

Phase diagram of random copolymers

C. D. Sfatos, A. M. Gutin, and E. I. Shakhnovich*

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

(Received 29 December 1992)

A two-letter random copolymer with attraction between similar monomers and repulsion between different ones is investigated using the replica method. This type of interaction favors microphase separation in a compact state of a polymer or in a melt. Frustrations between interactions and polymeric bonds may lead to a freezing transition in a phase where only a few conformations dominate and replica symmetry is broken. Our analysis reveals that stiff polymers have a frozen phase and do not undergo transitions to a phase with a microdomain structure. In flexible polymers, the microphase transition may occur before freezing. Then a new frozen phase with microdomain structure is found and studied. A complete phase diagram is constructed for the two-letter random copolymer.

PACS number(s): 61.41.+e, 87.15.Da, 64.60.Cn, 64.60.Kw

I. INTRODUCTION

In recent years the problem of random copolymers has attracted considerable attention [1]. Theoretical research was motivated by the highly unusual behavior of proteins. The key question in the protein research remains how a unique frozen conformation is encoded in the one-dimensional sequence of amino acids in the chain and how this conformation is reached in the folding process [2]. The first step to address this problem is to study the random heteropolymers and compare them with proteins to see which features come from general properties of polymeric structure and heterogeneity and which ones are due to evolutionary selection.

The simplest model to investigate the properties of polymeric structure and heterogeneity has been described by a Hamiltonian that contains a random quenched set of interaction potentials B_{ij} for monomers i, j which are in contact. In the spirit of the Sherrington-Kirkpatrick (SK) model [3] the B_{ij} interactions were taken as independent random values [4–6]. This model will be referred to as the *independent-interaction model*.

The independent-interaction model was solved and a frozen phase with replica symmetry breaking (RSB) was obtained [5,6]. In this frozen phase only a few conformations dominate. It was found [7] that for a significant fraction of random sequences only one conformation is populated in the frozen phase. This phase can then describe the protein native structure. In three dimensions the solution gave a one-step RSB. This means that the random-energy model (REM) of Derrida [8] is a good approximation for heteropolymers in three dimensions. This result justifies other approaches to the heteropolymer problem based on the REM [9].

The heteropolymer model is effectively infinite-ranged since it allows interactions between all possible pairs of monomers without restrictions with respect to the position of these monomers along the polymer chain. The infinite-range SK model probably is not appropriate for

the description of real spin glasses since the positions of the interacting sites are fixed on a lattice. Therefore, interactions between neighbors are intuitively much more important than long-range interactions. The polymer problem is fundamentally different from the spin-glass problem. In polymers the monomers are free to move in space as the polymer goes from the one configuration to the other. Hence, the strength of interactions between monomers is independent of their distance along the chain but depends only on the kind of the interacting monomers. Therefore, the infinite-range nature of the independent-interaction model is physically meaningful for the study of heteropolymers.

The heteropolymer problem, however, should be described by a random sequence [10], i.e., a set of random values $\{\sigma_i\}$ characteristic for each monomer. This model will be referred to as the *sequence model*. In this model the interaction potentials B_{ij} are correlated. The sequence model seems to be more realistic for the description of a real heteropolymer which consists of a random sequence of monomers. In the case of a “two-letter” random copolymer [11–15], the sequence model is the only one that can be used to describe the problem. In this model the random values $\{\sigma_i\}$ take only the values ± 1 . In the two-letter model, when similar kinds of monomers attract each other and different ones repel each other there is an energetic preference for separation between monomers of different kinds.

It was previously suggested [10] that the two-letter sequence model is not frustrated in analogy with the Mattis model of spin glasses [16]. This suggestion misses the importance of the polymeric effect. The two-letter sequence model is frustrated due to competition between the tendency for phase separation and the polymeric bonds. In polymers the thermodynamic variable is the position of monomers. Due to the polymeric effect the position of a monomer is not independent from the position of its neighbors. In a random sequence, if a monomer of kind A is placed inside an A -rich region it will bring along some monomers of kind B . Then some unfavorable A - B

contacts appear. This frustration is very important and as we will see in the present work it gives rise to a freezing transition with RSB.

Until recently such a frozen state had not been predicted. Only very weak microphase separation (MPS) was predicted without RSB [11]. On the level of mean-field theory, the MPS transition was found to be third order. A later discussion of fluctuations predicted a first-order transition [17]. The same approach was applied to the case of sequences with small correlations along the contour and similar mesophases were predicted [18–20]. However, another calculation [12] predicted RSB in a two-letter random copolymer in low dimensions using high-temperature expansion.

Recently we have performed a mean-field calculation where frozen states were predicted as a result of the frustration in the two-letter-code model [21]. The predicted RSB scheme was the same as in the previous solution of the independent-interaction model. On the level of mean field it was shown that when freezing occurs the MPS transition is prevented at any lower temperature.

In the present work we investigate the effect of contacts between neighboring monomers which become significant in flexible chains. We show that this effect can reduce the freezing temperature below the MPS transition temperature. Therefore, MPS can occur before freezing. In that case the frozen phase that appears at a lower temperature also has microdomain structure.

In Secs. II and III we present the solution of the sequence model and the resulting frozen phase. In Sec. III we also show how freezing prevents MPS. In Sec. IV we introduce a novel treatment of fluctuations of the order parameter that describes freezing and we demonstrate how an increase in flexibility can reduce the freezing temperature below the MPS transition temperature. In Sec. V we describe the MPS transition occurring before freezing and in Sec. VI we present the complete phase diagram and discuss the results obtained.

II. THE MODEL AND DEFINITION OF THE ORDER PARAMETERS

The random AB -type copolymer is described by a Hamiltonian that takes into account the self-interactions between monomers as

$$\mathcal{H} = \frac{1}{2} \sum_{i,j} B_{ij} U(\mathbf{r}_i - \mathbf{r}_j), \quad (2.1)$$

where the conformation of the polymer is described by the coordinates of its monomers $\{\mathbf{r}_i\}$ and $U(\mathbf{r}_i - \mathbf{r}_j)$ is a short-range potential. The binary interaction virial coefficient is [13]

$$B_{ij} = 2[B_0 + A(\sigma_i + \sigma_j) + \chi\sigma_i\sigma_j]. \quad (2.2)$$

The sequence of monomers is described by a quenched set of random values $\{\sigma_i\}$ with equal probabilities for the two types of monomers $\sigma_i = 1$ if monomer i is of type A and $\sigma_i = -1$ if it is of type B . When the interactions between similar monomers are equal ($B_{AA} = B_{BB}$) then $A = 0$. The composite Flory parameter $\chi = (B_{AA} + B_{BB})/2 - B_{AB}$ will be negative in the case of interest where similar monomers attract each other.

