

## ARTICLES

## Potts model on the Bethe lattice with mixed interactions

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A  $q$ -state Potts model on a Bethe lattice is considered in which the bonds at a given site may all have different interaction strengths, but in which all sites remain equivalent. We calculate the susceptibility of the system and hence the location of second-order phase transitions. The presence of first-order transitions is determined directly from the free energy. The formalism is then specialized to the case of a model crystalline random copolymer, in which the interchain interactions are weaker than the randomly varying intrachain interaction strengths. A comparison of the results of this treatment is made with the results of the mean-field theory of Lin *et al.* [Phys. Rev. E **47**, 981 (1993)].

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## I. INTRODUCTION

This work is an extension of that of Peruggi *et al.* [1], who gave an extensive analysis of the Potts ferro- and antiferromagnet on the Bethe lattice. Here we develop their work to allow the bonds at a given site to have different interaction strengths while still keeping all sites equivalent, as in the case of an anisotropic lattice. The problem arose in the modeling of phase transitions in ferroelectric random copolymers, an example of which is the system in which vinylidene fluoride and tetrafluoroethylene are combined in a copolymer containing 60% to 80% of vinylidene fluoride [2–4]. In Ref. [5] this system was represented by a three-state Potts model on a cubic lattice in which the interactions in one direction, that of the polymer chains, was much greater than that in the two perpendicular directions.

The Hamiltonian for this system is

$$\mathcal{H} = - \sum_{\text{intra}(i,j)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{\text{inter}(i,j)} J'_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the Potts spin vector  $\mathbf{S}_i$  is a unit vector allowed to have the  $q$  orientations  $0, 2\pi/q, \dots, 2\pi(q-1)/q$  in the plane perpendicular to the polymer chains. For the case of the fluorinated alkanes  $q$  is set equal to 3. The intrachain couplings  $J_{ij}$  are independently distributed random variables with probability density

$$\rho(J_{ij}) = p\delta(J_{ij} - J) + (1-p)\delta(J_{ij} + J) \quad (2)$$

corresponding to a random mixture of ferro- and antiferromagnetic couplings. The weaker interchain couplings are all ferromagnetic.

Lin *et al.* [5] treated the interchain interactions in a mean-field approximation, which reduced the problem to a linear chain with random interactions. This was solved with no further approximation by computer simulation. They found that a first-order transition occurs for the whole range  $[0,1]$  of  $p$ .

In this work we avoid the mean-field approximation but replace the random interaction by a suitably chosen mean value and then solve the model on a Bethe lattice exactly. This gives the correct mean value for the zero field susceptibility. It is found that as the concentration of antiferromagnetic interactions is increased, a critical point is reached at which the transition to the ferromagnetic state becomes second order. Since the replacement of the random interaction by a mean value is correct at  $p = 1$  and  $p = 0$ , it is almost certain that a similar effect would occur if the randomness were treated fully. Beyond this critical point further first-order transitions are found, but this work assumes that the order parameter has the same value on every site, which is almost certainly not the case in this region. Investigation of other types of order is deferred to a later date.

A general Bethe lattice model with arbitrary coordination number  $c$  is defined and its correlation functions are discussed in Sec. II. In this model all sites are equivalent, but there are  $c$  possibly different interaction strengths occurring at each site. The susceptibility is expressed in terms of the transmissivity variables in Sec. III and provides the means for locating second-order transitions. However, this is insufficient to determine first-order transitions, and for this purpose Sec. IV expresses the free energy as a function of the order parameter. A symmetry property of the free energy is shown to exist that yields an explicit form for the first-order transition curve in cer-

tain circumstances. Up until this point only nonrandom interactions have been considered and so in Sec. V application of the theory to the random copolymer problem is discussed. The results are compared with those of Lin *et al.* [5] in Sec. VI and finally the possibility of other types of order is considered in Sec. VII.

## II. THE MODEL AND ITS CORRELATION FUNCTIONS

### A. The Hamiltonian

Following Peruggi *et al.* [1] we consider the Bethe lattice  $L$  to be the limit of a regular sequence  $\{T_n\}_{n=1}^{\infty}$  of finite trees and denote the bonds and sites of  $T_n$  by  $B_n$  and  $S_n$ , respectively. The Potts Hamiltonian  $\mathcal{H}_n$  is defined by

$$-\frac{\mathcal{H}_n}{k_B T} = \sum_{(i,j) \in B_n} K_{ij} \delta_{\nu_i \nu_j} + H \sum_{i \in S_n} \delta_{\nu_i, 1}, \quad (3)$$

where the spin state variable  $\nu_i$  for the  $i$ th site takes on the values  $1, \dots, q$ .

### B. The order parameter and correlation functions

The ferromagnetic order parameter is  $p_r(i)$ , the probability that the spin on site  $i$  is in state  $r$ , so that

$$p_r(i) = \langle \delta_{\nu_i r} \rangle. \quad (4)$$

In calculating the susceptibility we shall require  $P_{rs}(i, j)$ , the probability that the spins on sites  $i$  and  $j$  are in states  $r$  and  $s$ , respectively,

$$P_{rs}(i, j) = \langle \delta_{\nu_i r} \delta_{\nu_j s} \rangle. \quad (5)$$

Because there is a unique chain of bonds  $C(i, j)$  connecting site  $i$  to site  $j$  on  $T_n$ , it is possible, following Peruggi *et al.* [1], to write  $P_{11}(i, j)$  in terms of the (1,1) element of a product of Markovian matrices, one for each bond in  $C(i, j)$ .

$$P_{11}(i, j) = p_1(i) \left[ \prod_{b \in C(i, j)} \mathbf{T}(b) \right]_{11}. \quad (6)$$

