

## Behavior of a random heteropolymer in mixed solvents

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I use a Landau theory to study the behavior of  $A-B$  heteropolymers with disordered sequences immersed in a binary solvent mixture. Segments of type  $A$  are preferentially solvated in one type of solvent, and those of type  $B$  prefer the other type of solvent. At high temperatures, the behavior is qualitatively the same as that in a single solvent. As the temperature approaches the critical temperature for solvent demixing, however, the chain conformational statistics change dramatically. A phase transition occurs driven by the long-range solvent density fluctuations. The transition is one where on scales larger than a preferred length the chain is collapsed and microphase ordered. On shorter scales it is disordered and exhibits self-avoiding walk statistics. In many circumstances this domain size acquires a limiting value and the system cannot order on shorter length scales by reducing temperature. The ordering disappears when the critical point is approached too closely. Predictions are made for scattering profiles that may be observed in neutron-scattering experiments.

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### INTRODUCTION

Over a quarter of a century ago, the behavior of a homopolymer chain in mixed solvents was first investigated. Pioneering studies carried out by Benoit and Dondos,<sup>1-3</sup> deGennes,<sup>4</sup> and Brochard and co-workers<sup>5,6</sup> elucidated an interesting new phenomenon when the temperature approached that corresponding to the incipient phase transition for the solvent mixture. The lessons that these scientists taught us have since been elaborated by many others. The studies of Vilgis, Sans, and Jannink<sup>7</sup> and the recent reports from the group led by Khokhlov<sup>8</sup> are particularly noteworthy.

The specific problem considered in these studies is the behavior of a homopolymer chain in a binary solvent mixture with both solvents being good solvents for the polymer segments. However, the polymer segments are preferentially solvated by one of the solvents ( $V_A$  and  $V_B$  are the segment-solvent interaction potentials, and  $V_A \neq V_B$ ). The question is: what are the chain conformational statistics as the temperature approaches that corresponding to the critical temperature of demixing for the solvent mixture? The major findings (in the infinitely dilute limit) may be summarized as follows. Since the polymer segments interact preferentially with one type of solvent, the solvent density fluctuations induce effective attractions between the polymer segments. These attractive interactions are spatially long ranged because the correlation function describing solvent density fluctuations is long ranged in the vicinity of the critical point. The attractive interactions drive chain collapse even though both solvents are good solvents for the chain segments. The collapse is only partial, however. This is because the short-range intersegment repulsions (the excluded volume effect) and long-range attractive interactions compete. The long-range interactions dominate only above a particular length scale ( $L$ ). On scales larger than  $L$ , the chain is collapsed and on smaller scales the statistics are those of a self-avoiding walk. The variation of  $L$  with temperature (or solvent-segment interac-

tion potentials) exhibits a nonclassical scaling exponent. This is simply a manifestation of the nonclassical exponent that describes the behavior of the solvent density fluctuations near criticality. In particular,  $L$  scales as  $\sim (V_A - V_B)^{2/(\eta-2)}$ , where  $\eta$  is the nonclassical exponent and equals 0.25 for three-dimensional systems.

The chain dimensions decrease as the critical point is approached. However, for finite chains, this trend changes as the critical temperature is approached more closely. This is because the size of solvent density fluctuations exceeds chain dimensions and the entire chain lives in a single good solvent. This results in reexpansion and self-avoiding-walk statistics for the entire chain. Thus, the variation of chain dimensions with temperature is nonmonotonic near the critical point; first it decreases as the critical temperature is approached and then reexpansion occurs when the critical point is approached too closely.

The preceding two decades have witnessed much interest in the behavior of copolymers with incompatible segments. For example, there have been innumerable studies of the phase behavior of block copolymers with ordered sequence distributions. In these materials, competing interactions between the different types of chain segments and frustration due to connectivity leads to interesting physical behavior in many contexts.<sup>9-13</sup>

More recently, attention has been focused on copolymers with disordered sequence distributions. In these macromolecules, competing interactions are frustrated not only by chain connectivity but also by the disordered (and quenched) sequence distribution. This additional source of frustration leads to interesting behavior, and these materials have been shown to be good model systems to study the effects of frustrating quenched randomness. They have been employed as simple models to study protein folding,<sup>14-17</sup> as models for biomimetic polymers,<sup>18-20</sup> and to study how frustrating quenched randomness influences microphase ordering in melts.<sup>21-23</sup>