In order to average over quenched disorder we use the replica trick which requires averaging the n th power of the partition function. We need to include the elastic term $g(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha)$ for replica α

$$g(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha) = \frac{1}{(2\pi a^2)^{3/2}} \exp\left[-\frac{(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha)^2}{2a^2}\right]. \quad (2.3)$$

Then the n -replica partition function is

$$\langle Z^n \rangle_{\text{av}} = \left\langle \int \mathcal{D}\mathbf{r}_j^\alpha g(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha) \exp\left(-\frac{B_0}{T} \sum_{i,j} U_{ij}^\alpha\right) \exp\left[-\sum_{\alpha} \sum_{i,j} \frac{\chi}{T} \sigma_i U(\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha) \sigma_j\right] \right\rangle_{\text{av}}, \quad (2.4)$$

where $\langle \rangle_{\text{av}}$ denotes an average over different sequences and $U_{ij}^\alpha = U(\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)$ with \mathbf{r}_i^α the position of the i th monomer in replica α . We can rewrite Eq. (2.4) as

$$\left\langle \int \mathcal{D}\mathbf{r}_j^\alpha g(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha) \exp\left(-\frac{B_0}{T} \sum_{i,j} U_{ij}^\alpha\right) \exp\left[b \sum_{\alpha} \int d\mathbf{R}_1 d\mathbf{R}_2 \sum_i \sigma_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) U(\mathbf{R}_1 - \mathbf{R}_2) \sum_j \sigma_j \delta(\mathbf{r}_j^\alpha - \mathbf{R}_2)\right] \right\rangle_{\text{av}} \quad (2.5)$$

with $b = -\chi/T$ to be positive in the case of interest, although this approach can be generalized to either sign of b .

By performing a Hubbard-Stratonovich transformation of the variable

$$\sum_i \sigma_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}),$$

the second exponential of Eq. (2.5) can be rewritten as

$$\int \mathcal{D}\Psi_\alpha(\mathbf{R}) \exp\left[-\frac{1}{4b} \sum_{\alpha} \int d\mathbf{R}_1 d\mathbf{R}_2 \Psi_\alpha(\mathbf{R}_1) \Psi_\alpha(\mathbf{R}_2) U^{-1}(\mathbf{R}_1 - \mathbf{R}_2) + \sum_{\alpha} \int d\mathbf{R} \Psi_\alpha(\mathbf{R}) \sum_i \sigma_i \delta(\mathbf{r}_i^\alpha - \mathbf{R})\right]. \quad (2.6)$$

Then we average over disorder. Instead of ± 1 we can consider a Gaussian distribution of σ_i 's as $\exp[-\sigma_i^2/2\tilde{\mu}^2]$. This corresponds to the fact that the interactions between different sites of the chain are not on the level of one monomer. Instead, parts of the chain interact due to the finite stiffness of the chain. Therefore, a coarse-grained field $\{\sigma_i\}$ with Gaussian distribution of the continuous variables σ_i can replace the discrete ± 1 values. However, this does not change the generality of our approach as it will be discussed later. Also, by taking Gaussian distribution we generalize this method for random sequences with more than two kinds of monomers.

After the disorder average we set

$$\Phi_\alpha(\mathbf{R}_2) = \frac{1}{2b} \int d\mathbf{R}_1 U^{-1}(\mathbf{R}_1 - \mathbf{R}_2) \Psi_\alpha(\mathbf{R}_1) \quad (2.7)$$

and obtain for the n -replica partition function

$$\left\langle \int \mathcal{D}\Phi_\alpha(\mathbf{R}) \exp \left[-\frac{B_0}{T} \sum_\alpha \int d\mathbf{R} \rho_\alpha^2(\mathbf{R}) \right] \right. \\ \times \exp \left[-b \sum_\alpha \int d\mathbf{R}_1 d\mathbf{R}_2 \Phi_\alpha(\mathbf{R}_1) \Phi_\alpha(\mathbf{R}_2) U(\mathbf{R}_1 - \mathbf{R}_2) \right. \\ \left. \left. + \mu^2 b^2 \sum_i \sum_{\alpha, \beta} \int d\mathbf{R}_1 d\mathbf{R}'_1 \Phi_\alpha(\mathbf{R}'_1) U(\mathbf{R}_1 - \mathbf{R}'_1) \int d\mathbf{R}_2 d\mathbf{R}'_2 \Phi_\beta(\mathbf{R}'_2) U(\mathbf{R}_2 - \mathbf{R}'_2) \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) \delta(\mathbf{r}_i^\beta - \mathbf{R}_2) \right] \right\rangle_{\text{th}}, \quad (2.8)$$

where $\langle \rangle_{\text{th}}$ represents a thermal average over all configurations of all replicas and includes multiplication by the elastic term $g(\mathbf{r}_{j+1}^\alpha - \mathbf{r}_j^\alpha)$. We also define $\mu = 2\tilde{\mu}$ and $\rho_\alpha(\mathbf{R}) = \sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R})$ the density of the system.

In addition to the B_0 attraction term there is a three-body repulsion that has not been explicitly included in our Hamiltonian. These two terms describe the transition to a globule [22]. We assume that the globule is maximally compact and with constant density. The transition is a purely homopolymeric effect and we will ignore these terms in what follows.

We introduce the order parameter

$$Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) = \sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) \delta(\mathbf{r}_i^\beta - \mathbf{R}_2). \quad (2.9)$$

$$\left\langle \int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_{\alpha, \beta} \sum_{\mathbf{k} \neq 0} [b\delta_{\alpha\beta} - \mu^2 b^2 Q_{\alpha\beta}(\mathbf{k})] \Phi_\alpha(\mathbf{k}) \Phi_\beta(-\mathbf{k}) \right] \right\rangle_{\text{th}}, \quad (2.11)$$

where V is the volume of the system, \mathbf{k} is the wave vector, $Q_{\alpha\beta}(\mathbf{k})$ and $\Phi(\mathbf{k})$ are the Fourier transforms of the order parameters. We consider only nonzero wave vectors because $\Phi(\mathbf{k} = 0) = 0$.

The parameter $Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2)$ represents the correlator between the conformations of two replicas. It shows the extent to which the conformation of replica α overlaps with the conformation of replica β . It is well known from the theory of the Sherrington-Kirkpatrick model that there is a correspondence between the overlap of replicas and the overlap of pure states [23]. In the case of polymers these pure states are the conformations of all possible folds.

If two folds are totally different then the corresponding $Q_{\alpha\beta}$ will be zero. In the opposite extreme, if two folds

From this definition we see that

$$\int d\mathbf{R}_1 Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) = \rho_\beta(\mathbf{R}_2). \quad (2.10)$$

Since we are considering the case of a collapsed chain of constant density throughout the globule the density must be independent of position. Therefore, Eq. (2.10) implies that $Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) = Q_{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2)$. This argument also applies to the case of an incompressible melt. With these definitions and by considering the potential $U(\mathbf{R}_1 - \mathbf{R}_2)$ as a δ function Eq. (2.8) becomes after Fourier transformation

are identical then $Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) = \rho \delta(\mathbf{R}_1 - \mathbf{R}_2)$ where ρ is the density. We can express the intermediate cases of similarity between folds by writing the order parameter in terms of a function $\varphi_{\alpha\beta}$ with unit scale [6] as

$$Q_{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2) = \frac{\rho}{R_t^3} \varphi_{\alpha\beta} \left(\frac{\mathbf{R}_1 - \mathbf{R}_2}{R_t} \right) \quad (2.12)$$

with $\int Q_{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2) d\mathbf{R}_1 d\mathbf{R}_2 = N$. This means that replicas repeat each other within some scale of fluctuations R_t as shown in Fig. 1.

We can evaluate Eq. (2.11) by switching to $Q_{\alpha\beta}$ variables. The corresponding entropy for this change of variables is

$$\ln S\{Q_{\alpha\beta}\} = \left\langle \delta \left(Q_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) - \sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) \delta(\mathbf{r}_i^\beta - \mathbf{R}_2) \right) \right\rangle_{\text{th}}. \quad (2.13)$$

According to the previous discussion this constraint corresponds to confinement of the chain within a tube of diameter R_t . The corresponding loss of entropy scales as $-1/R_t^2$. This result was obtained both from scaling arguments [24] and from rigorous calculation on the level of mean field [5,6].