The matrices in the product are ordered from  $i$  to  $j$  along the chain and

$$\mathbf{T}(b) = \begin{bmatrix} p_{11}(b) & 1 - p_{11}(b) \\ p_{21}(b) & 1 - p_{21}(b) \end{bmatrix}, \quad (7)$$

where  $p_{rs}(b)$  is the conditional probability that site  $j_b$  of the bond  $b$  is in state  $s$  given that site  $i_b$  of  $b$  is in state  $r$ . The quantity  $p_{rs}(b)$  is symmetric under the interchange of  $i_b$  and  $j_b$  but not  $r$  and  $s$ ,

$$p_r(i_b) p_{rs}(b) = P_{rs}(i_b, j_b) = P_{sr}(i_b, j_b) = p_s(i_b) p_{sr}(b). \quad (8)$$

We note the sum rule

$$\sum_{s=1}^q p_{rs}(b) = 1. \quad (9)$$

The  $q \times q$  matrix  $\mathbf{T}$  of Ref. [1] has been replaced by a  $2 \times 2$  matrix on the assumption that the ordering is such that all states other than state 1, which is singled out by the magnetic field, are equivalent. The same assumption yields the result

$$p_1(i_b)[1 - p_{11}(b)] = [1 - p_1(i_b)]p_{21}(b). \quad (10)$$

Also the  $\mathbf{T}$ -matrix parameters have been allowed to take on different values depending on the bond. This was unnecessary in [1] since the interaction parameters were the same for all bonds.

### C. Calculation of conditional probabilities and the order parameter for the Bethe lattice

For the Bethe lattice all sites have the same number of neighbors  $c$ , the coordination number. In [1]  $K_{ij} = K$ , but here we allow  $K_{ij}$  to take on one of the  $c$  values  $K^{(1)}, \dots, K^{(c)}$ . In order to preserve the equivalence of lattice sites we suppose that all  $c$  of the interactions occur at each site.

From now on, unless otherwise stated, the system parameters will be assumed to be such that  $p_r(i) = p_r$ , independently of  $i$ . This will be the case for the disordered phase and for ferromagnetic ordering. However, if negative interactions are present ordered states may occur, which invalidates this assumption even though the interactions have translational symmetry. We defer consideration of other types of order to a later date.

Equations (5)–(7) of Ref. [1] determine the conditional probabilities for a Bethe lattice model with constant interactions. The required generalizations to the present problem may be obtained by fixing attention on a particular bond with interaction strength  $K^{(\beta)}$  and representing the effect of the rest of the lattice by an effective magnetic field  $H^{(\beta)}$  acting on each spin belonging to the bond. This field includes the actual magnetic field  $H$ . The parameter  $\phi$  of Ref. [1] now depends on the chosen bond via its interaction strength and we define

$$\phi^{(\beta)} = \exp(-H^{(\beta)}). \quad (11)$$

The effective fields are expressible in terms of the order parameter  $p_1$  using the Boltzmann factors for the single bond, which leads to

$$\frac{(1 - p_1)}{p_1} = (q - 1) \phi^{(\beta)} \bar{\phi}^{(\beta)}, \quad (12)$$

where

$$\bar{\phi}^{(\beta)} = B(K^{(\beta)}, \phi^{(\beta)}) / A(K^{(\beta)}, \phi^{(\beta)}) \quad (13)$$

with

$$A(K, \phi) = e^K + (q-1)\phi, \quad (14)$$

$$B(K, \phi) = 1 + (e^K + q - 2)\phi.$$

The quantity  $\bar{H}^{(\beta)} = -\ln \bar{\phi}^{(\beta)}$  may also be interpreted as an effective field but arising from the interaction of spin 0 with the single branch  $\beta$  and excluding the external field. Hence  $-\ln(\phi^{(\beta)}\bar{\phi}^{(\beta)}) = H^{(\beta)} + \bar{H}^{(\beta)}$  is the total effective field acting on spin 0, which explains Eq. (12). The latter determines  $\phi^{(\beta)}$ , in terms of  $p_1$  and  $K^{(\beta)}$ , as the positive root of a quadratic and hence  $H^{(\beta)}$  using Eq. (11). Explicitly

$$p_1[1 + (q-2)e^{-K^{(\beta)}}]\phi^{(\beta)^2} - (1 - 2p_1)e^{-K^{(\beta)}}\phi^{(\beta)} - \frac{1-p_1}{q-1} = 0. \quad (15)$$

The conditional probabilities are obtained in terms of  $p_1$  and  $K^{(\beta)}$  via the effective fields

$$\begin{aligned} p_{11}^{(\beta)} &= \frac{e^{K^{(\beta)}}}{A(K^{(\beta)}, \phi^{(\beta)})}, \\ p_{21}^{(\beta)} &= \frac{1}{B(K^{(\beta)}, \phi^{(\beta)})}, \\ p_{22}^{(\beta)} &= \frac{e^{K^{(\beta)}}\phi^{(\beta)}}{B(K^{(\beta)}, \phi^{(\beta)})}. \end{aligned} \quad (16)$$

All other conditional probabilities are determined by the sum rule (9) and symmetry of the Hamiltonian. We note the following relations

$$1 - p_{11}^{(\beta)} = (q-1)p_{12}^{(\beta)}, \quad (17)$$

$$p_{11}^{(\beta)}p_{22}^{(\beta)} = e^{2K^{(\beta)}}p_{21}^{(\beta)}p_{12}^{(\beta)}. \quad (18)$$

The free energy will later be expressed in terms of the conditional probabilities and hence may be considered as a function of  $p_1$ .