In this paper, I consider the behavior of disordered heteropolymers in a binary solvent mixture. Specifically, I study linear disordered heteropolymers with two types of segments and random sequences (random heteropolymer or RHP). Let me label the two types of segments, A and B. In my model, the segments of type A prefer to interact with one type of solvent and those of type B exhibit preferential interactions with the other type of solvent. I develop a Landau theory to study this situation. Near the critical temperature for solvent demixing, due to the long-range solvent density fluctuations, the theory predicts a phase transition wherein partial collapse is accompanied by microphase ordering. On scales larger than a preferred length  $\xi$ , the chain is collapsed and microphase ordered; on shorter scales, the system is disordered and the chain exhibits self-avoiding walk (SAW) statistics. The coupling between the order parameters that describe collapse and microphase ordering leads to some unusual behavior. The instability that drives the phase transition occurs with a finite-wave vector, and I describe its dependence on system parameters. The scattering profiles that describe the fluctuations in the disordered phase are presented. These fluctuations are announcements of the chain conformational statistics expected in the ordered phase. In contrast to RHPs in a single solvent, as the critical temperature is approached, a preferred length scale emerges even in the disordered phase (manifested by a peak in the scattering intensity). Although detailed consideration of the ordered phase is postponed to a forthcoming communication, I discuss some conjectures regarding the ordered phase based on the form of the free-energy functional. As for homopolymers, when the range of solvent density fluctuations exceeds chain dimensions the chain re-expands and there is no microphase ordering.

This paper is organized as follows. In Sec. II, the model is described and the theory leading to the free-energy functional is developed. In Sec. III, I discuss the main predictions of the theory and their physical origin and significance. In Sec. IV, I offer some remarks focused on future experimental and theoretical studies that may help shed more light on the unusual behavior of RHPs in mixed solvents.

## MODEL DEVELOPMENT AND THEORY

In order to examine the essential physics, I consider flexible RHPs with  $l$  being the statistical segment length for both A- and B-type segments. The spatially short-range intersegment and segment-solvent interactions depend on the chemical identities of the segments and the solvent particles. The following Edwards Hamiltonian describes this physical situation:

$$\begin{aligned}
 & -\beta H[r(n); \theta(n); \rho_A(r)] \\
 &= -\frac{3}{2l} \int_0^N dn \left( \frac{dr(n)}{dn} \right)^2 \\
 & - \int_0^N dn \int_0^N dn' \left( \frac{a}{2} + \frac{b}{2} \theta(n) \theta(n') \right) \\
 & \times \delta(r(n) - r(n')) - \int_0^N dn \int dr \left( \frac{a'}{2} + \frac{b'}{2} \theta(n) \right) \\
 & \times \delta(r(n) - r) \zeta_A(r) - \beta H_{\text{solvent}}[\zeta_A(r)], \quad (1)
 \end{aligned}$$

where  $\mathbf{r}(n)$  is the spatial position of the  $n$ th segment,  $\theta(n)$  equals  $+1$  if the  $n$ th segment is of type A and equals  $-1$  otherwise,  $\zeta_A(\mathbf{r})$  is the density of solvent particles of type A, and  $H_{\text{solvent}}$  is the solvent Hamiltonian. The parameters  $a$ ,  $b$ ,  $a'$ , and  $b'$  are defined as follows:

$$\begin{aligned}
 a &= \frac{(U_{AA} + U_{BB} + 2U_{AB})}{2}, \\
 b &= \frac{(U_{AA} + U_{BB} - 2U_{AB})}{2}, \\
 a' &= \frac{(V_{AA} + V_{AB}) - (V_{BB} + V_{BA})}{2}, \\
 b' &= \frac{(V_{AA} + V_{BB} - V_{AB} - V_{BA})}{2}, \quad (2)
 \end{aligned}$$

where  $U_{ij}$  and  $V_{ij}$  denote the strengths of interactions between segments of type  $i$  and  $j$  and solvent particles of type  $i$  and segments of type  $j$ , respectively. In writing Eq. (1), I have assumed that the solvent particles fill space completely (i.e., the infinitely dilute chain limit).

It is important to understand the physical meaning of the parameters defined in Eq. (2). The parameter  $a$  is a measure of the effective repulsive intersegment interactions in the absence of the solvent.  $b$  measures the propensity of the A- and B-type segments to microphase segregate due to the bare intersegment interactions. The segment-solvent interactions also lead to two types of effective interactions:  $a'$  is a measure of the extent to which the segment-solvent interactions cause the RHP chain to prefer one solvent over the other, on average;  $b'$  reflects the extent to which segment-solvent interactions promote segregation of the two types of segments to different regions of space.