We can rewrite (2.11) in terms of $Q_{\alpha\beta}$,

$$\langle Z^n \rangle_{\text{av}} = \int \mathcal{D}Q_{\alpha\beta} \exp[-E\{Q_{\alpha\beta}\} + S\{Q_{\alpha\beta}\}]. \quad (2.14)$$

The effective energy term is given by

$$E\{Q_{\alpha\beta}\} = \ln \int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_{\alpha, \beta} \sum_{\mathbf{k} \neq 0} [b\delta_{\alpha\beta} - \mu^2 b^2 Q_{\alpha\beta}(\mathbf{k})] \Phi_\alpha(\mathbf{k}) \Phi_\beta(-\mathbf{k}) \right]. \quad (2.15)$$

The energy in terms of $Q_{\alpha\beta}(\mathbf{k})$ is found by the integration of the Gaussian integral and is followed by the mean field with respect to $Q_{\alpha\beta}$. The Gaussian integral gives

$$\int d\mathbf{k} \ln[\det P_{\alpha\beta}(\mathbf{k})] \quad (2.16)$$

with $P_{\alpha\beta}(\mathbf{k}) = b\delta_{\alpha\beta} - \mu^2 b^2 Q_{\alpha\beta}(\mathbf{k})$. We notice that the result in (2.16) corresponds to the summation of the ring diagrams in the high-temperature expansion approach of Ref. [12]. This means that only the ring diagrams contribute in the Gaussian case.

The determinant of the P matrix will be evaluated explicitly by using the Parisi ansatz [25] in Sec. III. In a qualitative approach, however, we can expand the determinant and get terms of the form

$$\sum_{(\alpha, \beta, \gamma, \dots)} \tilde{b}^{n-m} \int d\mathbf{k} Q_{\alpha\beta}(\mathbf{k}) Q_{\gamma\delta}(\mathbf{k}) \dots, \quad (2.17)$$

where \tilde{b} are the diagonal elements of the P matrix, n is the number of replicas, m is the number of Q terms, and the sum is taken over all pairs of different replicas. We can easily verify that

$$Q_{\alpha\beta}(\mathbf{k}) = \rho \tilde{\varphi}_{\alpha\beta}(R_t \mathbf{k}). \quad (2.18)$$

By setting $\mathbf{k}' = R_t \mathbf{k}$ the three-dimensional \mathbf{k} integral of Eq. (2.17) can be written as

$$\frac{\rho^m}{R_t^3} \int d\mathbf{k}' \tilde{\varphi}_{\alpha\beta}(\mathbf{k}') \tilde{\varphi}_{\gamma\delta}(\mathbf{k}') \dots$$

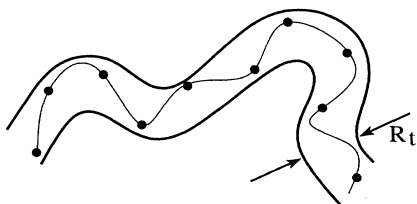


FIG. 1. A chain inside a tube corresponds to a fold defined to scale R_t .

We then see that the free energy behaves as

$$F\{R_t\} = -\frac{A_1}{R_t^2} + \frac{A_2}{R_t^3}. \quad (2.19)$$

In a mean-field theory for $n < 1$ replicas we must find the maxima of the free energy $F\{R_t\}$. From the form of Eq. (2.19) we can see (Fig. 2) that there are two such maxima at $R_t = \infty$ and at $R_t = v^{1/3}$ where v is the excluded volume.

Since the size of R_t corresponds to the degree of overlap between stable folds the existence of only two such maxima implies that the replicas should be divided into groups as follows: Replicas within each group will coincide at the microscopic scale. Replicas in different groups will have entirely different conformations. We can construct a Parisi-type hierarchical matrix for the order parameter with the form

$$Q_{\alpha\beta} = \begin{cases} \rho \delta(\mathbf{R}_1 - \mathbf{R}_2) & \text{for } \alpha, \beta \text{ in the same group} \\ 0 & \text{for } \alpha, \beta \text{ in different groups} \end{cases} \quad (2.20)$$

and carry out the calculation on the level of a mean field for $Q_{\alpha\beta}$. This is described in the next section.

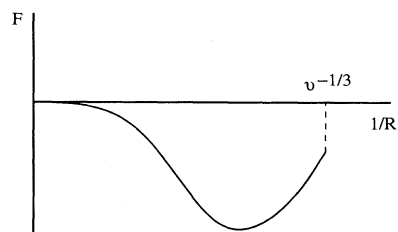


FIG. 2. Free energy of n replicas plotted vs the reciprocal scale ($1/R_t$) of the order parameter Q (for $n < 1$). The excluded volume $v^{1/3}$ is the limiting microscopic scale. Two values of R_t correspond to stable states, $R_t \rightarrow \infty$ and $R_t = v^{1/3}$. Intermediate values of R_t correspond to unstable states.

III. FREEZING TRANSITION PREVENTS MICROPHASE SEPARATION

In the preceding section we gave some qualitative arguments in order to introduce a RSB scheme for the order parameter $Q_{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2)$. According to Eq. (2.20) we have

$$Q_{\alpha\beta}(\mathbf{k}) = \begin{cases} \rho & \text{for } \alpha, \beta \text{ in the same group} \\ 0 & \text{for } \alpha, \beta \text{ in different groups} \end{cases} \quad (3.1)$$

In order to calculate Eq. (2.11) on the level of mean field with respect to $Q_{\alpha\beta}(\mathbf{k})$ we will transform to the continuous representation of the Parisi matrix [25]. If we set $M_{\alpha\beta}(\mathbf{k}) = -\mu^2 b^2 Q_{\alpha\beta}(\mathbf{k})$ for the off-diagonal elements, this matrix has eigenvalues [6,26]

$$\lambda(x) = \tilde{b} - \int_x^1 dy M(y) - xM(x), \quad (3.2)$$

where $\tilde{b} = b - \mu^2 b^2 \rho$, the diagonal elements of the matrix, and $M(x)$ is the Parisi function in the continuous representation of the hierarchical matrix in the $n \rightarrow 0$ limit. In that case

$$M(x) = \begin{cases} -\mu^2 b^2 \rho, & x > x_0 \\ 0, & x < x_0. \end{cases} \quad (3.3)$$

The parameter x_0 corresponds to the number of replicas inside one group. We can see from Eq. (3.2) that since $M(x) < 0$ and $0 < x_0 < 1$, RSB allows the eigenvalues of the $P_{\alpha\beta}$ matrix to remain positive and therefore the Gaussian integral (2.11) can be estimated. We need to calculate

$$\sum_{\mathbf{k} \neq 0} \ln[\det P_{\alpha\beta}] = \sum_{\mathbf{k} \neq 0} \sum_i g_i \ln \lambda_i$$

with λ_i the different eigenvalues and g_i the corresponding degeneracies. It can be seen from Eq. (3.1) that $Q_{\alpha\beta}(\mathbf{k})$ does not depend on the wave vector \mathbf{k} . Therefore, the sum over different \mathbf{k} 's will simply be replaced by a factor related to the excluded volume cutoff. In the continuous representation [26]

$$\ln[\det P_{\alpha\beta}] = - \int_0^1 \frac{dx}{x^2} \ln[\lambda(x)] \quad (3.4)$$

and combining (3.2) and (3.3)

$$\lambda(x) = \begin{cases} b - b^2 \mu^2 \rho x_0, & x < x_0 \\ b, & x > x_0. \end{cases} \quad (3.5)$$

