

# Walks with up to two monomers per site on the Bethe lattice: Interpolation between models with immediate reversals allowed and immediate reversals forbidden

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We generalize earlier calculations of the RA (immediate reversals allowed) and RF (immediate reversals forbidden) model with multiple monomers per site, including a parameter in the model, so that both cases studied before are particular cases of the model considered here. Also, we calculate the bulk free energy of the model using Gujrati's prescription, which leads to corrections in the localization of coexistence lines and qualitative changes in the phase diagram of the model. Thus, this calculation provides an example in which the use of the method of iterating recursion relations starting with natural initial conditions to locate coexistence loci is not trustworthy and may lead to qualitatively different results. A continuous collapse transition appears in all cases as a tricritical point.

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## I. INTRODUCTION

In the standard model for studying the collapse transition of linear polymers in poor solvents, the polymeric chains are represented by self- and mutually avoiding walks on a lattice, so that monomers are placed on lattice sites and polymer bonds on edges of the lattice, introducing attractive interactions between monomers on first-neighbor sites of the lattice that are not consecutive along a chain [self-attracting self-avoiding walks (SASAW's)] [1,2]. In the grand-canonical ensemble, the fieldlike variables are (i) the fugacity of a monomer  $z = \exp(\beta\mu)$ , where  $\beta = 1/k_B T$  and  $\mu$  is the chemical potential of a monomer, and (ii) the Boltzmann factor  $\omega = \exp(\beta\epsilon)$ , where  $-\epsilon$  is the attractive energy associated with two interacting monomers. At low values of  $\omega$  (high temperatures), a continuous polymerization transition is observed as the fugacity  $z$  is increased, between a nonpolymerized phase (empty lattice) and a polymerized phase, whose density of monomers vanishes and therefore is identified with an *extended* or coil-like phase. As the Boltzmann factor is increased (temperature is lowered), the polymerization transition becomes tricritical and then of first order, so that the nonpolymerized phase coexists with a polymerized phase of nonvanishing density of monomers, which is a *collapsed* or globular-like phase. In the canonical situation, the system is always at the border of the region in the parameter space occupied by the nonpolymerized phase, as is discussed in [3], and therefore the transition between the extended and the collapsed phases, which happens at the tricritical point, is continuous.

Some time ago, an alternative model for the collapse of polymer chains was proposed by Krawczyk *et al.* [4], where up to  $K > 1$  monomers may occupy the same lattice site and the monomer-monomer interaction is restricted to monomers on

the same site. Let us call this model MMS (multiple monomers per site). The model was studied using canonical simulation for  $K = 3$  on the square and the cubic lattices. Besides the case without additional restrictions for the walks, another case was studied in which, once a walk leaves a site to reach a first-neighbor site, it is not allowed to return immediately to the original site. These two versions of the model were called RA (immediate reversals allowed) and RF (immediate reversals forbidden), respectively. The only case for which the authors found an extended-collapse transition in the simulations was for the RF model on the cubic lattice, and this transition apparently is continuous in part of the border between the phases and discontinuous in the remaining part of this border, with both lines meeting at a tricritical point. The absence of a transition in two dimensions and for the RA model is a puzzling result.

A series of studies of these models on hierarchical lattices, such as the Bethe and Husimi lattices, were realized to find out the thermodynamic behavior of the MMS model, which emerges from the exact solutions on these lattices, which may be seen as approximate solutions of the same model on regular lattices [5]. Both versions of the MMS model were solved on the Bethe lattice for  $K = 2$  [6], and a diagram that resembles the one for the SASAW's model was found for the RF model, although an additional polymerized phase appeared with a predominance of double-occupied sites. Some differences were observed in the thermodynamic behavior of the RA model on the Bethe lattice, where no tricritical point was found. Here we correct and extend the results of that paper, introducing an additional parameter in the model that allows us to interpolate between both models studied there. Also, we do obtain the bulk free energy per site for the model using a prescription originally presented by Gujrati [7], which enables us to find better results for the coexistence loci as compared to the original ones, obtained using the recursion relations with *natural* initial conditions [8]. These changes lead to different phase diagrams, and for all cases studied here we obtain results that are similar

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to the phase diagram of SASAW's discussed earlier. Thus, our calculations show for the present model that the method used by us to obtain the former results may lead to results that differ from the correct ones. The model will be defined in Sec. II, and its solution in terms of recursion relations, as well as the calculation of the bulk free energy per site, are given. The thermodynamic behavior is discussed in Sec. III.