Further progress can be made by integrating out the solvent density fluctuations to obtain the influence functional.<sup>24</sup> This requires that we assume a form for the solvent Hamiltonian. In order to describe the solvent density fluctuations near the critical point correctly, a Gaussian Hamiltonian is inappropriate. However, as Vilgis, Sans, and Jannink<sup>7</sup> have demonstrated in the context of homopolymers in mixed solvents near critically, using a quadratic Hamiltonian with the proper form for the density-density correlation function leads to the correct phenomenology for chain conformational statistics. Following Vilgis, Sans, and Jannink,<sup>7</sup> I consider the solvent density fluctuations to be described by the following Hamiltonian:

$$\begin{aligned}
 & \exp[-\beta H_{\text{solvent}}] \\
 & \propto \exp \left[ -\frac{1}{2} \int dr \int dr' \delta \zeta_A(r) \chi^{-1}(r-r') \delta \zeta_A(r') \right], \quad (3)
 \end{aligned}$$

where,  $\chi(\mathbf{r}-\mathbf{r}') = \langle \delta \zeta_A(\mathbf{r}) \delta \zeta_A(\mathbf{r}') \rangle = \rho_0 \delta(\mathbf{r}-\mathbf{r}') + \chi_d(\mathbf{r}-\mathbf{r}')$ ;  $\chi_d$  is the distinct part of the correlation function, and will be chosen to properly represent the nature of the solvent density fluctuations (*vide infra*).

Using Eq. (3), it is straightforward to compute the functional integral over solvent density fluctuations. I obtain the effective Hamiltonian to be

$$\begin{aligned}
 -\beta H[r(n); \theta(n)] = & -\frac{3}{2l} \int_0^N dn \left( \frac{dr(n)}{dn} \right)^2 - \int_0^N dn \int_0^N dn' \left[ \left( \frac{a}{2} - \frac{a'^2 \rho_0}{8} \right) \delta(r(n) - r(n')) - \frac{a'^2}{8} \chi_d(r(n) - r(n')) \right] \\
 & - \int_0^N dn \int_0^N dn' \left[ \left( \frac{b}{2} - \frac{b'^2 \rho_0}{8} \right) \delta(r(n) - r(n')) - \frac{b'^2}{8} \chi_d(r(n) - r(n')) \right] \theta(n) \theta(n') + \frac{a' b'}{4} \\
 & \times \int_0^N dn \int_0^N dn' [\rho_0 \delta(r(n) - r(n')) + \chi_d(r(n) - r(n'))] \theta(n). \quad (4)
 \end{aligned}$$

In writing Eq. (4) I have ignored irrelevant constants that can be subsumed in normalization factors.

Equation (4) shows that the segment-solvent interactions induce effective intersegment interactions. Consider the second term first, which is homopolymeric in nature as there is no dependence on  $\theta$ . The bare homopolymeric interactions are short range and repulsive. These are renormalized by a short-range attractive term proportional to  $a'^2$ . Furthermore, an attractive term with the same spatial range as that which characterizes the solvent density fluctuations is also induced. Equation (4) suggests that a finite value of  $a'$  will promote chain collapse because of these attractive intersegment interactions. Given the physical meaning of  $a'$ , it is clear that the physical origin of these solvent-induced terms in the Hamiltonian, which lead to attractions between all chain segments, is that, on average, the chain prefers one solvent over another.

The third term in Eq. (4) tells us something about the more interesting heteropolymeric aspects of the physical problem under consideration. In the bare RHP, the term proportional to  $b$  drives microphase ordering. For example, if  $b$  is negative, segments of the same type are attracted to each other. Equation (4) shows that interactions with the fluctuat-

ing solvent density field renormalizes the bare RHP's short-range interaction driving microphase segregation. In addition, interactions with the spatial range of the solvent density fluctuations are also induced. These solvent-induced interactions are spatially long ranged near the critical point, and promote segregation of like segments on scales characteristic of the solvent density fluctuations. Physically, these terms reflect the preferential solvation of specific RHP segments by different types of solvent molecules.

The preceding discussion makes clear that the solvent-induced interactions promote chain collapse and microphase ordering. The best way to study how these two phenomena occur (and how they are coupled) is to introduce the following macroscopic order parameter fields: the total segmental density,  $\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})$ , where  $\rho_i(\mathbf{r})$  is the density of RHP segments of type  $i$ ;  $m(\mathbf{r}) = \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})$ , which is the appropriate order parameter field to monitor the onset of microphase ordering since, for simplicity, I will take the RHP composition to be symmetric.