The equilibrium value of  $p_1$  may be found in one of two ways: (a) by imposing the consistency condition [Eq. (19) below] that the order parameter have the same value on a given site and its neighboring sites or (b) as we show later, by minimizing the free energy with respect to  $p_1$ . The consistency equation may be written

$$\frac{(1-p_1)}{p_1} = (q-1)e^{-H} \prod_{\beta=1}^c \bar{\phi}^{(\beta)}. \quad (19)$$

### III. SUSCEPTIBILITY

#### A. General equations

The expected value of the magnetic moment of  $T_n$  is given by

$$\mathcal{M}_n = \sum_{i \in S_n} p_1(i) \quad (20)$$

and the magnetic susceptibility may be written as a sum of correlation functions

$$k_B T \chi_n = \partial \mathcal{M}_n / \partial H = \sum_{i, j \in S_n} \mathcal{G}(i, j), \quad (21)$$

where

$$\mathcal{G}(i, j) = P_{11}(i, j) - p_1(i)p_1(j). \quad (22)$$

To determine  $P_{11}(i, j)$  we require the eigenvalues and eigenvectors of  $\mathbf{T}(b)$ , defined by (7). If the  $i$ th eigenvalue is denoted by  $\lambda_i(b)$  and the corresponding left and right eigenvectors by  $\mathbf{e}_i(b)$  and  $\mathbf{f}_i(b)$  then

$$\lambda_1(b) = 1, \quad \mathbf{e}_1(b) = [p_1(i_b), [1 - p_1(i_b)]], \quad \mathbf{f}_1(b) = [1, 1]^T \quad (23)$$

and

$$\begin{aligned} \lambda_2(b) &= p_{11}(b) - p_{21}(b), \\ \mathbf{e}_2(b) &= [1, -1], \\ \mathbf{f}_2(b) &= [[1 - p_1(i_b)], -p_1(i_b)]^T, \end{aligned} \quad (24)$$

where we have used Eq. (10).

#### B. Uniform magnetization

In the case when the order parameter is the same for all sites, the eigenvectors of  $\mathbf{T}(b)$  are the same for all bonds and hence the matrix element in Eq. (6) may be evaluated to yield

$$\mathcal{G}(i, j) = P_{11}(i, j) - p_1^2 = p_1(1 - p_1) \prod_{b \in C(i, j)} \lambda_2(b). \quad (25)$$

The bulk susceptibility per lattice site  $\chi$  is defined for the Bethe lattice by fixing  $i$  in Eq. (21) to be some chosen site 0, thus

$$\chi = \frac{1}{k_B T} \sum_j \mathcal{G}(0, j). \quad (26)$$

The branches of the lattice meeting at 0 may be labeled by the type  $\beta$  of the bond leaving 0. Separating the term  $j = 0$  and partitioning the remaining terms of the sum according to which of these branches contains the site  $j$  gives

$$\chi = \frac{p_1(1-p_1)}{k_B T} + \sum_{\beta=1}^c \chi^{(\beta)}, \quad (27)$$

where

$$\chi^{(\beta)} = \frac{1}{k_B T} \sum_{j \in \text{branch}_\beta} \mathcal{G}(0, j). \quad (28)$$

Using (25) we see that all terms in the above sum contain a factor

$$t^{(\beta)} = p_{11}^{(\beta)} - p_{21}^{(\beta)}, \quad (29)$$

the eigenvalue of the  $\mathbf{T}$  matrix for the bond connecting 0 to the first atom in branch  $\beta$ , and using translational symmetry

$$\chi^{(\beta)} = t^{(\beta)} \left( \frac{p_1(1-p_1)}{k_B T} + \sum_{\beta'=1}^c \chi^{(\beta')} - \chi^{(\beta)} \right), \quad (30)$$

which leads to

$$k_B T \chi = p_1(1-p_1) \left/ \left[ 1 - \sum_{\beta=1}^c \frac{t^{(\beta)}}{1+t^{(\beta)}} \right] \right. . \quad (31)$$

The parameter  $t^{(\beta)}$  may be written

$$t^{(\beta)} = \frac{\phi^{(\beta)}(e^{K^{(\beta)}} - 1)(e^{K^{(\beta)}} + q - 1)}{A(K^{(\beta)}, \phi^{(\beta)})B(K^{(\beta)}, \phi^{(\beta)})}, \quad (32)$$

which in the case  $\phi^{(\beta)} = 1$  reduces to the usual transmissivity variable [6]

$$t^{(\beta)} = \frac{e^{K^{(\beta)}} - 1}{e^{K^{(\beta)}} + q - 1}. \quad (33)$$

At second-order-transition points,  $\chi^{-1} = 0$ , which, from (31), occurs when

$$\sum_{\beta=1}^c \frac{t^{(\beta)}}{1+t^{(\beta)}} = 1. \quad (34)$$

It may be that a first-order transition occurs before  $\chi^{-1} = 0$ , in which case the latter condition determines a spinodal point. This is the case for ferromagnetic interactions and  $q \geq 3$ .

#### IV. FREE ENERGY

##### A. General equations

Let  $P_\alpha$  be the probability of occurrence of a state  $\alpha$  of the whole lattice, with energy  $E_\alpha$ . The canonical free energy  $F$  is then given by the general formula

$$\frac{F}{k_B T} = -\ln Z = \frac{1}{k_B T} \sum_{\alpha} P_{\alpha} E_{\alpha} + \sum_{\alpha} P_{\alpha} \ln P_{\alpha}. \quad (35)$$

For the tree  $T_n$  this may be expressed in terms of the probabilities  $p_r(i)$  and  $P_{rs}(i, j)$  in the form

$$F_n = \sum_{(i,j) \in B_n} F(i, j) + \sum_{i \in S_n} F(i), \quad (36)$$

where

$$F(i, j)/(k_B T) = \sum_{r,s=1}^q P_{rs}(i, j) \ln P_{rs}(i, j) - K_{ij} \sum_{r=1}^q P_{rr}(i, j) \quad (37)$$

and

$$F(i)/(k_B T) = -H p_1(i) - \sigma(i) \sum_{r=1}^q p_r(i) \ln p_r(i). \quad (38)$$

Here  $\sigma(i) + 1$  is the coordination number of site  $i$ .