In order to calculate the free-energy density we need to evaluate the entropy change due to the constraint that the replica conformations satisfy Eq. (2.20). Replicas that belong to the same group coincide within a tube of width $R_t \sim \nu^{1/3}$. We know that because of the polymeric effect, after fixing one monomer we must place the next one in a volume a^3 . There are a^3/ν different ways

to do this so the corresponding entropy is $\ln(a^3/\nu)$ per monomer. However, for the second replica in the same group and all subsequent ones we must restrict the position of the next monomer to one place since the replica conformations coincide within the group. That will happen $x_0 - 1$ times in the group and for all n/x_0 groups. Therefore the corresponding loss of entropy is

$$S = N \frac{n}{x_0} (x_0 - 1) \ln \frac{\nu}{a^3} \quad (3.6)$$

and we will refer to it as Nns/x_0 in what follows. It is important to notice that the parameter s increases as flexibility increases. Combining (3.4) and (3.5) and adding the entropy contribution from Eq. (3.6) we obtain the free-energy density

$$\frac{f(x_0)}{n} = \ln b + \frac{\ln(1 - b\mu^2 \rho x_0)}{x_0} - \frac{s}{x_0}. \quad (3.7)$$

Optimization with respect to x_0 gives

$$-\frac{\gamma x_0}{1 - \gamma x_0} - \ln(1 - \gamma x_0) + s = 0 \quad (3.8)$$

with $\gamma = b\mu^2 \rho$.

This equation always has a solution $x_0 = g(s)/\gamma$ with $\gamma = \gamma'/T$ and $\gamma' = -\chi\mu^2 \rho$. Thus the solution has the form $x_0 = T/T_c$ below T_c . Above T_c we have $x_0 = 1$. According to the standard interpretation of the x_0 parameter [27]

$$x_0 = 1 - \sum_i P_i^2,$$

where P_i is the Boltzmann factor of each conformation. Freezing occurs when $x_0 < 1$. The smaller the value of x_0 the fewer the dominant conformations.

The transition temperature is $T_c = \gamma'/g(s)$. Equation (3.8) shows that any solution for x_0 satisfies $\gamma x_0 < 1$. From Eq. (3.8) we can obtain a solution in the lowest non-vanishing order in x_0 . Then $x_0 = s^{1/2}/\gamma$ or

$$x_0 = \frac{T}{\gamma'/s^{1/2}} \quad \text{and} \quad T_c = \gamma'/s^{1/2}. \quad (3.9)$$

It is now clear that RSB stabilizes the integral of Eq. (2.11) through Eq. (3.2) and prevents MPS. We can calculate the correlations $\langle m_\alpha(\mathbf{k}) m_\alpha(-\mathbf{k}) \rangle$ of the parameter $m_\alpha(\mathbf{R}) = \sum_i \sigma_i \delta(\mathbf{r}_i^\alpha - \mathbf{R})$ which shows the difference between densities of monomers A and B . We calculate the n -replica partition function after adding to the Hamiltonian a source term

$$\int d\mathbf{R} \sum_\alpha h_\alpha(\mathbf{R}) \sum_i \sigma_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}). \quad (3.10)$$

Integration of an expression similar to Eq. (2.11) gives

$$\prod_{\mathbf{k}} \exp \left[-\frac{1}{4b} \sum_\alpha h_\alpha(\mathbf{k}) h_\alpha(-\mathbf{k}) + \frac{1}{4} \sum_{\alpha, \beta} h_\alpha(\mathbf{k}) [P^{-1}]_{\alpha\beta} h_\beta(-\mathbf{k}) \right]. \quad (3.11)$$

Calculation of the second functional derivative results in

$$\langle m_\alpha(\mathbf{k})m_\alpha(-\mathbf{k}) \rangle = [P^{-1}]_{\alpha\alpha} - \frac{1}{b}. \quad (3.12)$$

The \mathbf{k} dependence vanishes because of the form of $Q_{\alpha\beta}(\mathbf{k})$ introduced in Eq. (3.1). Using the formula derived in [26] for the diagonal elements of the inverse Parisi matrix we find

$$\langle m_\alpha(\mathbf{k})m_\alpha(-\mathbf{k}) \rangle = \frac{\gamma}{b(1-\gamma x_0)}. \quad (3.13)$$

Above the freezing transition point $x_0 = 1$ and the correlation function increases (see Fig. 3) as the temperature decreases ($\gamma \sim 1/T, b \sim 1/T$). Below the freezing point γx_0 is independent of temperature and according to Eq. (3.8) $\gamma x_0 < 1$. Hence the MPS transition point is never reached. In the annealed case there is no freezing and $x_0 = 1$. Then we can see from Eq. (3.13) that there is a temperature at which the correlation function diverges signifying MPS as shown in Fig. 3.

It is important to notice that the above result comes from a mean-field treatment with respect to the order parameter $Q_{\alpha\beta}(\mathbf{R}_1 - \mathbf{R}_2)$. In the next section we will estimate the effect of fluctuations of this order parameter.

IV. EFFECT OF THE FLUCTUATIONS OF $Q_{\alpha\beta}$ ON FREEZING TEMPERATURE

In the preceding sections the potential was taken as a δ function and the \mathbf{k} dependence was omitted. Introduction of a finite range in the potential does not change the results obtained in Sec. III. In particular, the solution obtained from Eq. (3.8) for x_0 will always stabilize the Gaussian integral. Introduction of a range in the poten-

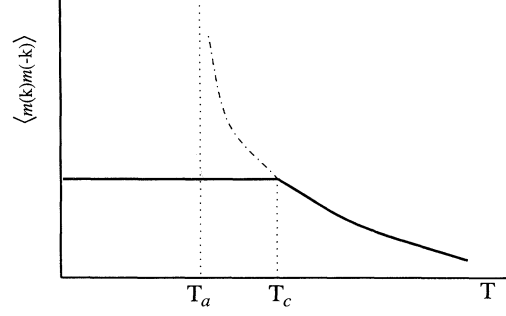


FIG. 3. The correlation function of the microphase-separation order parameter diverges at some temperature T_a for the annealed case. In the quenched case, the correlation function becomes independent of temperature. When freezing occurs first, it prevents microphase separation.

tial will simply replace the cutoff of the excluded volume by another cutoff. In order to investigate the effect of fluctuations we must introduce a finite range into the potential and set $U(\mathbf{k}) = 1 - c^2\mathbf{k}^2$, where c^2 is a surface tension coefficient which suppresses large wave vectors \mathbf{k} . We then set $b(\mathbf{k}) = b(1 - c^2\mathbf{k}^2)$.

