + 2K_2^2 A^2 (1 + K_2 B)$$
$$+ K_2^2 A^2 [K_2 + K_4 (B + C)] . \qquad (54)$$

The (semi) grand partition function is

$$\mathcal{Z} = g_0^2 + K_2 g_1^2 + 2K_2 g_0 g_2 + K_4 (g_2^2 + 2g_2 g_3) \qquad (55)$$

and the densities are

$$\rho_2 = \frac{K_2 A^2 + 2K_2 B}{1 + K_2 A^2 + 2K_2 B + K_4 B^2 + 2K_4 BC}, \qquad (56)$$

$$\rho_4 = \frac{K_4 (B^2 + 2K_2 BC)}{1 + K_2 A^2 + 2K_2 B + K_4 B^2 + 2K_4 BC} . \qquad (57)$$

Analyzing Eqs. (52) and (53) and considering Eqs. (56) and (57) we note the existence of the following fixed points associated with the corresponding phases.

(1) $A = B = 0$; $C \neq 0$. This phase corresponds to the nonpolymerized phase. As a consequence of having $C \neq 0$ the spinodal of the nonpolymerized phase will not be independent of K_4. This happens because of the inclusion of closed loops.

(2) A, B, $C \neq 0$. This fixed point is associated with the polymerized 1 phase.

(3) $A = 0$; B, $C \neq 0$. This phase corresponds to the polymerized 2 phase. Note that this phase, as a result of including closed loops, is no longer a frozen phase.

(4) $A = \infty$; $B \neq 0$, $C = 0$. This fixed point is unstable for all values of the parameters, therefore it does not correspond to a thermodynamic phase.

Except for the stability of the nonpolymerized phase, all stability regions and stability lines were calculated numerically. The first order line (determined by the equal areas rule) was also obtained numerically.

The phase diagram for this case is shown in Fig. 10. We found that the transition lines are no longer straight lines as in the Bethe lattice solution (Fig. 3). The multicritical behavior is also different. In this case a tricritical point is found in the polymerized 1–polymerized 2 line and the second order nonpolymerized–polymerized 1 line ends at the first order transition line. Then a critical end point appears. Their coordinates are

$$K_{2_{\text{TCP}}} = 0.333\,30, \quad K_{4_{\text{TCP}}} = 0.999\,90,$$
$$\qquad (58)$$
$$K_{2_{\text{CEP}}} = 0.327\,01, \quad K_{4_{\text{CEP}}} = 0.992\,54.$$

The stability line of the nonpolymerized phase is

$$K_{4_{\text{NP}}}(K_2) = \begin{cases} \frac{4}{27K_2^2} & \text{if } K_2 \leq K_2^t \\ \frac{4\sqrt{\frac{2-3K_2}{K_2}} - 8K_2 - 4}{\left(\sqrt{\frac{2-3K_2}{K_2}} - 1\right)^3} & \text{if } K_2 \geq K_2^t, \end{cases} \qquad (59)$$

where K_2^t is the positive real root of the polynomial

$$p(K_2) = \frac{K_2}{2} \left(9K_2^2 + 6K_2 + 4\right) - 1 \qquad (60)$$

that is obtained by imposing the condition $\lambda_{NP}^{(1)} = \lambda_{NP}^{(2)} = 1$, where λ_i ($i = 1, 2, 3$) are the eigenvalues of $\mathcal{M}$ corresponding to the nonpolymerized fixed point (note that for this fixed point we have $\lambda_{NP}^{(2)} = \lambda_{NP}^{(3)}$ for all values of K_2, K_4).