## II. DEFINITION OF THE MODEL AND SOLUTION IN TERMS OF RECURSION RELATIONS

Since the definition of the model and the method of its solution on the Bethe lattice are similar to the case discussed in [6], we will not include many details here for brevity. The model is defined on a Cayley tree with coordination number  $q$ ; the end point of the chains are placed on the surface of this tree. Each site of the tree may be visited at most two times, that is, up to  $K = 2$  monomers may occupy each site. Figure 1 in [6] shows a contribution that has some immediate returns and thus does not contribute to the partition function of the RF model. The statistical weight of a site is equal to 1 if the site is empty and  $\omega_i \kappa^j$  if  $i$  monomers are placed on the site and  $j$  immediate returns (hairpin configurations) are present at the site. When  $\kappa = 1$ , this model reduces to the RA model, and for  $\kappa = 0$ , no hairpin configurations are present and therefore the RF model is recovered. The statistical weight of a configuration is the product of the contributions of all sites of the lattice. As was done in [6], we assume the monomers located at the same site to be *distinguishable*. In later studies of related models on hierarchical lattices [3,9], this convention was changed to allow a direct comparison with the simulations.

To solve the model, as usual we consider rooted subtrees and define their partial partition functions (PPF's)  $g_k$  for fixed configurations of the root edge and site, indicated by  $k$ . The operation of connecting  $q - 1$  subtrees to a new root site and edge, obtaining a subtree with one more generation, leads to recursion relations for the PPF's; this operation is illustrated in Fig. 2 of [6]. For the present model, we need to consider six different root configurations ( $k = 0, 1, \dots, 5$ ), which are the same as those defined for the RA model in [6]. The recursion relations for the PPF's associated with these root configurations are similar to the ones of the RA model

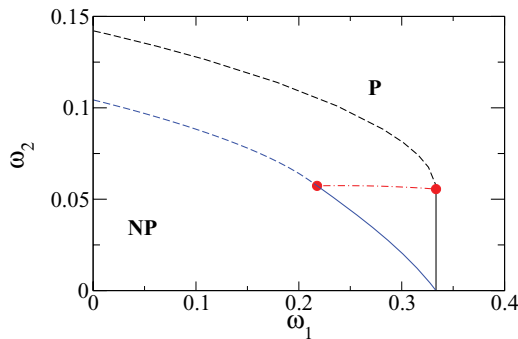


FIG. 1. (Color online) Phase diagram for the model. Lines at higher values of  $\omega_2$  correspond to the RF model  $\kappa = 0$  (black), the other lines to the RA model  $\kappa = 1$  (blue online), and the dot-dashed (red) line is the tricritical line as  $\kappa$  is varied. Solid lines are continuous transitions, dashed lines are lines of equal free energies.

studied before, but we need to keep track of the number of hairpins in the root site for each contribution. Let us use a particular contribution as an example, namely the third term in the recursion relation for  $g'_1$  (the prime denotes the additional generation), corresponding to expressions (2c) for the RF model and (7c) for the RA model in [6]. For the case we are considering here, this contribution is

$$g'_{1,3} = 2 \binom{q-1}{2} \times 2(2+\kappa) \omega_2 g_0^{q-3} g_1 g_2, \quad (1)$$

since there are two ways to connect the incoming bonds with no hairpin and one with one hairpin at the root site. We notice that expressions (2c) and (7c) in [6] are recovered for  $\kappa = 0$  and 1, respectively. We then proceed to define the ratios of the PPF's exactly as was done for the RA model in [6], dividing the other PPF's by  $g_0$ . Since  $g_3$  and  $g_4$  appear in the recursion relations only as the combination  $g_3 + 2g_4$ , we need to define four ratios only, the same as were defined for the RA model in [6]. The results for the recursion relations are

$$R'_1 = \left[ (q-1)\omega_1 R_1 + 6 \binom{q-1}{3} \omega_2 R_1^3 + 4 \binom{q-1}{2} (2+\kappa) \omega_2 R_1 R_2 + 4 \binom{q-1}{2} \omega_2 R_1 R_3 + 2(q-1)\omega_2 R_4 \right] \frac{1}{D}, \quad (2a)$$

$$R'_2 = 2 \left[ \binom{q-1}{2} R_1^2 + (q-1)R_2 \right] \frac{\omega_2}{D}, \quad (2b)$$

$$R'_3 = \left[ \kappa \omega_1 + 2 \binom{q-1}{2} \kappa \omega_2 R_1^2 + 2(q-1)\omega_2 (\kappa^2 R_2 + R_3) \right] \frac{1}{D}, \quad (2c)$$

$$R'_4 = \frac{2(q-1)\kappa \omega_2 R_1}{D}, \quad (2d)$$

where

$$D = 1 + \binom{q-1}{2} \omega_1 R_1^2 + 6 \binom{q-1}{4} \omega_2 R_1^4 + 6 \binom{q-1}{3} (2+\kappa) \omega_2 R_1^2 R_2 + 2 \binom{q-1}{2} (2+\kappa^2) \omega_2 R_2^2 + (q-1)\kappa \omega_1 R_2 + 6 \binom{q-1}{3} \omega_2 R_1^2 R_3 + 4 \binom{q-1}{2} \omega_2 R_2 R_3 + 4 \binom{q-1}{2} \kappa \omega_2 R_1 R_4. \quad (3)$$

