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Ferromagnetic phase transition in random Potts spin chains

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We study the ferromagnetic phase transition in a model consisting of one-dimensional three-state Potts spin chains with random intrachain couplings and comparatively weak ferromagnetic interchain couplings. Mean-field theory is employed to decouple approximately the interchain couplings. The transfer-matrix method is then used to study the resulting effectively one-dimensional random-bond Potts model. The free energy as a function of the ferromagnetic order is calculated numerically and a first-order ferromagnetic-paramagnetic phase transition is found over a wide range of degree of randomness.

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I. INTRODUCTION

There has recently been renewed interest in the problem of interacting Ising spins in the presence of disorder [1–5]. Some of this activity is prompted by the existence of experimental systems that appear to be well described by a disordered spin-$\frac{1}{2}$ Ising model [6,7]. A related problem is found in the study of phase transitions in ferroelectric random copolymers, an example of which is the system in which vinylidene fluoride and tetrafluoroethylene are combined in a ratio of from 60% to 80% vinylidene fluoride [8]. To describe the conformations of linear polymers having a carbon-chain backbone, an isomeric-state model is commonly adopted in which the torsional angle of a triad of carbon-carbon bonds can take on only three possible values. Such a system can then be modeled as an anisotropic three-state Potts model in three dimensions.

In this paper we study a simple analog of this system, and introduce a mean-field approximation to reduce the three-dimensional problem to an effectively one-dimensional system with long-range interactions. In practical application to random copolymers the justification for this step lies in the fact that the intrachain covalent bonds are appreciably stronger than the interchain van der Waals interactions. This model is presented in Sec. II, where a three-dimensional anisotropic three-state random-bond Potts model is described. Mean-field theory for this Potts model is introduced in Sec. III. In Sec. IV, the resulting effectively one-dimensional random-bond Potts model is studied via the transfer-matrix approach. In Sec. V, we calculate numerically the free energy as a function of the ferromagnetic order for various temperatures and compositions of randomness. According to the numerical results, a first-order ferromagnetic-paramagnetic phase transition is found over a wide range of compositions. Finally, we summarize and discuss our results in Sec. VI.

II. MODEL

We start with the following Hamiltonian of a three-dimensional anisotropic three-state random-bond Potts model:

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

where i and j represent coordinates of three-dimensional cubic lattice sites. $\mathbf{S}_i$ is the Potts spin which is a unit vector allowed to have three orientations (0, $2\pi/3$, and $4\pi/3$) on the plane perpendicular to the Potts spin chains. The quantity $\mathbf{S}_i \cdot \mathbf{S}_j$ is the scalar product of the two unit spin vectors and the J_{ij} represent the nearest-neighbor intrachain couplings and are random variables satisfying the same independent distribution $\rho(J_{ij}) = p\delta(J_{ij} - J) + (1-p)\delta(J_{ij} + J)$. Each intrachain coupling thus has probability p to be a ferromagnetic coupling and probability $1-p$ to be antiferromagnetic. The J'_{ij} represent the nearest-neighbor interchain couplings and are assumed to be uniform and of ferromagnetic type, so that $J'_{ij} = J' > 0$. We assume weak interchain coupling, and so we have $J' \ll J$. The sum $\sum_{\mathrm{intra}(i,j)}$ ($\sum_{\mathrm{inter}(i,j)}$) is the sum over all the nearest intrachain (interchain) neighbors. The ferromagnetic order is then given by the thermal and disorder average of the Potts spin:

$$\mathbf{m} = \overline{\langle \mathbf{S}_i \rangle} \ , \tag{2}$$

where $\langle\,\rangle$ is the thermal average and the bar represents the average over the random variables J_{ij}.

In the model defined by the Hamiltonian [Eq. (1)] the intrachain couplings are random, but the interchain couplings are not. This model has possible application to the first-order ferroelectric-paraelectric phase transition in random copolymers of vinylidene fluoride and tetrafluoroethylene [6–8]. The model is still not accessible to exact solution, and so we now turn to an approximate method, in which the term J'_{ij} is replaced by an infinite-range mean-field contribution.

III. MEAN-FIELD APPROXIMATION

In this section we will use the mean-field approximation to find a mean-field free energy as a function of the order parameter m from the Hamiltonian [Eq. (1)]. The ferromagnetic order of the system is determined by finding the value of m that minimizes the free energy.

