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A General Model of Random Copolymers in an Athermal Solution

Jong-Hoon Ryu[†] **and P. D. Gujrati***[,‡]

Departments of Polymer Science and Physics and Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325

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ABSTRACT: It is shown that a general model of athermal random copolymers in an equilibrium state is related to an appropriately generalized $n \to 0$ spin vector model, with each spin having $2n$ components. By adjusting various coupling constants in the model, one can control various densities such as bond densities of each type and copolymer density, average copolymer size, average block size, etc. The model is solved in a mean-field approximation to study the complete phase diagram and to calculate the free energy and the entropy and the entropy of mixing of copolymers in an athermal solution.

I. Introduction

The most important aspect of long-chain polymers is the excluded-volume effects which forbid polymer chains to overlap. In order to study excluded-volume effects, one starts with a simple model of polymer chains: The chains are described by self-avoiding random walks (SAW's), each of which has the constraint that it cannot return to sites already visited. If one is interested in long-range properties of polymers, then their chemical details are not expected to be important, and the above model seems to be quite appropriate. Here we assume that there are no long-range interactions except the excluded-volume effects. In 1972 de Gennes[1] pointed out an analogy between a self-avoiding random walk and a formal $n \to 0$ limit of an n-component φ^4 field theory in the absence of any external magnetic field. Later on, des Cloizeaux[2,3] extended the approach of de Gennes and succeeded in providing an analogy between a system of polymer chains with excluded volume in a solution and the φ^4 field theory in the presence of an external field as $n \to 0$. This analogy is found to be much more transparent if we restrict ourselves to a lattice and assume that the length of each spin is constrained to be $n^{1/2}$.[4−7] It has been argued that the activities for a bond and an end point of a SAW are given by K and H, respectively, where K and H are the ferromagnetic coupling constant and the magnetic field, respectively. However, Gujrati[8,9] pointed out that K and H do not serve as the activities for the polymer system. The latter are given by K/z and $H/z^{1/2}$, where $z = 1 + H^2$. He also showed that the polymer free energy W_p is different from the magnetic free energy W_0 in the $n \to 0$ limit and that W_p satisfies the proper convexity properties, even though W_0 does not.

Since Alfrey and Tobolsky[10] first treated the theory of equilibrium copolymerization, this complex problem has been approached kinetically[11−14] and thermodynamically.[15−19] Kennedy and Wheeler[19] proposed a model which incorporates excluded-volume effects for a random copolymer system by using the usual $n \to 0$ trick used for the description of the homopolymer system. Their correspondence is not only approximate but also not general.

In this study we discuss an exact correspondence between the equilibrium properties of random copolymers of A and B monomer units and an $n \to 0$ spin model, with each spin having $2n$ components. Our model is also very general. In order that the analysis can be carried out explicitly, we confine ourselves to a magnetic system and, therefore, a copolymer system on a lattice. Moreover, the length of each spin of the magnetic system is constrained to be $(2n)^{1/2}$. We express various interesting quantities of the copolymer system in terms of quantities describing the corresponding magnetic system. The model is solved in a mean-field approximation to study the phase diagram and to calculate the entropy and the entropy of mixing of copolymer chains in an athermal solution. If we follow the mapping proposed by Gujrati,[20] although not treated here, our model can be easily extended to describe the equilibrium system where the monomers and the copolymer coexist.

The equilibrium copolymerization problem considered here gives rise to a polydisperse system, the polydispersity being controlled by various activities. Hence, we cannot obtain this entropy by using the standard Flory method,[21] which is applicable to monodisperse systems. However, by following the extension proposed by Gujrati,[22] we can apply the Flory method to this case. Such an extension is quite cumbersome, while the method proposed here is straightforward and transparent. The results should be similar.

II. Definition of the Magnetic Model and Copolymer Analogy

Since this study is the extension of the previous work[9] to the copolymer system, we will briefly outline the magnetic model which we use to describe the copolymer system. There is a $2n$-component classical spin $\vec{S}_i$ with cubic symmetry at each site i on the lattice. Each spin $\vec{S}_i$ has the following orientations:

$$\vec{S}_i = \begin{cases} (\pm(2n)^{1/2}, 0, 0, \ldots, 0|0, 0, \ldots, 0) \\ (0, \pm(2n)^{1/2}, 0, \ldots, 0|0, 0, \ldots, 0) \\ \vdots \\ (0, 0, \ldots, 0|\pm(2n)^{1/2}, 0, 0, \ldots, 0) \\ (0, 0, \ldots, 0|0, 0, \ldots, 0, \pm(2n)^{1/2}) \end{cases}$$

Note that each spin has $4n$ different orientations. Each spin can also be symbolically expressed as

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[†] Department of Polymer Science and Maurice Morton Institute of Polymer Science.

[‡] Departments of Polymer Science and Physics and Maurice Morton Institute of Polymer Science.

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$$\vec{S}_i = (\sigma_i^{(\alpha)},\alpha=1,2,...,n|\tau_i^{(\alpha)},\alpha=1,2,...,n) = (\vec{\sigma}_i|\vec{\tau}_i)$$

where the $2n$ components of $\vec{S}_i$ are divided into two n-component spins, which are conveniently denoted by $\vec{\sigma}_i$ and $\vec{\tau}_i$. Because of the form of $\vec{S}_i$, $(\vec{\sigma}_i|\vec{0})$ can be considered as $\vec{\sigma}_i$ and, similarly, $(\vec{0}|\vec{\tau}_i)$ as $\vec{\tau}_i$. However, the two components $\vec{\sigma}_i$ and $\vec{\tau}_i$ are not independent: spins with orientations $(\vec{\sigma}_i\neq\vec{0}|\vec{\tau}_i\neq\vec{0})$ are not allowed. Thus, each site is occupied by either $\vec{\sigma}_i$ or $\vec{\tau}_i$. The length of each spin is constrained to be equal to $(2n)^{1/2}$:

$$\vec{\sigma}_i^2 = \sum_{\alpha=1}^{n}(\sigma_i^{(\alpha)})^2 = 2n, \qquad \text{if } \vec{\sigma}_i \neq 0 \tag{1a}$$

$$\vec{\tau}_i^2 = \sum_{\alpha=1}^{n}(\tau_i^{(\alpha)})^2 = 2n, \qquad \text{if } \vec{\tau}_i \neq 0 \tag{1b}$$