We consider the partition function in the form of Eq. (2.8). We again group replicas using the RSB pattern of Eq. (2.20). For replicas in the same group we replace the quantity $\sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1)\delta(\mathbf{r}_i^\beta - \mathbf{R}_2)$ by $\rho\delta(\mathbf{R}_1 - \mathbf{R}_2)$. On the mean-field level we will have $\langle \sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1)\delta(\mathbf{r}_i^\beta - \mathbf{R}_2) \rangle_{\text{th}} = 0$ for replicas in different groups. In order to investigate fluctuations of the $Q_{\alpha\beta}$ order parameter and interactions between replicas in different groups we need to expand the bilinear term $\Phi_\alpha(\mathbf{k})\Phi_\beta(-\mathbf{k})$ for replicas α, β in different groups as follows:

$$\left\langle \int \mathcal{D}\Phi_\alpha(\mathbf{R}) \exp \left[\mu^2 b^2 \sum_{(A,B)} \sum_i \sum_{\substack{\alpha \in A \\ \beta \in B}} \int d\mathbf{R}_1 d\mathbf{R}'_1 \Phi_\alpha(\mathbf{R}'_1) U(\mathbf{R}_1 - \mathbf{R}'_1) \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) \right. \right. \\ \left. \left. \times \int d\mathbf{R}_2 d\mathbf{R}'_2 \Phi_\beta(\mathbf{R}'_2) U(\mathbf{R}_2 - \mathbf{R}'_2) \delta(\mathbf{r}_i^\beta - \mathbf{R}_2) \right] \right\rangle_{\text{th}} \quad (4.1)$$

with (A, B) indicating a sum over all the possible different groups of replicas. By Fourier transformation

$$\left\langle \int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_\alpha \sum_{\mathbf{k} \neq 0} b(\mathbf{k}) \Phi_\alpha(\mathbf{k}) \Phi_\alpha(-\mathbf{k}) + \mu^2 \sum_{\alpha, \beta} \sum_i \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} b(\mathbf{k}_1) e^{i\mathbf{k}_1 \cdot \mathbf{r}_i^\alpha} \Phi_\alpha(\mathbf{k}_1) b(\mathbf{k}_2) e^{i\mathbf{k}_2 \cdot \mathbf{r}_i^\beta} \Phi_\beta(\mathbf{k}_2) \right] \right\rangle_{\text{th}}. \quad (4.2)$$

We now group replicas according to the scheme of Eq. (2.20), expand the bilinear term for replicas in different groups. The second-order term vanishes after the thermal average since replicas α and β belong to different groups. At fourth order, only terms with pairs of replicas from the same group will survive. Hence, from Eq. (2.8) we obtain

$$\left\langle \int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_A \sum_{\alpha, \beta \in A} \sum_{\mathbf{k} \neq 0} P_{\alpha\beta}(\mathbf{k}) \Phi_\alpha(\mathbf{k}) \Phi_\beta(-\mathbf{k}) \right] \right. \\ \left. \times \left\{ 1 + \frac{\mu^4}{2!} \sum_{(A,B)} \sum_{\substack{\alpha, \gamma \in A \\ \beta, \delta \in B}} \sum_{i,j} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4 \neq 0} b(\mathbf{k}_1) b(\mathbf{k}_2) b(\mathbf{k}_3) b(\mathbf{k}_4) e^{i(\mathbf{k}_1 \cdot \mathbf{r}_i^\alpha + \mathbf{k}_3 \cdot \mathbf{r}_j^\gamma)} \Phi_\alpha(\mathbf{k}_1) \Phi_\gamma(\mathbf{k}_3) \right. \right. \\ \left. \left. \times e^{i(\mathbf{k}_2 \cdot \mathbf{r}_i^\beta + \mathbf{k}_4 \cdot \mathbf{r}_j^\delta)} \Phi_\beta(\mathbf{k}_2) \Phi_\delta(\mathbf{k}_4) \right\} \right\rangle_{\text{th}}, \quad (4.3)$$

where $P_{\alpha\beta}(\mathbf{k}) = b(\mathbf{k})\delta_{\alpha\beta} - b^2(\mathbf{k})\mu^2\rho$. The first integral in Eq. (4.3) is the Gaussian integral that we calculated in Sec. III. The result was given in Eq. (3.7). We will denote this as $C(x_0)$. For the calculation including the fourth-order term we need to take the fourth variational derivative of the functional

$$\mathcal{F}[h(\mathbf{k})] = \int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_A \sum_{\alpha, \beta \in A} \sum_{\mathbf{k} \neq 0} P_{\alpha\beta}(\mathbf{k}) \Phi_\alpha(\mathbf{k}) \Phi_\beta(-\mathbf{k}) + V \sum_{\mathbf{k} \neq 0} \sum_A \sum_{\alpha \in A} h_\alpha^A(\mathbf{k}) \Phi_\alpha(-\mathbf{k}) \right]. \quad (4.4)$$

In the limit $h \rightarrow 0$ this gives

$$\frac{\delta^4 \mathcal{F}[h(\mathbf{k})]}{\delta h_\alpha^A(\mathbf{k}_1) \delta h_\gamma^A(\mathbf{k}_2) \delta h_\beta^B(\mathbf{k}_3) \delta h_\delta^B(\mathbf{k}_4)} = C(x_0) [P^{-1}]_{\alpha\gamma}^A(\mathbf{k}_1) \delta(\mathbf{k}_1 + \mathbf{k}_3) [P^{-1}]_{\beta\delta}^B(\mathbf{k}_2) \delta(\mathbf{k}_2 + \mathbf{k}_4) \quad (4.5)$$

and the integral of the fourth-order term will become

$$C(x_0) \left\langle \mu^4 \sum_{\mathbf{k}_1, \mathbf{k}_2} \sum_{(A, B)} \sum_{\substack{\alpha, \gamma \in A \\ \beta, \delta \in B}} \sum_{i, j} b^2(\mathbf{k}_1) b^2(\mathbf{k}_2) e^{i\mathbf{k}_1 \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\gamma)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_i^\beta - \mathbf{r}_j^\delta)} [P^{-1}]_{\alpha\gamma}^A(\mathbf{k}_1) [P^{-1}]_{\beta\delta}^B(\mathbf{k}_2) \right\rangle_{\text{th}}. \quad (4.6)$$

We will represent the elements of the inverse Parisi matrix $P^{-1}(\mathbf{k})$ as $p(\mathbf{k})$ for the off-diagonal elements and $\tilde{p}(\mathbf{k})$ for the diagonal elements, where

$$p(\mathbf{k}) = \frac{\gamma(\mathbf{k})}{b(\mathbf{k})[1 - \gamma(\mathbf{k})x_0]} \quad \text{and} \quad \tilde{p}(\mathbf{k}) = \frac{1 + \gamma(\mathbf{k})(1 - x_0)}{b(\mathbf{k})[1 - \gamma(\mathbf{k})x_0]}, \quad (4.7)$$

with $\gamma(\mathbf{k}) = b(\mathbf{k})\mu^2\rho$. Then Eq. (4.6) becomes

$$\begin{aligned} \mu^4 C(x_0) \frac{n}{x_0} \left(\frac{n}{x_0} - 1 \right) \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} b^2(\mathbf{k}_1) b^2(\mathbf{k}_2) [(x_0 - 1)x_0 p(\mathbf{k}_1) + x_0 \tilde{p}(\mathbf{k}_1)] \\ \times [(x_0 - 1)x_0 p(\mathbf{k}_2) + x_0 \tilde{p}(\mathbf{k}_2)] \left\langle \sum_{i, j} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_i^\beta - \mathbf{r}_j^\beta)} \right\rangle_{\text{th}}. \end{aligned} \quad (4.8)$$