##### B. The Bethe lattice

For the Bethe lattice the free energy becomes an extensive quantity and the free energy per lattice site  $\mathcal{F}$  is given by

$$\begin{aligned} \frac{\mathcal{F}}{k_B T} = & -H p_1 - \frac{(c-2)}{2} \\ & \times \left[ p_1 \ln p_1 + (1-p_1) \ln \left( \frac{1-p_1}{q-1} \right) \right] \\ & + \frac{1}{2} \sum_{\beta=1}^c [-K^{(\beta)} + p_1 \ln p_{11}^{(\beta)} + (1-p_1) \ln p_{22}^{(\beta)}]. \end{aligned} \quad (39)$$

After a lengthy calculation we find

$$\frac{1}{k_B T} \frac{\partial \mathcal{F}}{\partial p_1} = -H + \ln \left( \frac{(q-1)p_1}{1-p_1} \right) + \sum_{\beta=1}^c \ln \bar{\phi}^{(\beta)}. \quad (40)$$

Notice that this is zero when the consistency condition (19) is satisfied. Also, a further derivative with respect to  $p_1$  gives the inverse susceptibility in agreement with Eq. (31)

$$\frac{\partial^2 \mathcal{F}}{\partial p_1^2} = \chi^{-1}. \quad (41)$$

##### C. A symmetry property and the first-order transition

Figures 4 and 5 of Ref. [1] show the zero-field free energy as a function of  $p_1$ , for various fixed values of  $T$ , in the case that all the interaction parameters are ferromagnetic and equal. For the Ising model ( $q = 2$ ) the figure shows a standard second-order transition. The curves are symmetric about  $p_1 = \frac{1}{2}$  and above the critical temperature  $T_c$  there is a single minimum corresponding to the disordered equilibrium state. At  $T_c$  the curvature at the central minimum vanishes and below  $T_c$  the minimum splits into two symmetrically placed minima and  $p_1 = \frac{1}{2}$  is now a local maximum. The minima have equal free energy and correspond to the onset of ferromagnetic order in either state 1 or state 2. As  $T$  passes below  $T_c$  the order parameter varies continuously away from  $\frac{1}{2}$ .

For  $q \geq 3$  the transition in zero field is first order. Sufficiently far above  $T_c$  the curves are asymmetric with a single minimum at  $p_1 = \frac{1}{q}$ , which is the value corresponding to all states having equal probability. On approaching  $T_c$  a temperature  $T_2$  is reached at which a spinodal point appears (i.e., a point at which  $\chi^{-1} = 0$  but having a higher free energy than the minimum at  $p_1 = \frac{1}{q}$ ). Below

$T_2$  a second local minimum appears, but the disordered state is still the stable one until  $T_c$  is reached, at which point the two minima have equal free energy, the second one being at  $p_1 = 1 - \frac{1}{q}$ . Below  $T_c$  the second minimum becomes the stable one, corresponding to the ferromagnetic state, and the order parameter jumps by  $1 - \frac{2}{q}$  on passing through  $T_c$ . Continuing below  $T_c$  we find that the order parameter continues to increase.

Figure 6 of Ref. [1] shows the phase diagrams in the  $H$ - $T$  plane. For  $q = 2$  this is the usual phase diagram for a ferromagnet: a first-order line along  $H = 0$  and  $T < T_c$ , which terminates in the second-order transition point. For  $q \geq 3$  the first-order transition line leaves the  $H = 0$  axis at the zero-field first-order transition point  $T_c$ , and for  $T > T_c$  it moves into the  $H > 0$  region, terminating at a second-order transition point  $(T^*, H^*)$ . We shall find that a second-order transition point may also be recovered by making some of the interactions negative. For  $T < T_c$  the first-order transition line is still at  $H = 0$ . The phase boundary noted in Ref. [1] as lying in the  $H < 0$  region actually originates from a consideration of the metastable states that are found when one imposes the restriction  $p_2 = p_3$ . The true equilibrium state in this region corresponds to a situation where  $p_2 \neq p_3$ . A clear discussion of the full phase diagram of the three-state Potts model has been given by Fisher and Straley [7].

We now return to the zero-field free energy curves for  $q \geq 3$ . At the first-order transition temperature we noted that the two local minima have equal free energy and are symmetrically placed about  $p_1 = \frac{1}{2}$ . It turns out that at this temperature the whole curve is symmetric about the central point, i.e.,  $\mathcal{F}(1 - p_1) = \mathcal{F}(p_1)$ , and that this is also true along the whole first-order transition line. The latter may therefore be located using this symmetry condition.

We will show that the above discussion applies to the more general case of unequal ferromagnetic interactions and use the symmetry condition to generalize the first-order transition formula of Ref. [1]. First, we note that if we make the transformation  $p_1 \rightarrow 1 - p_1$ , then

$$p_{11}^{(\beta)} \rightarrow 1 - p_{21}^{(\beta)}, \quad p_{21}^{(\beta)} \rightarrow 1 - p_{11}^{(\beta)}, \quad (42)$$

and hence the variable  $t^{(\beta)}$  defined in Eq. (29) is invariant. Using Eq. (31) we see that  $\chi$  is also invariant and hence symmetric about  $p_1 = \frac{1}{2}$ . It follows from Eq. (41) that  $\mathcal{F}$  may be written as the sum of symmetric and antisymmetric functions, where the antisymmetric part is linear in  $p_1$ .