Equations (2) and (3) for  $\kappa = 1$  reduce to the recursion relations for the RA model described by Eqs. (11) and (12) in [6]. For  $\kappa = 0$ , Eq. (2d) leads to  $R_4 = 0$ . The value  $R_3$  also has hairpin configurations in the contributions to the nominator, so it also vanishes. With these constraints, the

recursion relations Eqs. (2a) and (2b) and (3) for  $\kappa = 0$  are identical to Eqs. (4) and (5) for the RF model given in Ref. [6].

The partition function of the model on the Cayley tree may be obtained if we consider the operation of attaching  $q$  subtrees to the central site of the lattice. The result is

$$\begin{aligned}
Y &= g_0^q + \binom{q}{2} \omega_1 g_0^{q-2} g_1^2 + 6 \binom{q}{4} \omega_2 g_0^{q-4} g_1^4 \\
&+ 6 \binom{q}{3} (2 + \kappa) \omega_2 g_0^{q-3} g_1^2 g_2 \\
&+ 2 \binom{q}{2} (2 + \kappa^2) \omega_2 g_0^{q-2} g_2^2 \\
&+ q \kappa \omega_1 g_0^{q-1} g_2 + 6 \binom{q}{3} \omega_2 g_0^{q-3} g_1^2 (g_3 + 2g_4) \\
&+ 4 \binom{q}{2} \omega_2 g_0^{q-2} g_2 (g_3 + 2g_4) \\
&+ 4 \binom{q}{2} \kappa \omega_2 g_0^{q-2} g_1 g_5. \tag{5}
\end{aligned}$$

In the thermodynamic limit, the solution of a model on the Cayley tree usually shows a behavior that is quite different from the one expected on regular lattices, since the number of surface sites represents a nonzero fraction of the total number of sites. Therefore, we study mean values calculated at the central site of the tree. The behavior of a model in the thermodynamic limit and in the central region of the Cayley tree has been named the Bethe lattice solution of this model [5]. Using the partition functions shown earlier, we then proceed to calculate the densities at the central site of the tree. The density of monomers is given by

$$\rho = \frac{P + 2Q}{1 + P + Q}, \tag{6}$$

where

$$P = \omega_1 \left[ \binom{q}{2} R_1^2 + q_2 \right], \tag{7a}$$

$$\begin{aligned}
Q &= \omega_2 \left[ 6 \binom{q}{4} R_1^4 + 6 \binom{q}{3} (2 + \kappa) R_1^2 R_2 + 2 \binom{q}{2} (2 + \kappa^2) R_2^2 \right. \\
&\left. + 6 \binom{q}{3} R_1^2 R_3 + 4 \binom{q}{2} R_2 R_3 + 4 \binom{q}{2} \kappa, R_1 R_4 \right]. \tag{7b}
\end{aligned}$$

It is supposed in the preceding expressions for the density of monomers at the central site that the ratios  $R_i$  have fixed-point values, so that the thermodynamic limit results are obtained. Since  $P$  and  $Q$  are non-negative, the density of monomers will be in the interval  $[0, 2]$ , as expected. The probability that the central site is occupied by a single monomer will be  $\rho_1 = P/(1 + P + Q)$ , and the probability to find two monomers at the central site is  $\rho_2 = Q/(1 + P + Q)$ . Finally, we may obtain the bulk grand-canonical free energy per site  $\phi_b$  on the tree using an argument proposed by Gujrati [7], and since it is discussed in [3] we refer the reader to that paper for the details.

The result is

$$\phi_b = \beta \phi_b = -\frac{1}{2} [q \ln D - (q - 2) \ln y], \tag{8}$$

where  $y = 1 + P + Q$  and  $D$  are calculated at the fixed point of the recursion relations.

### III. THERMODYNAMIC PROPERTIES OF THE MODEL

As discussed earlier, the thermodynamic properties of the model on the Bethe lattice are determined by the fixed-point values of the ratios, defined by the recursion relations, for fixed values of the parameters  $\omega_1$ ,  $\omega_2$ , and  $\kappa$ . As explained in Ref. [6], the nonpolymerized (NP) phase has the fixed-point values  $R_1^{(NP)} = R_2^{(NP)} = R_4^{(NP)} = 0$  and

$$R_3^{(NP)} = \frac{\kappa \omega_1}{1 - 2(q - 1)\omega_2}. \tag{9}$$

These values for the ratios actually correspond to  $\rho = 0$ , as may be seen using Eq. (6) for the density of monomers. The stability limit of the NP phase is obtained requiring that the largest eigenvalue of the Jacobian of the recursion relations, calculated at the fixed-point values of the ratios shown earlier, has an absolute value equal to 1. This leads to the following condition:

$$\omega_1^{(NP)}(\omega_2, \kappa) = \frac{[1 - 2(q - 1)\omega_2][1 + 4(q - 1)\kappa\omega_2^2]}{1 - 2[(q - 1) - \kappa(q - 2)]\omega_2}. \tag{10}$$