Rewriting the effective Hamiltonian in terms of these macroscopic fields, I obtain the following expression for the canonical partition function ( $Q$ ) for a given sequence distribution of the RHP:

$$\begin{aligned}
 Q[\theta(n)] = & \iint Dm(r) \iint D\rho(r) \exp \left[ - \left( \frac{a}{2} - \frac{a'^2 \rho_0}{8} \right) \int dr \rho^2(r) \right] * \exp \left[ - \left( \frac{b}{2} - \frac{b'^2 \rho_0}{8} \right) \int dr m^2(r) \right] \\
 & + \frac{a' b' \rho_0}{4} \int dr \rho(r) m(r) \left] * \exp \left[ \frac{1}{8} \int dr \int dr' (a' \rho(r) + b' m(r)) \chi_d(r - r') (a' \rho(r') + b' m(r')) \right] * \iint Dr(n) \right. \\
 & \times \exp \left[ - \frac{3}{2l} \int dn \left( \frac{dr(n)}{dn} \right)^2 \right] * \delta \left[ m(r) - \int dn \delta(r(n) - r) \theta(n) \right] * \delta \left[ \rho(r) - \int dn \delta(r(n) - r) \right]. \quad (5)
 \end{aligned}$$

In an experiment, RHP chains with different sequences (which belong to the same statistical distribution) are present in the solution. In order to compute properties that are typical for sequences that belong to a certain statistical distribution, averages over the quenched distribution of  $\theta(n)$  must be computed. The free energy needs to be

averaged since, as has been described many times before, the partition function is not self-averaging with respect to the sequence fluctuations.<sup>16-23</sup> I choose to perform the quenched average using the celebrated replica trick.<sup>25</sup> The  $n$ -replica partition function can be written conveniently as

$$\langle Q^n \rangle = \prod_{\alpha=1}^n \iint D\rho_{\alpha}(r) \iint Dm_{\alpha}(r) \times \exp \left[ \sum_{\alpha=1}^n -E[\rho_{\alpha}(r), m_{\alpha}(r)] + S_{\text{eff}}[\rho_{\alpha}(r), m_{\alpha}(r)] \right], \tag{6}$$

where

$$E[\rho_{\alpha}(r), m_{\alpha}(r)] = \left( \frac{a}{2} - \frac{a'^2 \rho_0}{8} \right) \int dr \rho_{\alpha}^2(r) + \left( \frac{b}{2} - \frac{b'^2 \rho_0}{8} \right) \int dr m_{\alpha}^2(r) - \frac{a' b' \rho_0}{4} \int dr \rho_{\alpha}(r) m_{\alpha}(r) - \frac{1}{8} \int dr \int dr' (a' \rho_{\alpha}(r) + b' m_{\alpha}(r)) \chi_d(r-r') (a' \rho_{\alpha}(r') + b' m_{\alpha}(r')), \tag{7}$$

and

$$\exp[S_{\text{eff}}] = \langle \exp[S[\rho_{\alpha}(r), m_{\alpha}(r)]] \rangle_{\theta} = \left\langle \prod_{\alpha=1}^n \int \int D r_{\alpha}(n) \times \exp \left[ -\frac{3}{2l} \sum_{\alpha=1}^n \int dn \left( \frac{dr_{\alpha}(n)}{dn} \right)^2 \right] * \times \delta \left[ \rho_{\alpha}(r) - \int dn \delta(r_{\alpha}(n) - r) \right] * \times \delta \left[ m_{\alpha}(r) - \int dn \delta(r_{\alpha}(n) - r) \theta(n) \right] \right\rangle_{\theta}, \tag{8}$$

where the angular brackets denote averaging over the distribution of  $\theta$ .

$S_{\text{eff}}$  is clearly the entropy corresponding to particular order parameter fields since it is the logarithm of the number of ways in which the system can arrange itself with these order parameter fields while obeying the constraints of connectivity and the quenched sequence fluctuations.  $E$  can, therefore, be interpreted to be the energy corresponding to particular order parameter fields. Equation (7) shows that the energy is very different from that for RHPs in a single solvent.<sup>21,22</sup> The new terms originate from interactions of the RHP segments with a fluctuating solvent density field. However, Eq. (8) shows that the effective entropy for given order parameter fields has the same form as that for a RHP in one solvent. Thus, methods employed to study RHPs in one solvent may be used to estimate the entropic contributions to the free-energy functional. In particular, I will employ Shakhnovich and Gutin's<sup>21</sup> adaptation of a method that was originally developed by Lifshitz<sup>26</sup> to compute Eq. (8). As this method is now well established, I shall only outline the calculation.