This symmetry may be made explicit using the relation

$$\ln p_{22}^{(\beta)} = \ln[1 - p_{21}^{(\beta)}] - \ln[1 + (q - 2)e^{-K^{(\beta)}}]. \quad (43)$$

Rearranging Eq. (39) we find

$$\mathcal{F} = \mathcal{F}^{\text{even}} + \mathcal{F}^{\text{odd}}, \quad (44)$$

where

$$\begin{aligned} \frac{\mathcal{F}^{\text{even}}}{k_B T} = & -\frac{1}{2}H - \frac{1}{2}(c - 2) \left[ p_1 \ln p_1 + (1 - p_1) \ln(1 - p_1) \right. \\ & \left. - \frac{1}{2} \ln(q - 1) \right] + \frac{1}{2} \sum_{\beta=1}^c \{ -K^{(\beta)} + p_1 \ln p_{11}^{(\beta)} \\ & + (1 - p_1) \ln(1 - p_{21}^{(\beta)}) \\ & - \frac{1}{2} \ln[1 + (q - 2)e^{-K^{(\beta)}}] \} \end{aligned} \quad (45)$$

and

$$\begin{aligned} \frac{\mathcal{F}^{\text{odd}}}{k_B T} = & \left( \frac{1}{2} - p_1 \right) \left[ H + \frac{(c - 2)}{2} \ln(q - 1) \right. \\ & \left. - \frac{1}{2} \sum_{\beta=1}^c \ln[1 + (q - 2)e^{-K^{(\beta)}}] \right]. \end{aligned} \quad (46)$$

Thus along the line

$$2H + (c - 2) \ln(q - 1) - \sum_{\beta=1}^c \ln[1 + (q - 2)e^{-K^{(\beta)}}] = 0, \quad (47)$$

the free energy is symmetric, and in the simple ferromagnetic case, the first-order transition curve will be a segment of this line. Equation (47) generalizes Eq. (19) of [1]. We shall see that when negative interactions are present, first-order transitions can occur without the above symmetry and vice versa.

## V. APPLICATION TO CRYSTALLINE RANDOM COPOLYMERS

### A. Phase diagram for two interaction strengths

In the polymer chain problem there are just two types of interaction, along and between the chains. We therefore specialize the formulas of the previous sections to  $c_1$  interactions of strength  $K_1$  and  $c_2$  of strength  $K_2$ . If for the moment we ignore the randomness of the intrachain interaction then  $c_1 = 4$  and  $c_2 = 2$  would be appropriate for the polymer problem on the simple cubic lattice.

Equations (47) and (34) yield the following conditions. The line along which the free energy is symmetric becomes

$$[1 + (q - 2)e^{-K_1}]^{c_1} [1 + (q - 2)e^{-K_2}]^{c_2} = e^{2H} (q - 1)^{c - 2} \quad (48)$$

and  $\chi^{-1} = 0$  along the line

$$\frac{c_1 t_1}{1 + t_1} + \frac{c_2 t_2}{1 + t_2} = 1, \quad (49)$$

where  $t_i$  is given by (32) with  $K^{(\beta)} = K_i$ .

The following discussion of the phase diagram is for  $q = 3$ ,  $c_1 = 4$ , and  $c_2 = 2$ , which are the parameters for the polymer problem. Figure 1 shows the line in the  $K_2$ - $K_1$  plane along which the symmetry condition (48), with

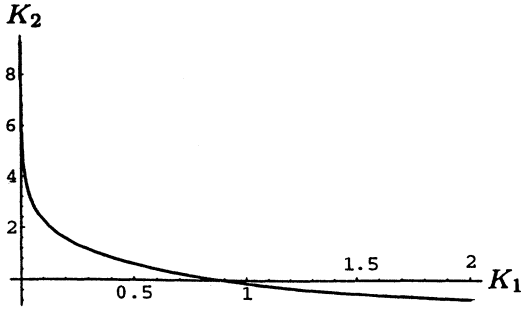


FIG. 1. First-order transition line in the  $K_2$ - $K_1$  plane along which the symmetry condition Eq. (48), with  $H = 0$ , holds. The parameters are chosen as  $q = 3$ ,  $c_1 = 4$ , and  $c_2 = 2$ .

$H = 0$ , holds. We call the graph  $K_{\text{sym}}(K_1)$ . A similar plot of the line along which  $\chi^{-1}$  vanishes, Eq. (49), lies very close to  $K_{\text{sym}}(K_1)$ . Calling this graph  $K_{\text{spinodal}}(K_1)$ , we plot the difference  $K_{\text{sym}}(K_1) - K_{\text{spinodal}}(K_1)$  in Fig. 2. The difference tends to a limit for large  $K_1$  as shown in Fig. 2(a). The difference is greater for  $c_1 = 6$  as shown in Fig. 2(b). At the point where the difference vanishes the susceptibility is diverging and the free energy curve as a function of  $p_1$  is very flat (Fig. 3). This is a second-order transition or critical point. For values of  $K_1$  below the critical value, the  $K_{\text{sym}}(K_1)$  curve is a first-order transition line, as shown by inspection of the free energy curves, which have two minima (see Fig. 3). Figure 4