This also means that

$$\vec{S}_i^2 = 2n \tag{1c}$$

The Hamiltonian of the constrained, homogeneous magnetic system is given by

$$\mathscr{H}_n = \sum_{\langle ij\rangle}(K_A\vec{\sigma}_i\cdot\vec{\sigma}_j + K_B\vec{\tau}_i\cdot\vec{\tau}_j + J\vec{\sigma}_i\cdot\vec{\tau}_j) + \sum_i(H_A\sigma_i^{(1)} + H_B\tau_i^{(1)}) \tag{2}$$

where K_A, K_B, and J are coupling constants for $\sigma-\sigma$, $\tau-\tau$, and $\sigma-\tau$ pairs, respectively, and H_A and H_B are magnetic fields applied in the $\alpha = 1$ directions of $\vec{\sigma}_i$ and $\vec{\tau}_i$, respectively. The first summation is over the nearest-neighbor pairs and a factor of $-1/k_BT$ has been absorbed in the definition of the Hamiltonian $\mathscr{H}_n$. Here k_B denotes the Boltzmann constant and T is the temperature of the magnetic system. The partition function is given by

$$Z_n = \mathrm{Tr}[\exp(\mathscr{H}_n)] = \prod_i \mathrm{Tr}_i[\exp(\mathscr{H}_n)] \tag{3}$$

where the product is over all sites i and the trace operation Tr_i over the spin configurations of $\vec{S}_i$ is defined as

$$\mathrm{Tr}_i[\psi] \equiv \frac{\sum_{\{\vec{s}_i\}}\psi}{\sum_{\{\vec{s}_i\}}1} = \frac{1}{4n}\sum_{\{\vec{s}_i\}}\psi \tag{4}$$

Here ψ is any function of $\vec{S}_i$. It is easily seen[9] that

$$\mathrm{Tr}_i[1] = 1$$

$$\mathrm{Tr}_i[(\sigma_i^{(\alpha)})^2] = \mathrm{Tr}_i[(\tau_i^{(\alpha)})^2] = 1 \qquad (\alpha = 1, 2, ..., n) \tag{5}$$

are the only nonvanishing averages in the $n \to 0$ limit for any i.

If we expand the partition function Z_n in a power series and represent each term in the expansion, following Gujrati,[9] as a diagram on the lattice (Figure 1), then the partition function Z_0 in the $n \to 0$ limit[9] becomes

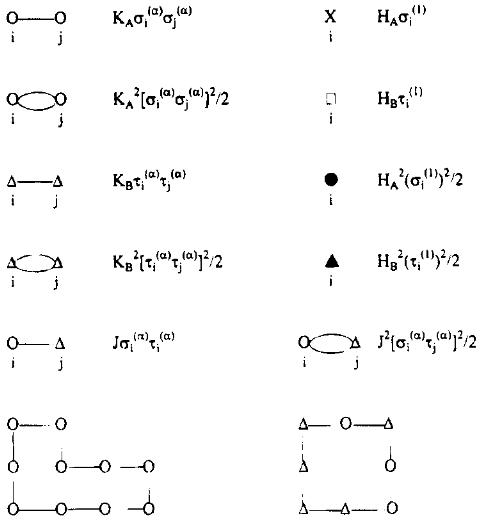

Figure 1. Graphical representation of various terms in Z_n. Closed loops vanish in the $n \to 0$ limit.

$$Z_0 = \mathrm{Tr}\left[\prod_{\langle ij\rangle}(1 + K_A\vec{\sigma}_i\cdot\vec{\sigma}_j + K_B\vec{\tau}_i\cdot\vec{\tau}_j + J\vec{\sigma}_i\cdot\vec{\tau}_j) \times \prod_k\left(1 + H_A\sigma_k^{(1)} + H_B\tau_k^{(1)} + \frac{1}{2}H_A^2(\sigma_k^{(1)})^2 + \frac{1}{2}H_B^2(\tau_k^{(1)})^2\right)\right] \tag{6}$$

Therefore, the only diagrams that contribute to Z_0 are those that contain any number of nonintersecting lines (consisting of three different types of bonds due to $K_A\sigma_i^{(1)}\sigma_j^{(1)}$, $K_B\tau_i^{(1)}\tau_j^{(1)}$, and $J\sigma_i^{(1)}\tau_j^{(1)}$) such that each line terminates on either a cross (×) or a square (□) at the two ends. In the following, we will use σ spins to represent A monomers and τ spins to represent B monomers. There can also be any number of filled circles and filled triangles at any sites not connected to these lines (SAW's). One such nonvanishing diagram is shown in Figure 2. Each bond of the SAW's gives a factor of K_A, K_B, or J for the three types, each SAW gives a factor H_iH_j $(i,j = \mathrm{A, B})$ from two chain ends of type i and j, and each filled circle and triangle contributes a factor of $H_A^2/2$ and $H_B^2/2$, respectively.