Let f be the free energy per spin of the system given by Eq. (1). From the well-known inequality $\langle e^x\rangle \geq e^{\langle x\rangle}$, one can find that

$$f \leq f_{\rm up} \equiv \frac{1}{N}\overline{\langle H\rangle_{H_{\rm eff}}} + f_{\rm eff} - \frac{1}{N}\overline{\langle H_{\rm eff}\rangle_{H_{\rm eff}}} \ , \qquad (3)$$

where $f_{\rm up}$ is an upper bound of the free energy f, N is the total number of Potts spins, $H_{\rm eff}$ is an effective Hamiltonian produced by a mean-field approximation, $f_{\rm eff}$ represents the free energy of the system with $H_{\rm eff}$, $\langle\,\rangle_{H_{\rm eff}}$ means the thermal average with respect to the effective Hamiltonian, and a bar stands for the average over the random variable J_{ij}. Choosing the effective Hamiltonian appropriately will give a useful estimate of the free energy f. We will use a mean-field consideration to introduce an effective Hamiltonian and then find an upper bound free energy ($f_{\rm up}$) of the system. This mean-field free energy is found to be a function of an order parameter m. Minimizing the mean-field free energy with respect to the order parameter m then yields the mean-field magnetization of the system.

Since the interchain coupling constant J' is much smaller than the intrachain coupling constant, it is reasonable to make an approximation for the terms involving all the interchain interactions in the Hamiltonian given by Eq. (1). We suppose that the system has a magnetization along the $\mathbf{z}$ direction, so that

$$\mathbf{m} = m\mathbf{z} \ , \qquad (4)$$

where $\mathbf{z}$ is a unit vector along the 0 direction in the plane perpendicular to the Potts spin chain, and m is the ferromagnetic order parameter. This spontaneous broken symmetry is assumed to produce a uniform field, $\mathbf{h} = h(m, K, J', p)\mathbf{z}$, acting on each individual Potts spin $\mathbf{S}_i$. The mean field $h(m, K, J', p)$ is a function of the ferromagnetic order parameter m, temperature parameter K ($K = J/T$ with temperature T and unit Boltzmann constant), interchain coupling J', and disorder parameter p. The resulting effectively one-dimensional Hamiltonian is then given by

$$H_{\rm eff} = -\sum_{{\rm intra}(i,j)} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j - h(m, K, J', p)\sum_i \mathbf{S}_i\cdot\mathbf{z} \ , \qquad (5)$$

where the sum $\sum_i$ is over all the lattice sites.

From Eqs. (1), (3), and (5) the mean-field free energy is

$$f_{\rm mean} \equiv f_{\rm up} = -2J'm^2 + h(m, K, J', p)m + f_{\rm eff} \ , \qquad (6)$$

where m is the magnitude of the spontaneous-broken-symmetry ferromagnetization and now satisfies the following mean-field equation:

$$m = \overline{\langle \mathbf{S}_i\cdot\mathbf{z}\rangle_{H_{\rm eff}}} \ . \qquad (7)$$

Equation (7) for the ferromagnetic order m determines the mean-field $h(m, K, J', p)$ as a function of the parameters m, K, J', and p. The effective free energy is

$$f_{\rm eff} = -\overline{\frac{1}{N\beta}\ln\,{\rm Tr}\,\exp[-\beta H_{\rm eff}]} \ , \qquad (8)$$

where $\beta = \frac{1}{T}$ is the inverse temperature.

Given the couplings J and J', the composition p, and the temperature T, Eqs. (5)–(8) indicate that the mean-field free energy is a function of m only. The magnetization can be obtained by finding the value of m that minimizes the mean-field free energy.

Combining Eq. (7) and the minimization condition of the mean-field free energy yields

$$h(m, K, J', p) = 4J'm \ . \qquad (9)$$

It is important to notice that Eq. (9) is only valid at the equilibrium state. Two approaches are possible for calculating the magnetization. The first is to find the minimum of the free energy, which is a function of the order parameter m, without applying Eq. (9); the second is to combine Eqs. (7) and (9) and solve them self-consistently. While the second approach has the advantage of being easily implemented, the first one has the advantage of yielding the free energy as a function of the order parameter. Since the order of the transition can be easily seen through observation of the free energy, and since the time required for the numerical calculation is not large, we employ the first approach in the numerical calculation of the magnetization.