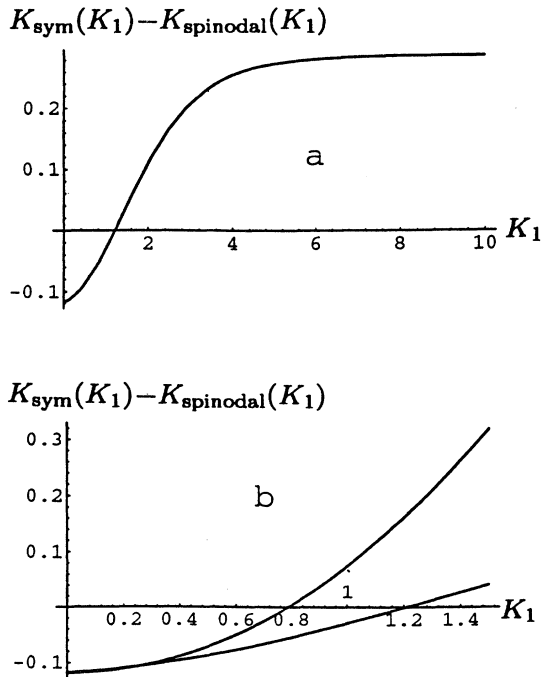


FIG. 2. Plot of the difference  $K_{\text{sym}}(K_1) - K_{\text{spinodal}}(K_1)$  as a function of  $K_1$ . (a) The parameters are  $q = 3$ ,  $c_1 = 4$ , and  $c_2 = 2$ . (b) The bottom curve has the same parameters as in (a) and the top curve has a different value of  $c_1$ , namely,  $c_1 = 6$ .

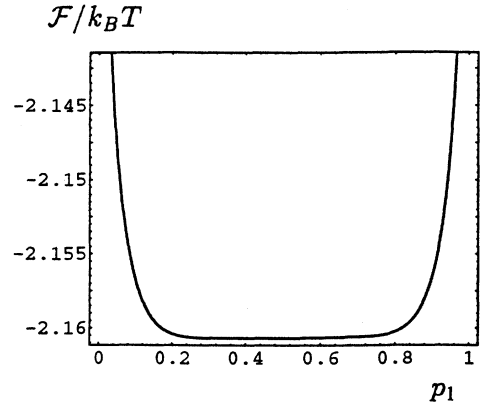


FIG. 3. Free energy as a function of the order parameter  $p_1$  at the critical point for  $q = 3$ ,  $c_1 = 4$ , and  $c_2 = 2$ .

shows the first-order transition line terminating at the critical point for values of  $c_1$  ranging from 2 to 6. Notice that for  $c_1 = 2$ , which corresponds to equal numbers of each type of bond at a given vertex, the critical point is at  $K_2 = 0$ . The coordinates of the critical point are listed in Table I. Besides this, each first-order transition line shares the same critical point at  $K_1 = 0$  and  $K_2 = \infty$ .

### B. Random intrachain interactions

Now suppose that some of the interaction parameters are independently distributed random variables. In the case  $\phi^{(\beta)} = 1$  (e.g., the zero-field disordered phase) the eigenvalues in (25) depend only on the corresponding interaction parameters and will also be independently distributed. Taking an average over the interaction variables, we find Eq. (25) to be still valid with the eigenvalues replaced by their average values. Equation (31) is also valid with  $t^{(\beta)}$  for the random bonds replaced by the average value  $\bar{t}$ . For random bonds with the distribution (2) appropriate to the polymer problem,

$$\bar{t} = pt_+ + (1-p)t_-, \quad (50)$$

where  $t_+$  and  $t_-$  are the values of  $t^{(\beta)}$  calculated from (33) using the ferro- and antiferromagnetic interaction

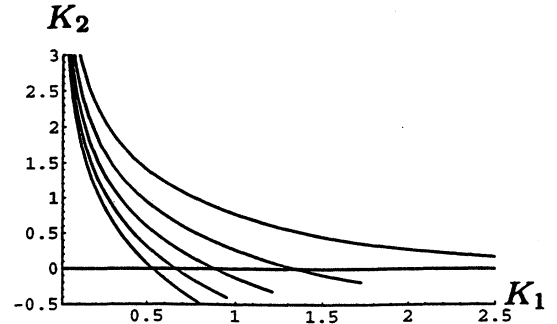


FIG. 4. First-order transition line [given by Eq. (48) with  $H = 0$ ] terminating at the critical point for values of  $c_1$  ranging from 2 to 6 (top to bottom).

TABLE I. Coordinates of the critical points.

$c_1$	$K_1$	$K_2$
2	$\infty$	0.000
3	1.724	-0.192
4	1.209	-0.317
5	0.950	-0.404
6	0.788	-0.469

parameters, respectively. Denoting by  $\bar{K}$  the value of the interaction parameter corresponding to  $\bar{t}$  via Eq. (33),

$$\bar{K} = -\ln\left(\frac{1-\bar{t}}{1+(q-1)\bar{t}}\right), \quad (51)$$

which is not the same as the average value of  $K^{(\beta)}$ . The difference is quite significant in locating the phase boundary. Figure 5 shows the value of  $\bar{K}$  as a function of  $p$  when the values of  $K^{(\beta)}$  are  $\pm 1$ .

When  $\phi^{(\beta)} \neq 1$ , factorization of the average of the product in (25) is not valid since the interaction variables are coupled via the effective-field variables. Consequently, an analytic treatment of the random problem appears not to be tractable. One possibility is to perform a computer simulation as in [5], but here we will replace the problem by a nonrandom problem in which the parameters for the random bonds are replaced by  $\bar{K}$  given by (51).

To make contact with the notation of Lin *et al.* [5] we take  $K_1 = \frac{qJ'}{(q-1)k_B T}$  and  $K_2 = \pm \frac{qJ}{(q-1)k_B T}$ , where in their numerical calculations they took  $J = 5J' = 1$  and  $k_B = 1$ . Using these values together with (51), the phase diagram of Sec. V A may be mapped onto the  $T$ - $p$  plane for comparison with Ref. [5] (see Fig. 6).