Consider the following quantity,  $Z_n[\phi_{\alpha}, \gamma_{\alpha}]$ :

$$Z_n = \left\langle \prod_{\alpha} \int \int D r_{\alpha}(n) \exp \left[ -\frac{3}{2l} \int dn \left( \frac{dr_{\alpha}(n)}{dn} \right)^2 - \sum_{\alpha} \int dr (\phi_{\alpha}(r) \rho_{\alpha}(r) + \gamma_{\alpha}(r) m_{\alpha}(r)) \right] \right\rangle_{\theta}. \tag{9}$$

Equation (9) makes clear that the fields  $\gamma$  and  $\phi$  are conjugate to the order parameters  $m$  and  $\rho$ . By rewriting Eq. (9) as functional integrals over the order parameter fields, it is easy to show that  $Z_n$  equals

$$Z_n = \prod_{\alpha} \iint D\rho_{\alpha}(r) Dm_{\alpha}(r) \times \exp \left[ -\sum_{\alpha} \int dr (\phi_{\alpha}(r) \rho_{\alpha}(r) + \gamma_{\alpha}(r) m_{\alpha}(r)) + S_{\text{eff}} \right]. \tag{10}$$

In the saddle-point approximation,

$$S_{\text{eff}} = \ln Z_n + \sum_{\alpha} \int dr (m_{\alpha}(r) \gamma_{\alpha}(r) + \phi_{\alpha}(r) \rho_{\alpha}(r)), \tag{11}$$

where the auxiliary fields satisfy the conditions

$$-\frac{\delta \ln Z_n}{\delta \gamma_{\alpha}(r)} = m_{\alpha}(r), \tag{12}$$

$$-\frac{\delta \ln Z_n}{\delta \phi_{\alpha}(r)} = \rho_{\alpha}(r).$$

Equations (11) and (12) allow computation of the entropy that I seek if  $Z_n$  is known.

In order to focus on the essential physics, I will restrict attention to the case where the fluctuations in  $\theta$  exhibit short-range correlations, and the composition is symmetric. Substituting the definitions of the order parameter fields in terms of the chain conformations  $[r_{\alpha}(n)]$  and carrying out the average over this equiprobable distribution for  $\theta$ , I can rewrite Eq. (9) as

$$Z_n = \prod_{\alpha} \iint D r_{\alpha}(n) \exp \left[ -\frac{3}{2l} \sum_{\alpha} \int dn \left( \frac{dr_{\alpha}(n)}{dn} \right)^2 - \sum_{\alpha} \int dn \phi_{\alpha}(r_{\alpha}(n)) + \int dn \ln \left( \cosh \sum_{\alpha} \gamma_{\alpha}(r_{\alpha}(n)) \right) \right]. \tag{13}$$

If interest is limited to sufficiently long chains, Eq. (13) can be evaluated using a ground-state dominance approximation. This is to say that  $Z_n$  equals  $\exp[-\lambda N]$ , where  $\lambda$  is the smallest eigenvalue of the following ‘‘Schrödinger equation:’’

$$\left[ -\frac{l^2}{6} \Delta + \sum_{\alpha} \phi_{\alpha}(r_{\alpha}) - \ln \cosh \left( \sum_{\alpha} \gamma_{\alpha}(r_{\alpha}) \right) \right] \psi = \lambda \psi. \tag{14}$$

Shakhnovich and Gutin<sup>21</sup> have computed  $\lambda$  using second-order perturbation theory. The answer is

$$\lambda = \sum_{\alpha} \bar{\phi}_{\alpha}(k=0) - \sum_{\alpha} \sum_{k \neq 0} \frac{\bar{\phi}_{\alpha}(k) \bar{\phi}_{\alpha}(-k)}{l^2 k^2} - \frac{1}{4} \sum_{\alpha \neq \beta} \sum_{k_1, k_2 \neq 0} \frac{\gamma_{\alpha}(k_1) \gamma_{\alpha}(-k_1) \gamma_{\beta}(k_2) \gamma_{\beta}(-k_2)}{l^2 (k_1^2 + k_2^2)}, \quad (15)$$

where

$$\bar{\phi}_{\alpha}(r) = \phi_{\alpha}(r) - \frac{1}{2} \gamma_{\alpha}^2(r), \quad (16)$$

and I have taken Fourier transforms.