Another fixed point of the recursion relations reported in Ref. [6] for the RF model is the double-occupied (DO) fixed point  $R_1^{(DO)} = 0$  and  $R_2^{(DO)} \neq 0$ . This fixed point exists only for the RF model, and it disappears for  $\kappa > 0$ . However (see later in the text), it does not correspond to a thermodynamic phase.

A third fixed point of the recursion relations Eqs. (2), which we may associate with the regular polymerized phase (P), corresponds to all ratios at nonzero values. The stability limits of the NP and the P phase are the same for small values of  $\omega_2$ , henceforth the transition between these phases is continuous in this region. For larger values of  $\omega_2$ , this transition becomes discontinuous. A tricritical line is found when  $\omega_1^{(TC)}$  is given by Eq. (10) and  $\omega_2^{(TC)}(\kappa)$  is a root of the polynomial of degree 7,

$$\begin{aligned}
&1/2 + [4\kappa(q - 2) - (q^2 - 1)]\omega_2 + \{2(q - 1)\}^3 \\
&+ [(9 - 4q)q^2 - 5]\kappa + 2[(3q - 10)q + 9]\kappa^2 \omega_2^2 \\
&+ 2(q - 1)((q - 1)^2 + 2(q - 1)^2(2q - 3)\kappa \\
&- \{2 + q[3 + q(3q - 7)]\}\kappa^2 + 3(q - 1)(q - 2)\kappa^3 \omega_2^3 \\
&+ (q - 1)^2[(2q - 1)(q - 1)^2/2 - 2(q - 1) \\
&\times (2q^2 - 4q + 3)\kappa \times (2q - 1)(5q^2 - 10q + 4)\kappa^2 \\
&- 4(q - 2)(q^2 + 2q - 4)\kappa^3 + (q - 2)^2\kappa^4] \omega_2^4 \\
&+ (q - 1)^3[(q - 1)^3 + 4(q - 1)^2\kappa - 2(q - 1) \\
&\times (q - 2)(2q - 3)\kappa^2 + (q - 2)(4q^2 - 6q - 13)\kappa^3 \\
&+ (q - 2)(q^2 + 4q - 10)\kappa^4] \omega_2^5 - (q - 1)^4[(q - 1)^2 \\
&+ 2(q - 1)(2q - 3)\kappa + (q - 2)(7q - 8)\kappa^2 \\
&- 4(q - 2)(2q - 3)\kappa^3 + 2(q - 2)^2\kappa^4] \omega_2^6 \\
&+ (q - 1)^5(q - 2)[(q - 1) + (q - 2)\kappa](2\kappa - 1)\kappa^3 \omega_2^7 = 0. \tag{11}
\end{aligned}$$

The roots of this polynomial are evaluated numerically, except for the RF model  $\kappa = 0$ , where the tricritical point is located at the values of  $\omega_1$  and  $\omega_2$  given by Eq. (24) in [6]. We may search for a DO fixed point, which should have the values  $R_1 = R_4 = 0$  and  $R_2, R_3 \neq 0$ . However, for this fixed point, we reach the unphysical conclusion  $R_2 = -\kappa \omega_1 / [2(q-1)\omega_2] < 0$ , indicating that the DO fixed point does not appear for  $\kappa \neq 0$ .

The phase diagram for the model is shown in Fig. 1. The first-order transition lines were calculated as the line where the two coexisting phases have the same free energy; for a detailed discussion, see Ref. [3]. In Ref. [6], we adopted an alternative procedure [8], iterating the recursion relations starting with the physical values for the partial partition functions for a subtree of generation “zero.” In particular, for the RA model we learn that the natural initial conditions procedure may lead us to wrongly conclude that the DO phase, which is never the phase of minimum free energy, is stable in part of the phase diagram. The conclusion that the transition was discontinuous

for all nonzero values of  $\omega_2$  was reached since we verified that the stability limit of the NP phase was coincident with the coexistence curve only at  $\omega_2 = 0$ , found using the natural initial conditions method. This is not true if the Gujrati ansatz is used, as is shown here, where for sufficiently low values of  $\omega_2$ , the polymerized phase that coexists with the NP phase has vanishing density, characterizing a critical line. As established in Ref. [3], both methods are not equivalent, and the correct first-order phase transition line must be obtained from the free energy of the model.

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