Let us consider a diagram having p SAW's consisting of $l = B_A + B_B + B_{AB}$ bonds, where B_A and B_B denote the number of $\sigma-\sigma$ and $\tau-\tau$ bonds, respectively, and B_{AB} the number of $\sigma-\tau$ bonds. These SAW's cover $p + l$ sites of the lattice. There are $N - (p + l)$ uncovered sites which may or may not be covered by the filled circles or triangles. The generating function for an uncovered site is given by

$$z = z(H_A,H_B) = 1 + \frac{1}{2}(H_A^2 + H_B^2) \tag{7}$$

The partition function Z_0 can now be written as follows:

$$Z_0(K_A,K_B,J,H_A,H_B) = z^N + \sum_{p\geq 1}\sum_{l\geq p} H_A^{e_A}H_B^{e_B}K_A^{B_A}K_B^{B_B}J^{B_{AB}}z^{N-(p+l)}U_{p,l} \tag{8}$$

and $U_{p,l}$ is the number of different ways of drawing p SAW's of total length l terminating on σ or τ ends. Here $2p = e_A + e_B$, where e_A denotes the number of σ ends, i.e., A-ends (crosses), and e_B the number of τ ends, i.e., B-ends (squares).

Now we identify a SAW with a copolymer chain. Let us first introduce the following five activities: η_A and η_B are the activities for an A and a B chain end,

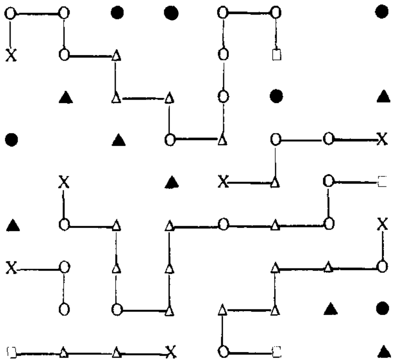

Figure 2. A typical example of the nonvanishing diagram appearing in Z_0. There are six SAW's of total length $l = 41$ and six filled circles and seven filled triangles that are not connected with the SAW's. Here empty sites can be considered as solvent molecules.

respectively, κ_A and κ_B are the activities for an A–A and a B–B bond, respectively, and γ is the activity for an A–B or B–A bond. We define the grand canonical partition function for the copolymer chains as follows:

$$Z_p(\kappa_A,\kappa_B,\gamma,\eta_A,\eta_B) = 1 + \sum_{p\geq 1}\sum_{l\geq p} \eta_A^{e_A}\eta_B^{e_B}\kappa_A^{B_A}\kappa_B^{B_B}\gamma^{B_{AB}}U_{p,l} \quad (9)$$

where we have used the quantity $U_{p,l}$ introduced in eq 8. A comparison of eqs 8 and 9 shows that

$$Z_0(K_A,K_B,J,H_A,H_B) = z^N Z_p(\kappa_A,\kappa_B,\gamma,\eta_A,\eta_B) \quad (10)$$

provided we make the following identifications:

$$\kappa_A = \frac{K_A}{z(H_A,H_B)}, \quad \kappa_B = \frac{K_B}{z(H_A,H_B)}, \quad \gamma = \frac{J}{z(H_A,H_B)}$$

$$\eta_A = \frac{H_A}{[z(H_A,H_B)]^{1/2}}, \quad \eta_B = \frac{H_B}{[z(H_A,H_B)]^{1/2}} \quad (11)$$

where $z(H_A,H_B)$ is given in eq 7.

We now proceed to calculate various interesting thermodynamic quantities characterizing the copolymer chains. It is easily shown that the chain end densities, ϕ_{eA} and ϕ_{eB}, and bond densities, ϕ_A, ϕ_B, and ϕ_{AB}, are given in the thermodynamic limit $N \to \infty$ by

$$\phi_{eA} = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_p}{\partial \ln \eta_A}\right) = \lim_{N\to\infty}\left(\frac{1}{N}\eta_A\frac{\partial}{\partial\eta_A}(\ln Z_0 - N\ln z)\right) = K_AH_A^2\epsilon_A + K_BH_A^2\epsilon_B + JH_A^2\epsilon_{AB} + \left(H_A + \frac{H_A^3}{2}\right)m_A + \frac{1}{2}H_A^2H_Bm_B - H_A^2 \quad (12)$$

$$\phi_{eB} = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_p}{\partial \ln \eta_B}\right) = \lim_{N\to\infty}\left(\frac{1}{N}\eta_B\frac{\partial}{\partial\eta_B}(\ln Z_0 - N\ln z)\right) = K_AH_B^2\epsilon_A + K_BH_B^2\epsilon_B + JH_B^2\epsilon_{AB} + \left(H_B + \frac{H_B^3}{2}\right)m_B + \frac{1}{2}H_B^2H_Am_A - H_B^2 \quad (13)$$

$$\phi_A = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_p}{\partial \ln \kappa_A}\right) = \lim_{N\to\infty}\left(\frac{1}{N}z\kappa_A\frac{\partial \ln Z_0}{\partial K_A}\right) = K_A\epsilon_A \quad (14)$$

$$\phi_B = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_p}{\partial \ln \kappa_B}\right) = \lim_{N\to\infty}\left(\frac{1}{N}z\kappa_B\frac{\partial \ln Z_0}{\partial K_B}\right) = K_B\epsilon_B \quad (15)$$

$$\phi_{AB} = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_p}{\partial \ln \gamma}\right) = \lim_{N\to\infty}\left(\frac{1}{N}z\gamma\frac{\partial \ln Z_0}{\partial J}\right) = J\epsilon_{AB} \quad (16)$$

where

$$m_A = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_0}{\partial H_A}\right), \quad m_B = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_0}{\partial H_B}\right)$$

$$\epsilon_A = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_0}{\partial K_A}\right), \quad \epsilon_B = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_0}{\partial K_B}\right),$$

$$\epsilon_{AB} = \lim_{N\to\infty}\left(\frac{1}{N}\frac{\partial \ln Z_0}{\partial J}\right) \quad (17)$$