IV. TRANSFER-MATRIX ANALYSIS

The transfer-matrix technique has been widely used in studying the one-dimensional disordered Ising spin system [1-5]. In this section we use this technique to study the one-dimensional random-bond three-state Potts model in the presence of a uniformal external field [see the Hamiltonian $H_{\rm eff}$ given by Eq. (5)].

Given the one-dimensional Hamiltonian $H_{\rm eff}$, the corresponding 3×3 transfer matrix is

$$\mathbf{T}_\pm = \begin{pmatrix} e^{-\frac{3}{2}\bar{h}} & e^{-\frac{3}{2}K_\pm-\frac{3}{2}\bar{h}} & e^{-\frac{3}{2}K_\pm-\frac{3}{2}\bar{h}} \\ e^{-\frac{3}{2}K_\pm} & 1 & e^{-\frac{3}{2}K_\pm} \\ e^{-\frac{3}{2}K_\pm-\frac{3}{2}\bar{h}} & e^{-\frac{3}{2}K_\pm-\frac{3}{2}\bar{h}} & e^{-\frac{3}{2}\bar{h}} \end{pmatrix} , \qquad (10)$$

where $\mathbf{T}_\pm$ are the two possible transfer matrices with $+$ representing the ferromagnetic bond and $-$ the antiferromagnetic bond, where $K_\pm \equiv \pm K$ is the coupling strength J divided by temperature T, and $\bar{h}$ is the effective mean field $h(m, K, J', p)$ divided by temperature. In writing the above transfer matrix we have omitted a common factor of $e^{K_\pm + \bar{h}}$ which does not affect our calculation of the magnetization m but which will be accounted for in the calculation of the effective free energy. The transfer matrix is arranged in a way such that the first, second, and third columns (or rows) correspond to the $2\pi/3$, 0, and $4\pi/3$ orientations of the Potts spins.

We define a sequence of partition functions

$$\begin{bmatrix} Z_{\searrow n+1} \\ Z_{\uparrow n+1} \\ Z_{\swarrow n+1} \end{bmatrix} = \mathbf{T}_n \begin{bmatrix} Z_{\searrow n} \\ Z_{\uparrow n} \\ Z_{\swarrow n} \end{bmatrix} , \tag{11}$$

where $\mathbf{T}_n$ is the random transfer matrix associated with the nth bond and can be either $\mathbf{T}_+$ (with probability p) or $\mathbf{T}_-$ (with probability $1 - p$) depending on the type of the associated bond. For a free boundary system the initial partition functions are defined by

$$\begin{bmatrix} Z_{\searrow 0} \\ Z_{\uparrow 0} \\ Z_{\swarrow 0} \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} . \tag{12}$$

Since $\mathbf{T}_n$ is a random matrix, Eq. (11) introduces a sequence of random partition functions, which is a sequence of random three-dimensional vectors. To study this sequence of random partition functions, let us introduce the spherical coordinates (r_n, θ_n, φ_n) for the partition function at a given step n, so that

$$r_n \begin{bmatrix} \sin\theta_n \cos\varphi_n \\ \cos\theta_n \\ \sin\theta_n \sin\varphi_n \end{bmatrix} \equiv \begin{bmatrix} Z_{\searrow n} \\ Z_{\uparrow n} \\ Z_{\swarrow n} \end{bmatrix} . \tag{13}$$

The advantages of introducing spherical coordinates are twofold. First, it separates the common factor r_n, which is irrelevant in the calculation of the magnetization but on the other hand uniquely determines the effective free energy. This permits a reduction in the dimensions of the random partition functions from 3 to 2. Second, it utilizes a symmetry preserved by the random matrix $\mathbf{T}_n$, reducing further the dimensions of the random vector from 2 to 1. This symmetry lies in the fact that the matrices have an invariant vector subspace which is composed of all the vectors having the form $\begin{bmatrix} x \\ z \\ x \end{bmatrix}$. This then says that φ_n is fixed and is equal to $\pi/4$. After these considerations, we find the following iteration relation between θ_{n+1} and θ_n:

$$\begin{aligned} \theta_{n+1} &= g_\pm(\theta_n) \\ &\equiv \arctan \frac{e^{-\frac{3}{2}\bar{h}} \left[\sqrt{2} e^{-\frac{3}{2}K_\pm} + \left(1 + e^{-\frac{3}{2}K_\pm}\right) \tan\theta_n\right]}{1 + \sqrt{2} e^{-\frac{3}{2}K_\pm} \tan\theta_n} . \end{aligned} \tag{14}$$