By substitution of (4.7) in (4.8)

$$n\mu^4 C(x_0)(n - x_0) \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{b(\mathbf{k}_1)b(\mathbf{k}_2)}{[1 - \gamma(\mathbf{k}_1)x_0][1 - \gamma(\mathbf{k}_2)x_0]} \left\langle \sum_{i, j} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_i^\beta - \mathbf{r}_j^\beta)} \right\rangle_{\text{th}}. \quad (4.9)$$

The MPS transition temperature T_a is the temperature at which the coefficient of the Gaussian term in (4.3) changes sign. Before freezing $x_0 = 1$. Thus $[1 - \gamma(\mathbf{k})x_0] \sim 0$ near T_a . Away from T_a we can consider $[1 - \gamma(\mathbf{k})x_0] \sim 1$ independent of \mathbf{k} . Then (4.8) separates as

$$\begin{aligned} b^4 \mu^4 \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} C(x_0) \frac{n}{x_0} \left(\frac{n}{x_0} - 1 \right) [(x_0 - 1)x_0 p + x_0 \tilde{p}]^2 \left\langle \sum_{i, j} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_i^\beta - \mathbf{r}_j^\beta)} \right\rangle_{\text{th}} \\ = \frac{b^2 \mu^4 C(x_0)(n - x_0)}{(1 - \gamma x_0)^2} \left\langle \sum_{i, j} \delta(\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha) \delta(\mathbf{r}_i^\beta - \mathbf{r}_j^\beta) \right\rangle_{\text{th}}, \end{aligned} \quad (4.10)$$

with α and β in different groups. The thermal (configurational) average in (4.10) is the number of common contacts in different folds α, β . The overlap is mainly due to the contacts of neighboring monomers which is neglected in the mean-field theory for $Q_{\alpha\beta}$ and becomes important when the flexibility of the chain increases. We denote this overlap as $N\epsilon$ where ϵ is the small parameter of our perturbation expansion. With this correction the expression for the free energy becomes

$$\frac{f(x_0)}{n} = \ln b + \frac{\ln(1 - \gamma x_0)}{x_0} - \frac{s}{x_0} + \frac{\epsilon \gamma^2 x_0}{(1 - \gamma x_0)^2}. \quad (4.11)$$

Expanding to the lowest nonvanishing order for x_0 and taking $\partial f(x_0)/\partial x_0 = 0$, we obtain

$$x_0 = \frac{1}{\gamma} \left(\frac{s}{1 - \epsilon} \right)^{1/2} \quad (4.12)$$

and therefore the freezing temperature is

$$T_c = T_c^*(1 - \epsilon)^{1/2}, \quad (4.13)$$

where T_c^* is the freezing temperature derived on the level of the mean field for $Q_{\alpha\beta}$ in Sec. III.

The fluctuations $\langle Q_{\alpha\beta}^2 \rangle$ due to overlaps between replicas in different groups result in a decrease of the freezing temperature. The more flexible the polymer chain the more important the overlaps due to neighboring monomer contacts. Therefore, with increasing flexibility the freezing temperature will decrease. However, the temperature T_a at which the MPS transition occurs is independent of flexibility and at some critical flexibility the MPS transition point will occur before freezing. We then have to examine freezing on the background of microdomain structure.

We notice that near T_a the \mathbf{k} dependence of the term $[1 - \gamma(\mathbf{k})x_0]$ cannot be ignored. Then the \mathbf{k} integral of (4.8) must be taken including the contribution of $\gamma(\mathbf{k})$. First we take the configurational average. We recall that this includes multiplication by the elastic term of Eq. (2.3). The configurational average will give

$$\left\langle \sum_{i,j} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_i^\beta - \mathbf{r}_j^\beta)} \right\rangle_{\text{th}} = \frac{1}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)}. \quad (4.14)$$

The $[1 - \gamma(\mathbf{k})x_0]$ term can be approximated by $\tau + \mathbf{k}^2$ where $\tau = (T - T_a)/T_a$. Then the \mathbf{k} integral is

$$\int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)(\mathbf{k}_1^2 + \tau)(\mathbf{k}_2^2 + \tau)} \sim \ln \tau, \quad (4.15)$$

i.e., diverges logarithmically near T_a .

$$\int \mathcal{D}\Phi_\alpha(\mathbf{k}) \exp \left[-V \sum_A \sum_{\alpha, \beta \in A} \sum_{\mathbf{k} \neq 0} P_{\alpha\beta}(\mathbf{k}) \Phi_\alpha(\mathbf{k}) \Phi_\beta(-\mathbf{k}) \right] \times \left\{ M + \frac{N\mu^4}{2!} \sum_{(A,B)} \sum_{\substack{\alpha, \gamma \in A \\ \beta, \delta \in B}} \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{b^2(\mathbf{k}_1)b^2(\mathbf{k}_2)}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)} \Phi_\alpha(\mathbf{k}_1) \Phi_\gamma(-\mathbf{k}_1) \Phi_\beta(\mathbf{k}_2) \Phi_\delta(-\mathbf{k}_2) \right\}, \quad (5.1)$$

where M is the number of all replica conformations of all groups and can also be written as $\exp(Nns/x_0)$. We return everything to the exponent and perform a mean-field calculation for $\Phi_\alpha(\mathbf{k})$. The free-energy density per replica is

$$\frac{f[x_0; m(\mathbf{k})]}{n} = \frac{\rho}{x_0} \sum_{\mathbf{k} \neq 0} [x_0 \tilde{b}(\mathbf{k}) - x_0(x_0 - 1)b^2(\mathbf{k})\mu^2 \rho] m^2(\mathbf{k}) - \frac{s}{x_0} - x_0^4 \left(\frac{n - x_0}{x_0^2} \right) \frac{\mu^4}{2!} \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{b^2(\mathbf{k}_1)b^2(\mathbf{k}_2)}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)} m^2(\mathbf{k}_1) m^2(\mathbf{k}_2), \quad (5.2)$$

where $\tilde{b}(\mathbf{k}) = b(\mathbf{k}) - b^2(\mathbf{k})\mu^2 \rho$. We have introduced $m(\mathbf{k})$ to denote the mean-field value of $\Phi(\mathbf{k})$ independent of the replica index and $m^2(\mathbf{k}) = m(\mathbf{k})m(-\mathbf{k})$. The MPS transition occurs at the temperature at which the coefficient of the quadratic term becomes negative for one or more modes. The above expression for free energy can be rewritten as

V. FREEZING ON THE BACKGROUND OF THE DOMAIN STRUCTURE

In this section we will consider the case of a polymer flexible enough that the freezing temperature T_c will be shifted below the temperature T_a at which MPS occurs. T_a is the temperature at which the Gaussian integral in Eq. (2.11) diverges or, equivalently, the correlation function $\langle m_\alpha(\mathbf{k})m_\alpha(-\mathbf{k}) \rangle$ in Eq. (3.13) diverges. From now on we refer to T_a as the MPS transition temperature.

In this case we have a nonzero value of the order parameter $\Phi(\mathbf{k})$ before freezing. The amplitude corresponds to the degree of phase separation. The wave vectors describe the domain structure and the domain sizes. Starting from the general expression in Eq. (2.8) for the n -replica partition function we obtain the free energy in the form of a Landau expansion around the mean-field value of $\Phi(\mathbf{k})$. We group replicas in n/x_0 groups corresponding to the different folds introducing the same pattern of RSB as before. This way we include the possibility that the system will freeze after the MPS transition. This will happen if x_0 can become less than unity at some finite temperature.