Here m_A and m_B are the magnetizations of σ and τ spins per site, respectively, and ϵ_A, ϵ_B, and ϵ_{AB} denote the interaction energies between $\sigma-\sigma$, $\tau-\tau$, and $\sigma-\tau$ spins, respectively. From the above five densities, other interesting quantities can also be calculated as follows:

$$\phi_p = \frac{1}{2}(\phi_{eA} + \phi_{eB}) \quad (18)$$

$$\phi_{sA} = \frac{1}{2}(\phi_{eA} + \phi_{AB}), \quad \phi_{sB} = \frac{1}{2}(\phi_{eB} + \phi_{AB}) \quad (19)$$

$$\langle L_A\rangle = \frac{2\phi_A}{\phi_{eA} + \phi_{AB}}, \quad \langle L_B\rangle = \frac{2\phi_B}{\phi_{eB} + \phi_{AB}} \quad (20)$$

$$\langle N_s\rangle = \frac{\phi_{sA} + \phi_{sB}}{\phi_p} = 1 + \frac{\phi_{AB}}{\phi_p} \quad (21)$$

Here ϕ_p denotes the number density of copolymer chains, $\langle L_A\rangle$ and $\langle L_B\rangle$ denote the average lengths of A- and B-blocks, respectively, ϕ_{sA} and ϕ_{sB} denote the number densities of A- and B-blocks, respectively, and $\langle N_s\rangle$ is the average number of segments per copolymer chain.

III. Mean-Field Approximation and Phase Diagrams

Let $\vec{m}_{n,A}$ and $\vec{m}_{n,B}$ be the average magnetizations of $\vec{\sigma}_i$ spins and $\vec{\tau}_i$ spins, respectively, and $\vec{\xi}_{i,A}$ and $\vec{\xi}_{i,B}$ be the fluctuations from $\vec{m}_{n,A}$ and $\vec{m}_{n,B}$, respectively. Then, following Gujrati,[23] we can rewrite the Hamiltonian $\mathscr{H}_n$ in the following way:

$$\mathscr{H}_n = \sum_{\langle ij\rangle}(\vec{\xi}_{i,A}\cdot\vec{\xi}_{j,A} + \vec{\xi}_{i,B}\cdot\vec{\xi}_{j,B} + \vec{\xi}_{i,A}\cdot\vec{\xi}_{j,B}) - Nf_n + \sum_i(\vec{\sigma}_i\cdot\vec{x}_n + \vec{\tau}_i\cdot\vec{y}_n) \quad (22)$$

where

$$f_n = \frac{q}{2}(K_A\vec{m}^2_{n,A} + K_B\vec{m}^2_{n,B} + J\vec{m}_{n,A}\cdot\vec{m}_{n,B})$$

$$\vec{x}_n = qK_A\vec{m}_{n,A} + \frac{q}{2}J\vec{m}_{n,B} + \vec{H}_A$$

$$\vec{y}_n = qK_B\vec{m}_{n,B} + \frac{q}{2}J\vec{m}_{n,A} + \vec{H}_B$$

and q is the coordination number of the lattice. Because of the presence of the magnetic fields, the only nonvanishing components of $\vec{\sigma}_i$ and $\vec{\tau}_i$ spins are in the directions of the applied fields. Thus, in the following the scalar notations instead of the vector ones will be used. We will take $m_{n,\mathrm{A}}$ and $m_{n,\mathrm{B}}$ to be nonnegative in the following. This amounts to choosing H_A and H_B nonnegative.

In the mean-field approximation,[23] we neglect the first term of eq 22. Then, all the correlations between sites i and j are thrown away and the calculation becomes straightforward since each spin can be treated as noninteracting. The free energy per site ω_n, equal to $(\ln Z_n)/N$ in the thermodynamic limit $N \to \infty$, is given by

$$\omega_n = -f_n + \ln D_n$$

where

$$D_n = \frac{\cosh[(2n)^{1/2}x_n] + \cosh[(2n)^{1/2}y_n] + 2(n-1)}{2n} \tag{23}$$

Note that our free energy ω_n differs by a factor of $-k_\mathrm{B}T$ compared to the conventional free energy F_n: $\omega_n = -F_n/k_\mathrm{B}T$. Therefore, we maximize ω_n, which is equivalent to minimizing F_n. Maximizing ω_n with respect to both $m_{n,\mathrm{A}}$ and $m_{n,\mathrm{B}}$, we find that $m_{n,\mathrm{A}}$ and $m_{n,\mathrm{B}}$ are given by

$$m_{n,\mathrm{A}} = \frac{\sinh[(2n)^{1/2}x_n]}{(2n)^{1/2}D_n}, \qquad m_{n,\mathrm{B}} = \frac{\sinh[(2n)^{1/2}y_n]}{(2n)^{1/2}D_n} \tag{24}$$

In the $n \to 0$ limit these equations become

$$m_\mathrm{A} \equiv m_{0,\mathrm{A}} = \frac{x}{1 + \frac{1}{2}x^2 + \frac{1}{2}y^2}, \qquad m_\mathrm{B} \equiv m_{0,\mathrm{B}} = \frac{y}{1 + \frac{1}{2}x^2 + \frac{1}{2}y^2} \tag{25}$$

and the free energy ω_0 is given by

$$\omega_0 = -\frac{q}{2}(K_\mathrm{A}m_\mathrm{A}^2 + K_\mathrm{B}m_\mathrm{B}^2 + Jm_\mathrm{A}m_\mathrm{B}) + \ln\left(1 + \frac{1}{2}x^2 + \frac{1}{2}y^2\right) \tag{26}$$

where $x = \lim_{n\to 0} x_n$ and $y = \lim_{n\to 0} y_n$. Therefore, in the mean-field approximation various energies per site defined in eq 17 are given by

$$\epsilon_\mathrm{A} = \frac{\partial\omega_0}{\partial K_\mathrm{A}} = \frac{q}{2}m_\mathrm{A}^2, \qquad \epsilon_\mathrm{B} = \frac{\partial\omega_0}{\partial K_\mathrm{B}} = \frac{q}{2}m_\mathrm{B}^2, \qquad \epsilon_\mathrm{AB} = \frac{\partial\omega_0}{\partial J} = \frac{q}{2}m_\mathrm{A}m_\mathrm{B} \tag{27}$$