Since all the partition functions are positive, all the angles $\{\theta_n\}$ are confined in $(0, \ \pi/2)$. Equation (14) generates a sequence of random angles $\{\theta_n\}$. When $n \to \infty$, they will satisfy a well-defined angle distribution function $\rho(\theta)$ [2,4] on $[0, \ \pi/2]$, which gives the probability density of finding θ_n within $(\theta \ , \theta + d\theta)$ and is determined by the iterative functions $g_\pm$ and the composition p. Analytic solutions for the angle distribution function $\rho(\theta)$ are, in general, not available, and so we resort to numerical methods.

Our next step is to establish relations between the thermal quantities (the magnetization m and the effective free energy) and the angle θ. One can verify that the ferromagnetic order m satisfies

$$m = \overline{\frac{1 - \frac{1}{2}\tan\theta_1 \tan\theta_2}{1 + \tan\theta_1 \tan\theta_2}} , \tag{15}$$

where θ_1 and θ_2 are angles, each satisfying independently the angle distribution function $\rho(\theta)$. The bar indicating the average over the random variable J_{ij} is now replaced by the average over the angle distribution.

To calculate the effective free energy, let us further define

$$\lambda_n \equiv \frac{r_n}{r_{n-1}} . \tag{16}$$

It is worth noting that as far as the random variables are concerned, λ_n is a function only of θ_{n-1} and the random coupling ($J_{n,n-1}$) associated with sites n and $n - 1$ on the same chain and is given by

$$\begin{aligned} \lambda_n^2(\theta_{n-1}) = e^{-\frac{3h}{T}} \Bigg[&\left(1 + e^{-\frac{3J_{n,n-1}}{2T}}\right) \sin\theta_{n-1} \\ &+ \sqrt{2} e^{-\frac{3J_{n,n-1}}{2T}} \cos\theta_{n-1} \Bigg]^2 \\ &+ \left[\sqrt{2} e^{-\frac{3J_{n,n-1}}{2T}} \sin\theta_{n-1} + \cos\theta_{n-1}\right]^2 , \end{aligned} \tag{17}$$

where h is the mean field. The effective free energy can now be found to be

$$f_{\text{eff}} = [-h - J(2p - 1)] - T\,\overline{\ln\lambda(\theta)} , \tag{18}$$

where $\lambda(\theta)$ is given by Eq. (17) with θ_{n-1} replaced by θ, and the average is over both the distributions $[\rho(J_{ij})$ and $\rho(\theta)]$ of the random coupling and random angle. The terms in the square brackets in the above equation come from the contribution of the common factor that was extracted from the transfer matrix. Equations (6) and (14)–(18) are our basic starting point for calculating the free energy numerically in the next section.

V. NUMERICAL RESULTS

In this section, we present the numerical results of a calculation of the free energy. Starting from the iterative relation [Eq. (14)], one can generate an angle distribution function $\rho(\theta)$ and hence the magnetization m and the effective free energy through Eqs. (15) and (18). Finally, the mean-field free energy can be found via Eq. (6).

For the numerical simulation we have chosen $J = 5J' = 1$. Figure 1 shows the mean-field free energy as a function of the ferroelectric order parameter m for various temperatures at a composition $p = 0.9$. Figure 1(a) shows that at high temperature, the only minimum occurs at $m = 0$, indicating that there is no ferroelectric order. However, at low temperature, the state with $m = 0$ becomes unstable, and two minima at nonzero m (one positive and one negative) appear, implying the existence of a ferroelectric phase. The one that has the lowest free energy is located at positive m. There is thus a paramagnetic-ferromagnetic phase transition when the temperature is lowered through a certain transition temperature. A careful examination of the free energy in the vicinity of the transition temperature [Fig. 1(b)] shows that the transition is weakly of first order.

Figure 2 shows schematically the ferromagnetic order as a function of the temperature. When the temperature is larger than a certain temperature T_1, the only stationary point is at $m = 0$ which is also a minimum and has the lowest free energy. When the temperature is lowered below T_1 but higher than the transition temperature T_c, two more stationary points at m_l (> 0 and unstable) and m_u ($> m_l$ and metastable) appear, but the state with $m = 0$ still has the lowest free energy. If the temperature is further reduced to a temperature smaller than T_c and larger than another temperature T_2, the state at m_u possesses the lowest free energy, leaving other properties unchanged. Finally, if the temperature is smaller than T_2, then the state at m_l becomes negative and metastable while that at $m = 0$ becomes unstable, but with that at m_u continuing to have the lowest free energy. The figure also shows that the transition from the stable branch $m = 0$ to the most stable branch $m = m_u$ is of first order in contrast with the usual Ising spin system where the upper branch $m = m_u$ and the lower branch $m = m_l$ are symmetric about the branch $m = 0$, and all transitions are of second order.