The strategy now is to combine Eq. (15) with Eq. (12) to obtain the auxiliary fields in terms of the order parameter fields of interest. Shakhnovich and Gutin did this for compact states only, i.e., they assumed that the overall segment density was uniform and exhibited no fluctuations. Obviously, I have to allow overall density fluctuations. Taking the appropriate functional derivatives, I obtain the following coupled equations that must be solved simultaneously to obtain  $\gamma_{\alpha}$  and  $\phi_{\alpha}$  in terms of  $m_{\alpha}(\mathbf{k})$  and  $\rho_{\alpha}(\mathbf{k})$ :

$$\rho_{\alpha}(k) = -2 \frac{\phi_{\alpha}(-k)}{l^2 k^2} + \sum_{k_1} \frac{\gamma_{\alpha}(k_1) \gamma_{\alpha}(k-k_1)}{l^2 k^2}, \quad (17)$$

$$m_{\alpha}(k) = -\gamma_{\alpha}(k) - \frac{1}{4} \sum_{k_1} \sum_{\alpha \neq \beta} \frac{\gamma_{\alpha}(k) \gamma_{\beta}(k_1) \gamma_{\beta}(-k_1)}{l^2 (k^2 + k_1^2)} + \frac{1}{2} \sum_{k_1} \frac{\phi_{\alpha}(-k_1) \gamma_{\alpha}(k_1 - k)}{l^2 k_1^2} + \frac{1}{2} \sum_{k_1} \frac{\phi_{\alpha}(k_1) \gamma_{\alpha}(-k_1 - k)}{l^2 k_1^2} - \frac{1}{4} \sum_{k_1, k_2} \frac{\gamma_{\alpha}(k_1 - k) \gamma_{\alpha}(k_2) \gamma_{\alpha}(-k_1 - k_2)}{l^2 k_1^2}. \quad (18)$$

Solving Eqs. (17) and (18) for the auxiliary fields in terms of the order parameters, using the definition  $Z_n = \exp[-\lambda N]$ , and Eqs. (11) and (15) allows calculation of the entropy  $S_{\text{eff}}$ . Combining the resulting expression with Eq. (7) (the energy) yields the Landau free-energy functional that I seek up to quartic order. The entropy will contain interesting terms that reflect how the constraints of connectivity and the disordered sequence distribution influence chain collapse and microphase ordering. For example, the equations I have derived already show that a quartic term proportional to the strength of the sequence fluctuations will arise, which varies as  $\sim 1/(k_1^2 + k_2^2)$ . Such a term is a signature of the constraints imposed by the quenched fluctuations characterizing the sequence distribution.<sup>21-23</sup> The quartic terms will play a crucial role in determining the physics immediately following the phase transition and the behavior of the ordered phase.

Simple algebraic steps allow calculation of the entropy to quartic order (*vide supra*). However, I will postpone analysis of the full quartic free-energy functional to a later communication. This is because the results of such an analy-

sis are pertinent to the nature of the ordered phase, and would be most illuminating if comparisons could be made with experiments or Monte Carlo simulations.<sup>27</sup> In this paper, I will focus on the stability limit of the disordered phase and the nature of the structure factor in the disordered phase. The features revealed by this analysis are announcements of the nature of the ordered phase and the instability that drives a phase transition leading to partial chain collapse and microphase ordering.

In order to study the stability limit and nature of the disordered phase, I need to compute the entropy (and so, the free-energy functional) up to quadratic order only. Following the steps that I described immediately following Eq. (18), and keeping only the quadratic terms, I obtain  $S_{\text{eff}}$  to be

$$S_{\text{eff}} = -\frac{1}{2} \sum_{\alpha} \sum_k m_{\alpha}(k) m_{\alpha}(-k) - \frac{1}{4} \sum_{\alpha} \sum_k l^2 k^2 \rho_{\alpha}(k) \rho_{\alpha}(-k). \quad (19)$$

Combining Eqs. (7) and (19) obtains the replicated free-energy functional. I then take the replica symmetric solution since the order parameters of concern carry only one replica index. This obtains the following free-energy functional up to quadratic order:

$$F[m(k), \rho(k)] = \sum_k \left[ \frac{a}{2} - \frac{a'^2 \rho_0}{8} + \frac{l^2 k^2}{4} - \frac{a'^2 \chi_d(k)}{8} \right] \times \rho(k) \rho(-k) + \sum_k \left[ \frac{b}{2} - \frac{b'^2 \rho_0}{8} + \frac{1}{2} + c^2 k^2 - \frac{b'^2 \chi_d(k)}{8} \right] m(k) m(-k) - \sum_k \left[ \frac{a' b' \rho_0}{4} + \frac{a' b' \chi_d(k)}{4} \right] m(k) \rho(-k). \quad (20)$$

In writing Eq. (20), I have added a standard term to the energy which is proportional to the surface tension  $c^2$  and penalizes microphase segregation on small scales.