We consider Eq. (4.3). The condition of translational invariance for the density of a maximally compact globule discussed after Eq. (2.10) implies $\mathbf{k}_1 = -\mathbf{k}_3$ and $\mathbf{k}_2 = -\mathbf{k}_4$ for replicas in the same group. Under these conditions we perform the thermal average. This is the configurational average including the elastic term of Eq. (2.3). Because of the later term the thermal average over all conformations of replicas will introduce a factor $e^{-\mathbf{k}^2 a^2 |i-j|}$ and after summation over all pairs of monomers we obtain

$$\frac{f[x_0; m(\mathbf{k})]}{n} = \rho \sum_{\mathbf{k} \neq 0} [b(\mathbf{k}) - x_0 b^2(\mathbf{k})\mu^2 \rho] m^2(\mathbf{k}) - \frac{s}{x_0} + \frac{\mu^4}{2} x_0^3 \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{b^2(\mathbf{k}_1)b^2(\mathbf{k}_2)}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)} \times m^2(\mathbf{k}_1) m^2(\mathbf{k}_2). \quad (5.3)$$

The mean-field value will be calculated by optimization of Eq. (5.3). It turns out to be more convenient to differentiate with respect to

$$\Psi(\mathbf{k}) = 2b(\mathbf{k})\Phi(\mathbf{k}). \quad (5.4)$$

Then Eq. (5.3) becomes

$$\begin{aligned} \frac{f[x_0; \Psi(\mathbf{k})]}{n} &= \rho \sum_{\mathbf{k} \neq 0} \left(\frac{1}{4b(\mathbf{k})} - \frac{x_0 \mu^2 \rho}{4} \right) \Psi^2(\mathbf{k}) - \frac{s}{x_0} \\ &+ \frac{\mu^4 x_0^3}{32} \sum_{\mathbf{k}_1, \mathbf{k}_2 \neq 0} \frac{\Psi^2(\mathbf{k}_1) \Psi^2(\mathbf{k}_2)}{a^2(\mathbf{k}_1^2 + \mathbf{k}_2^2)}. \end{aligned} \quad (5.5)$$

By variation $\delta(f/n)/\delta\Psi(\mathbf{k}) = 0$ we obtain

$$\Psi(\mathbf{k}) \left\{ \left(\frac{1}{b(\mathbf{k})} - x_0 \mu^2 \rho \right) \rho + \frac{\mu^4 x_0^3}{8a^2} \sum_{\mathbf{k}_1 \neq 0} \frac{\Psi^2(\mathbf{k}_1)}{\mathbf{k}^2 + \mathbf{k}_1^2} \right\} = 0. \quad (5.6)$$

One solution of this equation is

$$\Psi(\mathbf{k}) = \Psi_0 \Delta(\mathbf{k} - \mathbf{k}_0). \quad (5.7)$$

where Δ is Kronecker's delta. By substitution of this into Eq. (5.5) and optimization with respect to Ψ_0 and \mathbf{k}_0 , we find

$$\Psi_0 = \frac{(4/3)(1 - \gamma x_0)a}{\rho^{1/2} b^{1/2} x_0^{3/2} \mu^2 c} \quad (5.8)$$

and

$$|\mathbf{k}_0| = \frac{(1 - \gamma x_0)^{1/2}}{\sqrt{3c\rho^{1/2}}}, \quad (5.9)$$

with $\gamma = b\mu^2\rho$.

From Eqs. (5.4), (5.7), and (5.8) we have

$$m(\mathbf{k}) = \frac{(2/3)(1 - \gamma x_0)a}{\rho^{1/2}(bx_0)^{3/2}\mu^2 c} \Delta(\mathbf{k} - \mathbf{k}_0), \quad (5.10)$$

reproducing the results obtained in [11] for $x_0 = 1$. By substitution of Eqs. (5.10) and (5.9) in Eq. (5.3) we can see that

$$F \sim \frac{b(1 - \gamma x_0)^3 a^2}{\rho(bx_0)^3 \mu^4 c^2} - \frac{s}{x_0} \quad (5.11)$$

and therefore the MPS transition is of third order. In order to find the condition for freezing from Eq. (5.11) we take $(\partial f/\partial x_0) = 0$. Then

$$\frac{\rho a^2}{c^2} \left(1 - \frac{1}{\gamma x_0} \right)^2 = s \quad (5.12)$$

and setting $\gamma = \gamma'/T$ we obtain the freezing transition temperature at which $x_0 = 1$ as

$$T_c = \gamma' \left(1 - \frac{s^{1/2} c}{\rho^{1/2} a} \right) \quad (5.13)$$

or, since $\gamma' = T_a$

$$T_c = T_a \left(1 - \frac{s^{1/2} c}{\rho^{1/2} a} \right). \quad (5.14)$$

Therefore, freezing is possible after MPS. The calculation and the conclusions of this section are based on the fact that we are close enough to the MPS transition temperature T_a so that $(1 - \gamma x_0)$ is small, but also far enough from this point so that a mean field with respect to Φ_α gives satisfactory results.

VI. DISCUSSION

In the present work we solved the sequence model in random heteropolymers making use of the replica technique. We have predicted a frozen phase with the same RSB scheme as in the solution of the independent-interaction model. In a frozen phase with RSB there is a small number of thermodynamically relevant conformations that dominate [27]. It was also shown [28] that there is a significant probability that the ground-state conformation will be nondegenerate. This single conformation will be thermodynamically dominant in the frozen phase. Therefore, we see that the frozen phase with RSB in the sequence model also describes qualitatively the protein unique structure.

In the mean-field approximation, according to this RSB scheme the different folds (pure states) will not have any common contacts and therefore the energies, given by $\sum_{i,j} B_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j)$ will be independent from each other as in the REM. These different folds correspond to well-defined minima in conformation space. Therefore, these states form a discrete bottom part of the energy spectrum [7]. There are also the unfolded states which form a continuum in the upper part of the spectrum.

In the two-letter sequence model, in addition to the freezing order parameter $Q_{\alpha\beta}$ there is a one-replica order parameter Φ_α . This parameter has the meaning of local density difference between monomers of kind A and kind B and describes microphase separation (MPS). In Sec. II we have derived a coupling between these two order parameters described by Eq. (2.11). When Φ_α is integrated out and a mean-field calculation is performed with respect to $Q_{\alpha\beta}$, freezing prevents MPS. This was shown clearly in Eq. (3.13) and in Fig. 3 since the correlation function $\langle m_\alpha(\mathbf{k}) m_\alpha(-\mathbf{k}) \rangle$ becomes independent of temperature below T_c .

In an early study [29] de Gennes had described the effect of disorder introduced to a periodic block copolymer. On the same level of approximation with our mean field it was shown that MPS disappears when randomness increases beyond some threshold value related to the period.

On the level of mean field, however, we neglect contacts between monomers neighboring along the sequence. In flexible chains these contacts cannot be ignored. In order to take them into account we developed a method that goes one step beyond mean field. This method was described in Sec. IV. There we considered two folds from

different groups which have no common contacts between distant monomers, i.e., in the mean-field sense, but have $N\epsilon$ common contacts between neighboring monomers ignored in the mean-field approximation. In Eq. (4.13) we have shown that an increase of ϵ reduces the freezing temperature T_c . Then T_c can be shifted below MPS. Therefore, in flexible polymers MPS can occur before freezing.