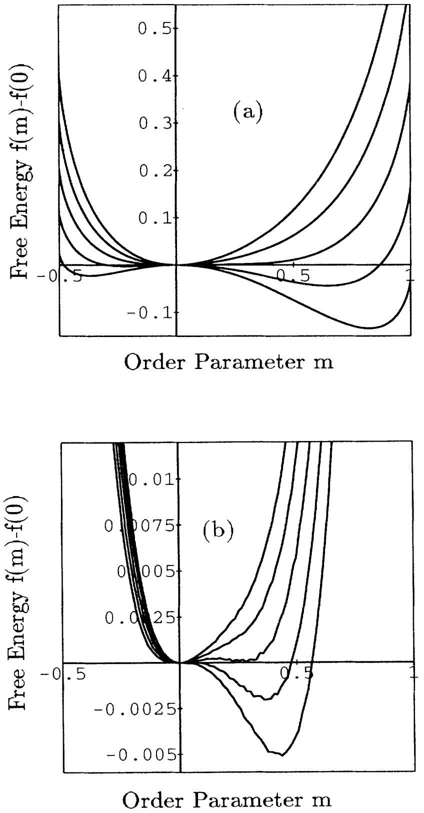

FIG. 1. This figure shows free energy as a function of the order parameter m at various temperatures. The composition p is equal to 0.9. The curves correspond, from top to bottom, to temperatures 3.5, 3.0, 2.5, 2.0, and 1.5 in (a), and 2.55, 2.50, 2.45, 2.40, and 2.35 in the expanded figure (b).

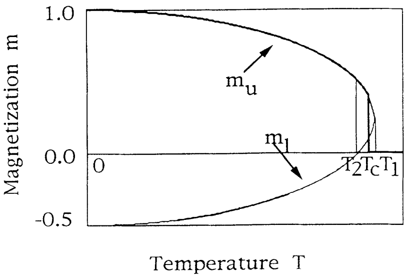

FIG. 2. This figure shows schematically the magnetization as a function of the temperature.

In Fig. 3, we plot the transition temperature as a function of the composition p. Unlike the case of the usual spin-glass system, here the ferromagnetic-paramagnetic phase transition exists for all compositions as a consequence of the mean-field approximation.

VI. CONCLUSIONS

We have studied the ferromagnetic-paramagnetic phase transition of a three-dimensional anisotropic three-state random-bond Potts model. Mean-field theory has been employed to decouple the comparatively weak ferroelectric couplings between the random Potts spin chains, reducing the model to an effectively one-dimensional random-bond three-state Potts model in the presence of the uniform mean field. The symmetry of the transfer-matrix permits us to simplify greatly the problem from finding an angular distribution function of two spherical

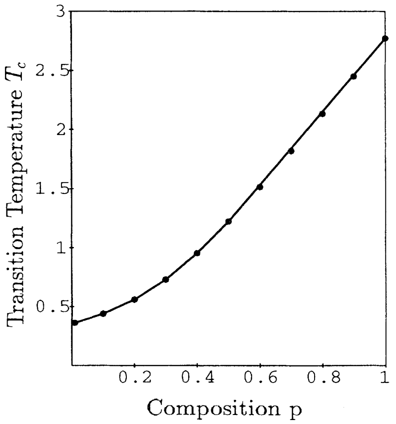

FIG. 3. This figure shows the transition temperature as a function of the composition p.

angles θ and φ from which the average free energy and magnetization may be determined. A first-order ferromagnetic phase transition at all compositions is found from a numerical calculation of the free energy. As expected, the transition to the ferromagnetic phase with positive magnetization (corresponding to the most stable branch) is of first order. The weak ferromagnetic coupling between the random Potts spin chains prevents the system from being a spin-glass system. The uniform mean field adopted in this version of the theory prevents us from finding a helical phase. A future improvement to the present theory is planned to introduce a random mean field.

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