V. CONCLUSIONS

A model of branched polymers with annealed mixture of polyfunctional monomers is solved exactly on Bethe and Husimi lattices. In the Bethe lattice solution we studied the phase diagrams of the polymer model, in general and for many particular cases. We have to emphasize the variety of diagrams that may be obtained modifying
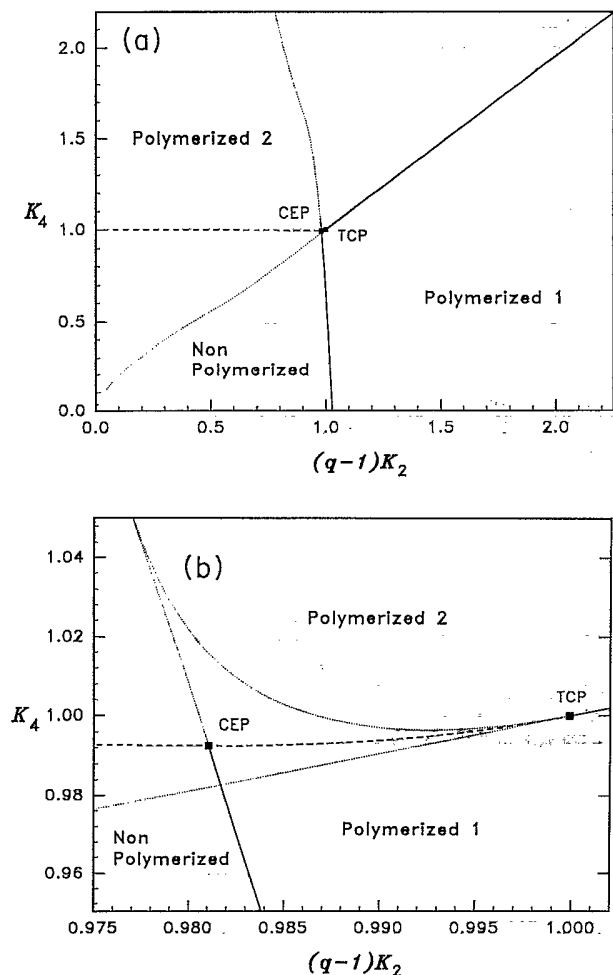

FIG. 10. (a) K_4 against $(q - 1)K_2$ phase diagram for the Husimi lattice with coordination number $q = 4$. The full lines represent second order transitions and the dashed line locates the first order transitions. The stability (spinodals) curves are also shown (dotted lines). The critical end point (CEP) and the tricritical point (TCP) are difficult to distinguish at this scale. (b) Amplification of the CEP-TCP region.

the relation between the coordination of the lattice q and the number of incoming polymer bonds on a site n and m. The existence of two ordered phases for some values of q, m, and n is reported. For $n = 2$, a condition for the existence of a second ordered phase is established. This condition is verified in other problems that present a second ordered phase, e.g., our model on the Husimi lattice and silhouettes of dynamical trails on a Sierpinski gasket [8].

The Bethe lattice solution has some peculiar features. When $m = q$, the second polymerized phase is a frozen phase. We also show that, for $n = 2$, the second order line between the nonpolymerized and the polymerized 1 phases is independent of K_m for all cases. This feature of the second order line is present in several models that have the SAW as a particular limit. The SASAW model [11] and the n-vectorial model with four spin interactions [7] studied on the Bethe lattice present the same behavior for the second order phase transition line. For both models this line depends on the second thermodynamic parameter when treated on the Husimi lattice (which is a better mean-field-like approximation than the Bethe lattice).

On the Husimi lattice of coordination number $q = 4$, we study the particular case of two nonzero fugacities corresponding to two (K_2) and four (K_4) incoming bonds on a site, which approximates silhouettes of trails on the two-dimensional square lattice. The results obtained for our model on the Husimi lattice are qualitatively similar to the calculations on the Bethe lattice, but some important differences must be emphasized. The phase diagram on the Husimi lattice seems more realistic, both polymerized phases are not frozen, and the second order line between the nonpolymerized–polymerized 1 phases depends in this case on the value of K_4, because of the inclusion of closed loops. The multicritical behavior is also different. The Θ-like point is a bicritical point on the Bethe lattice, but on the Husimi lattice it is a critical end point and a tricritical point appears on the phase transition line between both polymerized phases.

It is not clear that such a phase diagram with two ordered phases is possible only on treelike lattices. In the Husimi lattice (and only in this lattice) a mapping between the model of polymerization with crosslinks and the SASAW exists [14]. Therefore, on the Husimi lattice, the SASAW has a second polymerized phase; however, it is known that this phase does not appear for the SASAW problem on regular two-dimensional lattices [15,16], fractal lattices [17], and on the treelike Bethe lattice [11]. Then, one might ask if the second polymerized phase is present in the square lattice solution or not.

The problem of silhouettes of dynamical trails, which is equivalent to our model with K_2 and K_4 nonzero for lattices with coordination number equal to 4, was studied recently on the Sierpinski gasket (a fractal lattice with fractal dimension less than 2 and coordination number equal to 4) [8]. In this reference two polymerized phases and the existence of a new multicritical point between these phases are reported. Two polymerized phases in two dimensions were also found in two-tolerant trails [8], vesicles [18] and self-attracting self-avoiding loops [19].

A preliminary study of our model on the square lattice using transfer-matrix techniques [20] also supports the idea that the phase diagram shown in Fig. 8 is qualitatively correct for the square lattice, but the nature of the multicritical behavior is an open question and new studies of this phase transition would be interesting.

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