This free-energy functional and the form of the quartic terms [which can easily be obtained from Eqs. (17) and (18)] form the basis for my discussion of the physical behavior of the system under consideration.

## RESULTS AND DISCUSSION

Now I must choose a form for the correlation function which properly describes solvent density fluctuations. At temperatures sufficiently far away from the critical point, the correlation function that describes solvent density fluctuations is short ranged; i.e.,  $\chi_d = 0$ . In this case, Eq. (20) shows that an instability with a finite-wave vector is not possible by considering the quadratic term in the free-energy functional. In fact, I recover the quadratic term of the free-energy functional obtained earlier for linear RHPs in a single solvent<sup>21,22</sup> except for trivial renormalization of the excluded volume

and Flory parameters. This renormalization simply reduces the excluded volume parameter, and increases the propensity for microphase ordering.<sup>28</sup> The reason that an instability with a preferred length scale cannot occur in this case is that the sequence is not characterized by a natural length scale.<sup>21-23</sup>

In the vicinity of the critical point, the correlations in solvent density fluctuations decay as  $A/|\mathbf{r}-\mathbf{r}'|^{1+\eta}$ . The qualitative physical behavior can be studied by taking  $\eta$  to equal its classical value of zero; note, however, that this approximation does change the scaling exponents. With this approximation,  $\chi_d(\mathbf{k})$  equals  $A/k^2$ . Substituting this expression for  $\chi_d$  into Eq. (20), the form of the quadratic term of the free-energy functional changes dramatically. The long-range correlations between solvent density fluctuations near the critical point induce long-range attractions between all segments of the polymer. This Coulombic term which promotes chain collapse is proportional to the parameter  $a'^2$ , which measures the extent to which the entire chain (on average) prefers one solvent over another. This physics is similar to that observed for homopolymers in mixed solvents near the critical point. However, the second and third terms in the quadratic part of the free-energy functional reflect a competing effect. Long-range solvent density fluctuations also induce a Coulombic term that encourages microphase separation; i.e., a term proportional to  $b'^2$  promotes the segregation of A- and B-type segments of the heteropolymer on large scales. The parameter  $b'$  measures the extent to which particular RHP segments are preferentially solvated in a given solvent. These two long-range driving forces for chain collapse (i.e., attractions between all segments) and microphase ordering (i.e., effective repulsions between unlike segments) compete. The interplay between this competition and the constraints imposed by chain connectivity, the disordered sequence distribution, and surface tension causes a natural length scale to emerge, and an instability with a finite-wave vector becomes possible. The resulting phase transition is one where partial chain collapse is accompanied by microphase ordering. The finite-wave vector corresponding to the unstable mode is a measure of the domain size below which the system is disordered. On scales smaller than the domain size there is no microphase ordering and chain statistics are that of a SAW; on scales larger than the domain size, the chain is collapsed and microphase segregated. Thus, consideration of the concentration fluctuations in the disor-

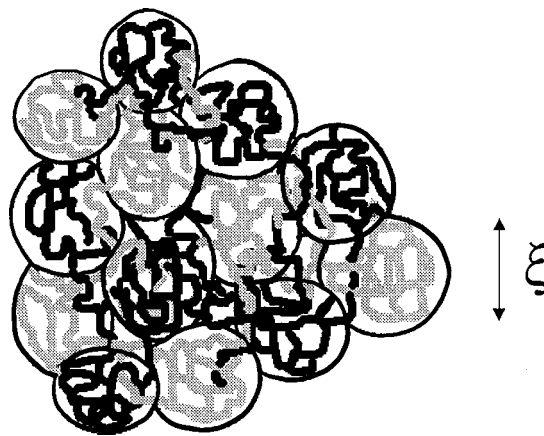


FIG. 1. Schematic representation of the ordered phase. On scales larger than  $\xi$ , the chain is collapsed and microphase ordered. Due to the disordered sequence, the domains are only predominantly (not exclusively) comprised of A- or B-type segments (represented by black or gray colors). On scales shorter than  $\xi$ , there is no microphase ordering and the conformational statistics are those of a self-avoiding walk.

dered phase suggest that the ordered phase should look like that shown schematically in Fig. 1. As I shall comment later, the nature of the ordered phase immediately following the phase transition will be strongly influenced by the quartic terms.