## VI. COMPARISON WITH THE MEAN-FIELD APPROXIMATION

Lin *et al.* [5] obtained the phase boundary for ferromagnetic ordering of the random copolymer using a mean-field approximation for the interchain interactions. This reduced the problem to a linear chain with random interactions, which they solved without further approximation using a computer simulation. They found that the

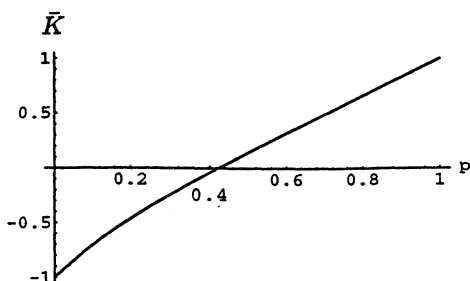


FIG. 5. Plot of the average value of  $K$  [given by Eq. (51)] as a function of  $p$ .

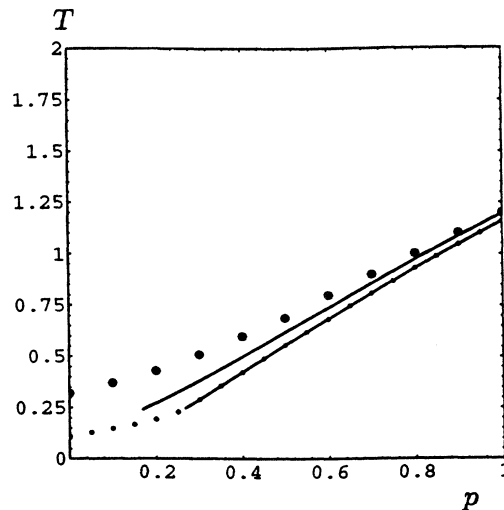


FIG. 6. Dimensionless transition temperature as a function of concentration  $p$ , calculated from various approaches. The parameters are chosen as  $q = 3$ ,  $c_1 = 4$ , and  $c_2 = 2$ . The big dots are from the calculation in Ref. 5, the top solid curve is calculated from the mean-field theory in Sec. VI A, the lower solid curve is the result from Sec. V B, and the small dots show the numerical results from Sec. VII.

transition was first order over the whole concentration range, which differs qualitatively from the result of the previous section. In order to make a comparison, we first show how one or more of the effective fields  $\bar{H}^{(\beta)}$  and the corresponding  $H^{(\beta)}$  may be replaced using a mean-field approximation.

### A. Mean-field theory as a limit

The mean-field approximation ignores the fluctuations in the effective fields. This may be achieved for  $\bar{H}^{(\beta)}$  by first replacing the branch  $\beta$  at each site by  $n_\beta$  branches, then setting the interaction parameter  $K^{(\beta)} = \hat{K}^{(\beta)}/n_\beta$ , and finally taking the limit  $n_\beta \rightarrow \infty$ .

In [5] the parameter  $m = \langle \mathbf{S}_i \cdot \mathbf{z} \rangle$  was used. In our notation

$$m = \frac{qp_1 - 1}{q - 1}. \quad (52)$$

Equation (15) combined with (12) yields a quadratic for  $\bar{\phi}^{(\beta)}$  which, in terms of  $m$ , may be written

$$[1 + (q-1)m]\bar{\phi}^{(\beta)2} + [(q-2) - 2(q-1)m]e^{-K^{(\beta)}}\bar{\phi}^{(\beta)} - (1-m)[1 + (q-2)e^{-K^{(\beta)}}] = 0. \quad (53)$$

It follows that

$$\hat{\phi}^{(\beta)} \equiv \lim_{n_\beta \rightarrow \infty} (\bar{\phi}^{(\beta)})^{n_\beta} = e^{-m\hat{K}^{(\beta)}}. \quad (54)$$

The free energy equation (39) may be written in the form

$$\begin{aligned} \frac{\mathcal{F}}{k_B T} = & -H p_1 + p_1 \ln p_1 + (1 - p_1) \ln \left( \frac{1 - p_1}{q - 1} \right) \\ & - \frac{1}{2} \left[ p_1^2 + \frac{(1 - p_1)^2}{q - 1} \right] \hat{K} \\ & + \frac{1}{2} \sum_{\beta=1}^{c'} \{ (2p_1 - 1) \ln \bar{\phi}^{(\beta)} - \ln [p_1 B(K^{(\beta)}, \phi^{(\beta)})] \}, \end{aligned} \quad (55)$$

with

$$\hat{K} = \sum_{\beta=c'+1}^c \hat{K}^{(\beta)}, \quad (56)$$

where the sum is over branches for which the effective field has been replaced by the mean field.

The equilibrium value of the magnetization  $m$  is given by

$$\frac{(1 - m)}{1 + (q - 1)m} = e^{-H - \hat{K}m} \prod_{\beta=1}^{c'} \bar{\phi}^{(\beta)}, \quad (57)$$

where  $\bar{\phi}^{(\beta)}$  is determined by (53). The above equation is obtained either by minimization of (55) or by substituting (54) in (19). In the case that all branches are treated in the mean-field approximation, (57) reduces to the expected result

$$m = \frac{(1 - e^{-H - \hat{K}m})}{1 + (q - 1)e^{-H - \hat{K}m}}. \quad (58)$$

The expression on the right-hand side is just the magnetization of an isolated atom in the mean field  $H + \hat{K}m$ .