Using eqs 25 and 27, all independent densities can be calculated as follows:

$$\phi_\mathrm{A} = \frac{q}{2}K_\mathrm{A}m_\mathrm{A}^2, \qquad \phi_\mathrm{B} = \frac{q}{2}K_\mathrm{B}m_\mathrm{B}^2, \qquad \phi_\mathrm{AB} = \frac{q}{2}Jm_\mathrm{A}m_\mathrm{B}$$

$$\phi_\mathrm{eA} = \frac{H_\mathrm{A}^2}{2}(qK_\mathrm{A}m_\mathrm{A}^2 + qK_\mathrm{B}m_\mathrm{B}^2 + qJm_\mathrm{A}m_\mathrm{B} + H_\mathrm{A}m_\mathrm{A} + H_\mathrm{B}m_\mathrm{B} - 2) + H_\mathrm{A}m_\mathrm{A}$$

$$\phi_\mathrm{eB} = \frac{H_\mathrm{B}^2}{2}(qK_\mathrm{A}m_\mathrm{A}^2 + qK_\mathrm{B}m_\mathrm{B}^2 + qJm_\mathrm{A}m_\mathrm{B} + H_\mathrm{A}m_\mathrm{A} + H_\mathrm{B}m_\mathrm{B} - 2) + H_\mathrm{B}m_\mathrm{B} \tag{28}$$

Magnetic fields H_A and H_B control the number of copolymer chains, and coupling constants K_A, K_B, and J determine the bond densities of each type. When $J = 0$, for example, there are no A–B bonds, and thus only blends of two different homopolymers exist. When magnetic fields are very small, we have only a few chains; see eqs 12 and 13. Furthermore, if the values of coupling constants are also small, there exist only a few chains of small lengths. This phase, called the unpolymerized or dilute phase, has zero bond densities in the thermodynamic limit as the magnetic fields become zero. However, as the values of the coupling constants increase, there appear critical values, above which at least one of the bond densities becomes nonzero even if the magnetic fields are zero. These phases of nonzero bond densities are called polymerized or dense phases of homopolymers if $J = 0$ or copolymers if J is nonzero.

The analysis of the solutions of these two coupled equations (eq 25) reveals various phase diagrams. Here three cases will be examined according to the values of H_A, H_B, and J.

(a) Phase Diagram When $H_\mathrm{A} = H_\mathrm{B} = J = 0$. Let us define $k_\mathrm{A} = qK_\mathrm{A}$, $k_\mathrm{B} = qK_\mathrm{B}$, and $j = qJ$. Substituting $x = k_\mathrm{A}m_\mathrm{A}$ and $y = k_\mathrm{B}m_\mathrm{B}$ into eq 25 yields

$$m_\mathrm{A}(k_\mathrm{A}^2m_\mathrm{A}^2 + k_\mathrm{B}^2m_\mathrm{B}^2 + 2 - 2k_\mathrm{A}) = 0$$

$$m_\mathrm{B}(k_\mathrm{A}^2m_\mathrm{A}^2 + k_\mathrm{B}^2m_\mathrm{B}^2 + 2 - 2k_\mathrm{B}) = 0$$

It is easily seen that there are four different sets of solutions according to the values of k_A and k_B as follows:

(i) $m_\mathrm{A} = m_\mathrm{B} = 0$ when $k_\mathrm{A} \le 1$ and $k_\mathrm{B} \le 1$

(ii) $m_\mathrm{A} = 0$, $m_\mathrm{B} = \dfrac{[2(k_\mathrm{B} - 1)]^{1/2}}{k_\mathrm{B}}$ when $k_\mathrm{B} > k_\mathrm{A}$ and $k_\mathrm{B} > 1$

(iii) $m_\mathrm{A} = \dfrac{[2(k_\mathrm{A} - 1)]^{1/2}}{k_\mathrm{A}}$, $m_\mathrm{B} = 0$ when $k_\mathrm{A} > k_\mathrm{B}$ and $k_\mathrm{A} > 1$

(iv) $m_\mathrm{A} = m_\mathrm{B} = \dfrac{[2(k - 1)]^{1/2}}{k}$ when $k_\mathrm{A} = k_\mathrm{B} = k$ and $k > 1$

The resulting phase diagram is shown in Figure 3a. As seen in Figure 3a, there exist three different phases: (i) unpolymerized phase (dilute phase), where $m_\mathrm{A} = m_\mathrm{B} = 0$, (ii) homopolymerized B phase (dense B phase), where $m_\mathrm{A} = 0$ and $m_\mathrm{B} > 0$, and (iii) homopolymerized A phase (dense A phase), where $m_\mathrm{A} > 0$ and $m_\mathrm{B} = 0$. Here it should be noted that $\phi_\mathrm{A} = k_\mathrm{A}m_\mathrm{A}^2/2$, $\phi_\mathrm{B} = k_\mathrm{B}m_\mathrm{B}^2/2$, and $\phi_\mathrm{AB} = jm_\mathrm{A}m_\mathrm{B}/2$ (see eq 28). There is, of course, no copolymerized phase when $j = 0$. When $k_\mathrm{A} = k_\mathrm{B} = k$ and $k > 1$, there occur first-order phase transitions between two different homopolymer phases. One example of these transitions is shown in Figure 4a, where the bond density ϕ_A jumps from zero to a finite value as soon as k_A becomes larger than k_B. Note that this

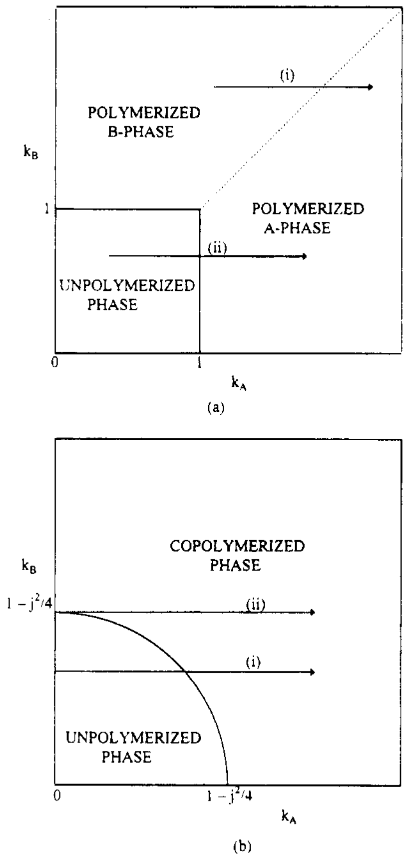

Figure 3. Phase diagrams: (a) when $H_A = H_B = j = 0$; (b) when $H_A = H_B = 0$ and $0 < j < 2$.