A frozen phase can appear at lower temperature. This new frozen phase has a domain structure with A - and B -rich regions. Hence we have obtained a richer phase diagram shown in Fig. 4. The maximally compact state G is a homopolymericlike globule without definite structure [22]. The transition from G to MPS is a very weak transition without latent heat and with a smooth increase of the MPS order parameter Φ from zero to a finite value. On the level of mean field this is found to be a third-order transition. The transition from G to the frozen phase (FP) or the frozen phase with domain structure (MPS+FP) is thermodynamically of second order, without latent heat but with a jump in the order parameter Q .

There is a critical flexibility at which $T_a = T_c$. The behavior of the system in this area as well as the value of this critical flexibility cannot be estimated by low-order deviations from the mean field and interesting critical phenomena may appear in this region.

In order to understand physically why freezing prevents MPS in stiff polymers and why MPS occurs in flexible polymers we compare the "energy spectra" of stiff and flexible polymers [Figs. 5(a) and 5(b)]. Freezing transition occurs when the system reaches a conformation that corresponds to an energy level in the discrete part of the spectrum of Fig. 5(a). The number of such conformations is of order one and therefore, at the freezing transition point T_c the entropy per monomer becomes zero. This implies that all the thermodynamic quantities stop

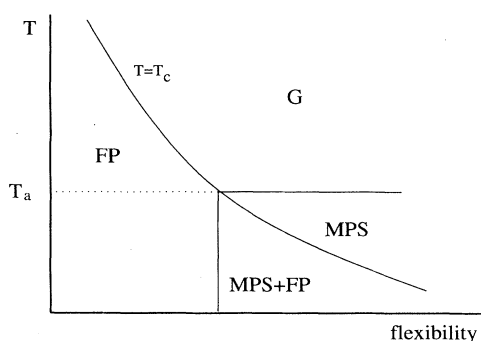


FIG. 4. Phase diagram for random copolymers. By G we denote a compact globular state without definite fold. The FP denotes a frozen phase without domain structure. MPS denotes the microphase separation with A - and B -rich microdomains. FP+MPS denotes a frozen state with microdomains. We see that for "flexible" chains freezing occurs after phase separation on the background of a microdomain structure. The shaded area is around the point where the freezing transition temperature equals the MPS transition temperature. The behavior of the system in this area cannot be estimated by low-order corrections to mean-field theory.

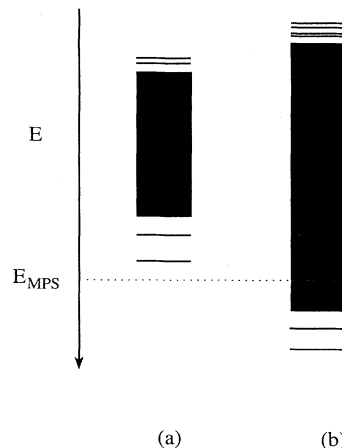


FIG. 5. Energy spectrum of (a) a stiff polymer and (b) a flexible polymer. E_{MPS} is the energy threshold below which structures with MPS exist. We distinguish the continuous and discrete part of the spectrum. Freezing corresponds to the transition from the discrete to the continuous part. The gray color labels states with MPS.

to depend on temperature. Physically this means that the system has reached the bottom of its conformational set and there are no conformations with lower energies. MPS conformations have low energies and for a stiff polymer the energy corresponding to the MPS conformation lies below the border of the spectrum. In other words, there are no MPS conformations in the conformational set of a stiff polymer. However, as flexibility increases the number of conformations increases and the lowest-energy level of the spectrum in Fig. 5 is shifted down. At some critical flexibility it reaches a value of energy corresponding to MPS. Below that point the conformational set of a polymer will also contain MPS conformations. These conformations will occupy the lower part of the spectrum [Fig. 5(b)]. This includes the bottom of the continuous part of the spectrum and all the discrete part. In this case the decrease of the temperature will lead first to MPS without freezing [transition from the black to the gray part in the spectrum in Fig. 5(b)]. Further decrease of temperature leads to freezing to the set of MPS frozen conformations [transition to the discrete part of the spectrum in Fig. 5(a)]. Therefore we see that increase of the flexibility decreases the temperature of the freezing transition T_c . When T_c becomes lower than the MPS transition temperature T_a the scenario of transitions is described by Fig. 5(b) rather than by Fig. 5(a).

We notice that in order to perform the disorder average in Eq. (2.5) we considered a Gaussian distribution for the characteristic values $\{\sigma_i\}$. Instead, if we had taken $\sigma_i = \pm 1$ we would have obtained a term

$$\sum_i \ln \left[\cosh \left(2b \sum_{\alpha} \int d\mathbf{R} \delta(\mathbf{r}_i^{\alpha} - \mathbf{R}) \Phi_{\alpha}(\mathbf{R}) \right) \right] \quad (6.1)$$

and with high-temperature expansion to the order $b^2 \sim 1/T^2$ we get the same Gaussian integral as in Eq. (2.11).

The higher-order terms of the expansion were neglected. Here we will discuss why these terms do not change the results presented above.

First we examine the effect on the RSB scheme proposed. The Φ^4 term includes multiple replica coupling

$$\sum_i \delta(\mathbf{r}_i^\alpha - \mathbf{R}_1) \delta(\mathbf{r}_i^\beta - \mathbf{R}_2) \delta(\mathbf{r}_i^\gamma - \mathbf{R}_3) \delta(\mathbf{r}_i^\delta - \mathbf{R}_4). \quad (6.2)$$

In three dimensions this term does not change the arguments that lead to the step-function type of $Q(x)$ since it contributes to the free energy by a term $1/R_t^3$. Therefore, the free energy still has only two maxima at scales $R_t = \infty$ and $R_t = v^{1/3}$.

We must also examine the effect of these fourth-order terms to the T_c . Since $\Phi(\mathbf{k} = 0) = 0$ we find that the only nontrivial term is $\Phi_\alpha^4(\mathbf{R})$. We calculate the contribution of this term to the free energy at order $1/T^4$. In a way similar to that described for the calculation of Eq. (4.5) we find that this contribution to the free energy is

$$nC(x_0) \frac{\rho(2b)^4}{12} \left[\frac{1 + \gamma(1 - x_0)}{b(1 - \gamma x_0)} \right]^2. \quad (6.3)$$

It seems that the fourth-order term due to discreteness has the same effect as the fourth-order term in Eq. (4.9) due to the polymeric effect. However, these terms become important near T_a . Then from Eqs. (4.14) and (4.15) we see that the polymeric term is much more important and the effect of the other term can be ignored.

The sequence model is a more realistic description of heteropolymers than the independent-interaction model. Also it predicts new phases impossible to reveal in the independent-interaction model. It is remarkable that the RSB scheme in the sequence model is the same as in the independent-interaction model. As discussed above, this means that the REM is a good approximation of the system. However, the interpretation of the x_0 parameter here may not be straightforward as in the independent-interaction model as shown in [28].

On the basis of the results obtained here we can briefly discuss the anticipated behavior of a two-letter random copolymer with short-range correlations along the sequence. In this model the contacts between neighbors cannot be ignored. It should be expected that they are very important so that MPS will precede freezing. The MPS transition in this model was described in [18,19] but the freezing transition, if any, is a very interesting problem which is under current investigation.

ACKNOWLEDGMENTS

This work was supported by the David and Lucille Packard Fund. Acknowledgement is made also to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

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- * Electronic address: eugene@diamond.harvard.edu
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