The symmetry line that contains the mean-field boundary is now

$$2H + (c' - 2) \ln(q - 1)$$

$$+ \hat{K} \frac{q - 2}{q - 1} - \sum_{\beta=1}^{c'} \ln[1 + (q - 2)e^{-K^{(\beta)}}] = 0 \quad (59)$$

and, in the  $m = 0$  domain, the susceptibility diverges along the line

$$\frac{\hat{K}}{q} + \sum_{\beta=1}^{c'} \frac{t^{(\beta)}}{1 + t^{(\beta)}} = 1. \quad (60)$$

## B. The copolymer problem

To make a comparison with the previous result [5] for the random copolymer problem, we chose  $c' = 2$ ,  $\hat{K} = \sum_{\beta=c'+1}^c \hat{K}^{(\beta)} = 4K_1$ . The result for the phase boundary is shown in Fig. 6. We find that the results of the two approaches are very close and in fact at  $p = 1$  they give the same solutions.

## VII. OTHER TYPES OF ORDERING

What happens after the first-order transition line terminates at a critical point? Analytically it has not been possible to describe the remaining section of the transition line by a single equation. However, numerically it is fairly easy to obtain this section. We have plotted the result in Fig. 6 with the same parameters, using the free energy as a function of  $p_1$  given by Eq. (39). It is found that the transition line is composed of two sections, which join together at the critical point. The first section coincides with the analytical expression given by Eq. (48), as expected. The transition along this section is from  $p_1 = \frac{1}{3}$  to  $p_1 > \frac{1}{3}$ . The second section is another first-order transition line, marking a transition from  $p_1 = \frac{1}{3}$  to  $p_1 < \frac{1}{3}$ . The transition exists for the whole range of the composition variable  $p$ . This is qualitatively in agreement with the result in Ref. [5]. The difference between the transitions along the two sections indicates that below the transition line just discussed there should be another first-order transition line separating the two phases with  $p_1 > \frac{1}{3}$  and  $p_1 < \frac{1}{3}$ . This line should start from the critical point and end at a certain point ( $p = \frac{1}{7}$ , to be obtained below) on the zero-temperature axis. We do not calculate this line, as the free energy, Eq. (39), was calculated on the assumption that the order parameter has only one component and is uniform and the phase with  $p_1 < \frac{1}{3}$  for low temperature and concentration  $p$  may therefore be a metastable one. To see some evidence of this, we study the zero-temperature entropy as a function of the concentration. In the following discussion we will use the same parameters as before.

First, we consider the two special cases  $p = 1$  and  $p = 0$ , where there is no randomness. For  $p = 1$ ,  $K_2$  is positive and we find the asymptotic behavior of the order parameter, when  $T \rightarrow 0$ , goes as

$$p_1 \sim 1 - 2e^{-4K_1 - 2K_2} \quad (61)$$

and the corresponding equilibrium free energy is

$$\frac{\mathcal{F}}{k_B T} = -2K_1 - K_2 + o(T), \quad (62)$$

where  $o(T)$  represents terms of higher order with respect to  $T$  when  $T \rightarrow 0$ . This yields zero entropy at zero temperature as is expected.

For  $p = 0$ ,  $K_2$  is negative and the order parameter goes as

$$p_1 \sim 2^5 e^{-4K_1}. \quad (63)$$

The corresponding "equilibrium" free energy is

$$\frac{\mathcal{F}}{k_B T} = -2K_1 + 2 \ln 2 + o(T), \quad (64)$$

which results in a negative zero-temperature entropy  $S/k_B = -2 \ln 2$ . This indicates that the phase with  $p_1 \sim 2^5 e^{-4K_1} < \frac{1}{3}$  is a metastable one.

Next, we consider the case where  $(1 - p)p$  is positive.  $K_2$  must now be replaced by its average value, which is

given by Eq. (51). When  $T \rightarrow 0$ , it reaches a finite value given by

$$\begin{aligned}\bar{K}_2 &= -\ln \frac{1-p}{(q-1)p} + o(e^{-K_2/T}) \\ &= -\ln \frac{1-p}{2p} + o(e^{-K_2/T}).\end{aligned}\quad (65)$$

A careful asymptotic analysis yields the following  $p$ -dependent order parameter:

$$p_1 = \begin{cases} \frac{2^5(1-p)^2}{(1+p)^2} e^{-4K_1} & \text{for } p < \frac{1}{7} \\ 1 - \frac{(1-p)^2}{2p^2} e^{-4K_1} & \text{for } p > \frac{1}{7} \end{cases}\quad (66)$$

and the equilibrium free energy

$$\frac{\mathcal{F}}{k_B T} = \begin{cases} 2 \ln 2 - \ln \frac{1+p}{1-p} - 2K_1 & \text{for } p < \frac{1}{7} \\ \ln \frac{1-p}{2p} - 2K_1 & \text{for } p > \frac{1}{7}. \end{cases}\quad (67)$$

The zero-temperature entropy is then given by

$$\frac{S}{k_B} = \begin{cases} -2 \ln 2 + \ln \frac{1+p}{1-p} & \text{for } p < \frac{1}{7} \\ -\ln \frac{1-p}{2p} & \text{for } p > \frac{1}{7}. \end{cases}\quad (68)$$

From this we find that the entropy is negative for low composition ( $p < \frac{1}{3}$ ). Again, the phase with  $p_1 < \frac{1}{3}$  always has a negative zero-temperature entropy. It is thus plausible to think that the first-order transition line given by Eq. (48) should give a good description for the system when  $p > \frac{1}{3}$ . However, when  $p < \frac{1}{3}$ , one should look for other types of symmetry-breaking schemes, such as ferromagnetic order with more than one component, antiferromagnetic order, or spin-glass order.

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