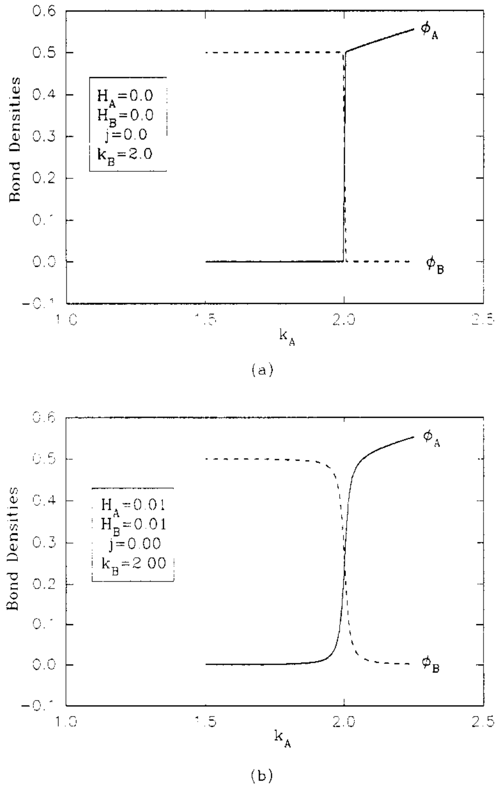

Figure 4. (a) First-order phase transition between two homopolymerized phases along the trajectory (i) in Figure 3a. (b) First-order phase transition disappears when magnetic fields become nonzero.

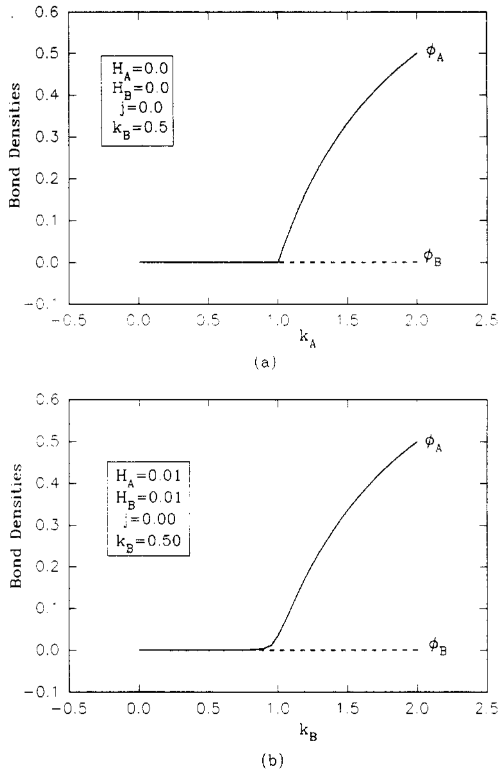

Figure 5. (a) Continuous phase transition occurs between unpolymerized and polymerized phases along the trajectory (ii) shown in Figure 3a. (b) No phase transition occurs when magnetic fields are nonzero.

discontinuity disappears, as seen in Figure 4b, when the magnetic fields become nonzero. Otherwise, there exist continuous phase transitions between the unpolymerized phase and the polymerized A or B phases, one example of which is shown in Figure 5a. When the magnetic fields become nonzero, the continuous phase transition disappears as shown in Figure 5b.

(b) Phase Diagram When $H_A = H_B = 0$ and $J \neq 0$. Let $m_A/m_B = x/y = r$. Solving eq 25 gives

$$\frac{1}{2}jr^2 + (k_B - k_A)r - \frac{1}{2}j = 0$$

whose solution is given by

$$r = \frac{k_A - k_B}{j} + \left[1 + \left(\frac{k_A - k_B}{j}\right)^2\right]^{1/2}$$

since $r \geq 0$. Substituting $x = ry$ and eq 25 into $y = jm_A/2 + k_B m_B$ yields

$$y[(r^2 + 1)y^2 - (jr + 2k_B - 2)] = 0$$

Therefore, we have two different sets of solutions:

(i) $x = y = 0$

(ii) $x = ry$ and $y = \left[\frac{jr + 2(k_B - 1)}{r^2 + 1}\right]^{1/2}$

It can be easily shown that $m_A = m_B = 0$ is the only solution when $jr + 2(k_B - 1) \leq 0$. Thus, we have the following condition for the copolymerized phases (dense phases):

$$k_A + k_B \geq 2 - [j^2 + (k_A - k_B)^2]^{1/2} \qquad (29)$$

Figure 3b shows the phase diagram when both magnetic

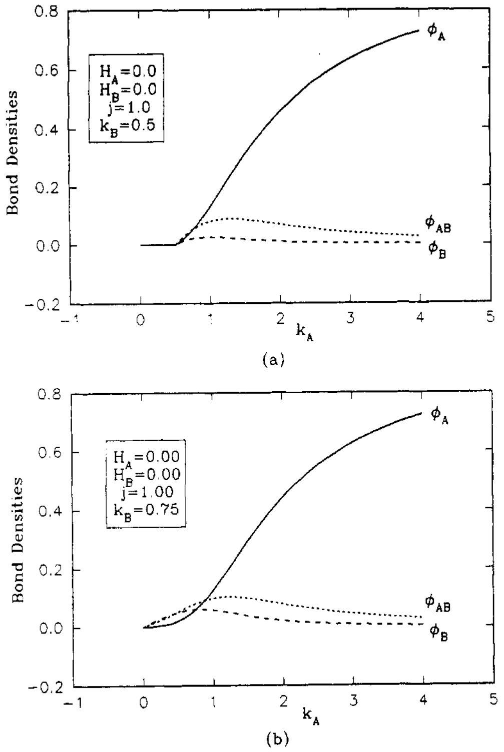

Figure 6. (a) Continuous phase transition occurs between unpolymerized and copolymerized phases along the trajectory (i) in Figure 3b. (b) No phase transition occurs along the trajectory (ii) in Figure 3b.

fields are zero and j is nonzero. It should be noted that only the copolymerized phase exists when $j \geq 2$, since the condition (29) is always satisfied. Figure 6 shows a continuous phase transition between the unpolymerized and copolymerized phases when $H_A = H_B = 0$ and $j = 1$.

(c) Phase Diagram When One of the Magnetic Fields and *J* Are Zero. Let us consider the case when $H_B = j = 0$ and $H_A > 0$. Substituting $x = k_A m_A + H_A$ and $y = k_B m_B$ into eq 25 and solving the resulting equations gives two kinds of solutions as follows:

(i) $m_A > 0$ and $m_B = 0$ when $k_B \leq k_A$

(ii) $m_A = \dfrac{H_A}{k_B - k_A}$ and $m_B = 0$ or $[2(k_B - 1)k_A^2 + 4k_B(1 - k_B)k_A + (2k_B - 2 - H_A^2)k_B^2]^{1/2}/[k_B(k_B - k_A)]$ when $k_B > k_A$

Further analysis of the expression inside the square root of m_B in solution (ii) shows that the critical line when $H_B = j = 0$ is given by

$$k_{A,C} = k_B\left[1 - \frac{H_A}{[2(k_B - 1)]^{1/2}}\right] \quad \text{and} \quad k_B \geq 1 + \frac{H_A^2}{2} \qquad (30)$$

and is shown in Figure 7. The continuous phase transition between the unpolymerized B phase and the polymerized B phase through this critical line is shown in Figure 8. Due to the presence of the magnetic field H_A, m_A is always larger than zero even if $k_A = 0$. It is also easily seen that there is no phase transition when both magnetic fields are nonzero because the magnetizations m_A and m_B are always nonzero. The same situation occurs when one of the magnetic fields is zero and j nonzero.

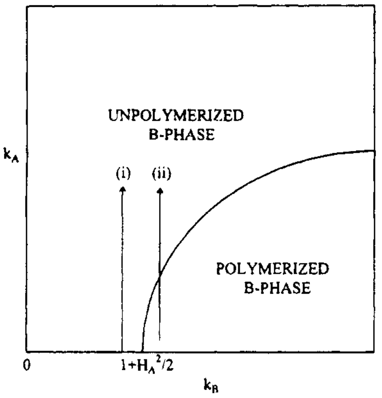

Figure 7. Schematic phase diagram when $j = 0$ and one of the magnetic fields (in this case H_B) is zero.

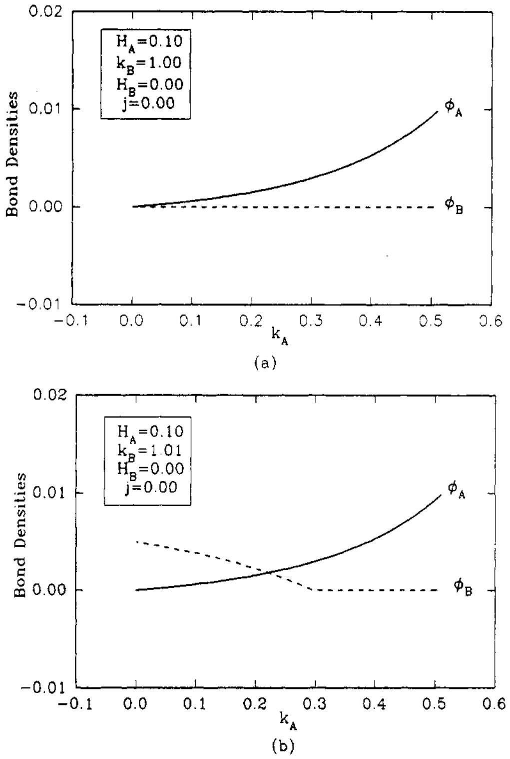

Figure 8. (a) No phase transition occurs along the trajectory (i) in Figure 7. (b) Continuous phase transition occurs between unpolymerized B phase and polymerized B phase along the trajectory (ii) in Figure 7.

IV. Entropy of Copolymers in an Athermal Solution

In the mean-field approximation the free energy per site of the magnetic system in the $n \to 0$ limit is obtained as eq 26. The entropy per site S of copolymer chains in an athermal solution can be calculated by using the Legendre transformation:

$$S = \omega_0 - \phi_0 \ln z - \phi_A \ln K_A - \phi_B \ln K_B - \phi_{AB} \ln J - \phi_{eA} \ln H_A - \phi_{eB} \ln H_B \qquad (31)$$

The derivation of eq 31 is straightforward. From eq 10, we note that

$$\omega_0 = \ln z + \omega_p$$

where ω_p is the free energy per site of the polymer system. From eq 9, we observe that

$$\omega_{\mathrm{p}} = S + \phi_{\mathrm{A}} \ln \kappa_{\mathrm{A}} + \phi_{\mathrm{B}} \ln \kappa_{\mathrm{B}} + \phi_{\mathrm{AB}} \ln \gamma + \phi_{\mathrm{eA}} \ln \eta_{\mathrm{A}} + \phi_{\mathrm{eB}} \ln \eta_{\mathrm{B}}$$

Using eq 11 in this equation yields eq 31. After some tedious algebra, the coupling constants and the magnetic fields can be expressed in terms of densities, and the final expression for the entropy is given by

$$S = (\phi_{\mathrm{A}} + \phi_{\mathrm{B}} + \phi_{\mathrm{AB}}) \ln(q/e) + \phi_{\mathrm{p}} \ln 2 - \phi_0 \ln \phi_0 - \phi_{\mathrm{A}} \ln \phi_{\mathrm{A}} - \phi_{\mathrm{B}} \ln \phi_{\mathrm{B}} - \phi_{\mathrm{AB}} \ln \phi_{\mathrm{AB}} - \phi_{\mathrm{eA}} \ln \phi_{\mathrm{eA}} - \phi_{\mathrm{eB}} \ln \phi_{\mathrm{eB}} - (\phi_{\mathrm{mA}} - \phi_{\mathrm{eA}}) \ln(\phi_{\mathrm{mA}} - \phi_{\mathrm{eA}}) - (\phi_{\mathrm{mB}} - \phi_{\mathrm{eB}}) \ln(\phi_{\mathrm{mB}} - \phi_{\mathrm{eB}}) + 2(\phi_{\mathrm{A}} + \phi_{\mathrm{AB}}/2) \ln(\phi_{\mathrm{A}} + \phi_{\mathrm{AB}}/2) + 2(\phi_{\mathrm{B}} + \phi_{\mathrm{AB}}/2) \ln(\phi_{\mathrm{B}} + \phi_{\mathrm{AB}}/2) \quad (32)$$

where

$$\phi_{\mathrm{mA}} = \phi_{\mathrm{A}} + \frac{1}{2}(\phi_{\mathrm{eA}} + \phi_{\mathrm{AB}}), \quad \phi_{\mathrm{mB}} = \phi_{\mathrm{B}} + \frac{1}{2}(\phi_{\mathrm{eB}} + \phi_{\mathrm{AB}}), \quad \phi_0 = 1 - (\phi_{\mathrm{mA}} + \phi_{\mathrm{mB}})$$

Here ϕ_{mA} and ϕ_{mB} are the A-monomer density and the B-monomer density, respectively, and ϕ_0 is the solvent density. When $H_{\mathrm{A}} = H_{\mathrm{B}} = 0$, $\phi_{\mathrm{eA}} = \phi_{\mathrm{eB}} = 0$. For nonzero ϕ_{A} and ϕ_{B}, we must have a copolymer chain of an infinite molecular weight in the system. In this case, the entropy is expressed as follows:

$$S_\infty = (\phi_{\mathrm{A}} + \phi_{\mathrm{B}} + \phi_{\mathrm{AB}}) \ln(q/e) - \phi_0 \ln \phi_0 - \phi_{\mathrm{A}} \ln \phi_{\mathrm{A}} - \phi_{\mathrm{B}} \ln \phi_{\mathrm{B}} - \phi_{\mathrm{AB}} \ln \phi_{\mathrm{AB}} + \phi_{\mathrm{mA}} \ln \phi_{\mathrm{mA}} + \phi_{\mathrm{mB}} \ln \phi_{\mathrm{mB}} \quad (33)$$

By subtracting the contribution from the disorientation of copolymer chains in the melt state ($\phi_0 = 0$), the entropy of mixing can also be obtained by

$$\Delta S = S - \phi_{\mathrm{m}} S\left(\frac{\phi_{\mathrm{A}}}{\phi_{\mathrm{m}}}, \frac{\phi_{\mathrm{B}}}{\phi_{\mathrm{m}}}, \frac{\phi_{\mathrm{AB}}}{\phi_{\mathrm{m}}}, \frac{\phi_{\mathrm{eA}}}{\phi_{\mathrm{m}}}, \frac{\phi_{\mathrm{eB}}}{\phi_{\mathrm{m}}}\right) = -\phi_0 \ln \phi_0 - \frac{\phi_{\mathrm{m}}}{M} \ln \phi_{\mathrm{m}} \quad (34)$$

where $M = \phi_{\mathrm{m}}/\phi_{\mathrm{p}}$ is the number-average molecular weight of the copolymer chains and $\phi_{\mathrm{m}} = \phi_{\mathrm{mA}} + \phi_{\mathrm{mB}}$ is the total monomer density. This expression is the same as the Flory expression for the entropy of mixing of homopolymer solutions.[21] From this it is evident that the important factors determining the entropy of mixing in athermal solutions are not the composition of the copolymer chains but (i) the solvent volume fraction and (ii) the average molecular weight of the polymer chains at the level of Flory-like mean-field approximation.

V. Conclusion

It has been shown that a general model of athermal random copolymers in an equilibrium state is related to an $n \to 0$ spin vector model, with each spin having $2n$ components. Our correspondence is not only exact but also more general compared to the result obtained by Kennedy and Wheeler.[19] The most important use of the model lies in that it allows us to describe the general aspects of equilibrium copolymerizations in the case when all monomers have been incorporated into the copolymer chains. Although not treated here, our model can be easily extended to describe the equilibrium systems where the monomers and the copolymer coexist.

The model has been solved in a mean-field approximation to study the phase diagram and to calculate the entropy of copolymers in an athermal solution. When $j = 0$ (homopolymers only), both the first-order and continuous phase transitions can occur in the absence of any external magnetic fields: The first-order phase transitions can occur only between two different homopolymerized phases, and only continuous phase transitions occur between the unpolymerized and polymerized phases. When j is nonzero, the first-order phase transitions cannot occur due to the presence of A−B bonds. When $0 < j < 2$, we have only continuous transitions provided both magnetic fields are zero. In other words, polymers must be infinitely large for transitions to occur. The transitions disappear as soon as one of the magnetic fields becomes nonzero. We have also obtained the expression for the entropy of the athermal copolymer solution by using the Legendre transformation of the magnetic free energy in the $n \to 0$ limit. As expected, the entropy of mixing does not depend upon the average composition of copolymer chains and is identical to the Flory expression for the homopolymer solutions except that in our case M is the number-average molecular weight.

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