In order to further explore the nature of the instability at the phase transition, the domain size, and the nature of the ordered phase, let me begin by diagonalizing the matrix of quadratic coefficients in Eq. (20). The eigenvalues will provide the condition for the stability limit of the disordered phase, and the eigenvectors will shed light on the nature of the unstable concentration fluctuations that drive the phase transition.

The eigenvalues  $\lambda_1$  and  $\lambda_2$  of the matrix of quadratic coefficients in Eq. (20) are given by

$$\lambda_{1,2} = \frac{\alpha}{2} \left[ 1 \pm \sqrt{1 - \frac{4\beta}{\alpha^2}} \right], \quad (21)$$

$$\alpha(k) = \frac{4(b+1) - b'^2\rho_0 + 4a - a'^2\rho_0}{8} + \left( c^2 + \frac{l^2}{4} \right) k^2 - \frac{(a'^2 + b'^2)A}{8k^2}, \quad (22)$$

$$\beta(k) = \frac{(4(b+1) - b'^2\rho_0)(4a - a'^2\rho_0) - c^2a'^2A - 2b'^2Al^2 - a'^2b'^2\rho_0^2}{64} + \left( \frac{c^2l^2}{4} \right) k^4 + \left( \frac{(4(b+1) - b'^2\rho_0)l^2 + 4c^2(4a - a'^2\rho_0)}{32} \right) k^2 - \left( \frac{(4(b+1) - b'^2\rho_0)a'^2A + (4a - a'^2\rho_0)b'^2A + 16a'^2b'^2\rho_0A}{64k^2} \right). \quad (23)$$

The wave vector corresponding to the dominant scale over which concentration fluctuations occur is one that minimizes the smaller of the two eigenvalues in Eq. (21). The eigenvector which belongs to the smaller eigenvalue tells us the way in which fluctuations in the order parameters  $\rho$  and  $m$  must be coupled for the instability to occur. The conditions that correspond

to the phase transition can be obtained by setting the smaller eigenvalue equal to zero. Numerical solution of the equations I have derived allows all these issues to be examined as a function of various parameters. Some essential physical ideas are, however, clarified by considering certain approximations that allow analytical calculation.

The combination of parameters  $\alpha$  and  $\beta$  must be greater than zero for an instability to originate from the quadratic term of the free-energy functional. If this condition does not hold, one of the eigenvalues is always negative, and the quartic terms are needed for stability. Physically, this simply says that when there are long-range driving forces for collapse and microphase ordering due to solvent density fluctuations, and the parameters that drive both these phenomena are sufficiently large, entropic constraints due to connectivity and sequence disorder need to be considered beyond quadratic order for stability. For  $\alpha$  and  $\beta$  larger than zero,  $\lambda_2$  is the smaller eigenvalue. The optimal wave vector  $k^*$  is given by  $(\partial\lambda_2/\partial k)_{k=k^*}=0$ .

The combination of parameters  $4\beta/\alpha^2$  can vary between zero and unity. In the spirit of considering approximations that reveal the essential physics, let me focus attention on the limits which bracket this range; i.e.,  $(1-4\beta/\alpha^2)$  is either close to unity or zero. In these circumstances,  $k^*$  satisfies the equation

$$\alpha \frac{\partial\beta}{\partial k} = 2\beta \frac{\partial\alpha}{\partial k}. \quad (24)$$

Since the spatial length scale that we are concerned with is much larger than the segmental scale and much smaller than chain dimensions, roughly speaking, the meaningful range of wave vectors is  $1/N < l^2 k^2 < 1$ . For large  $N$ , this implies that terms of order  $k^5$  and higher can be ignored since  $k$  is small. Making this approximation obtains the following result for the variation of  $q^* = k^{*2}$  with different parameters:

$$q^* = \frac{A_1 B_3 - 2B_1 A_3}{6(B_2 A_3 - A_2 B_3)} \times \left[ 1 \pm \sqrt{1 + \frac{12A_3 B_3 (B_2 A_3 - A_2 B_3)}{(A_1 B_3 - 2B_1 A_3)^2}} \right], \quad (25)$$

where  $A_i$  and  $B_i$  are defined as follows:

$$\alpha = A_1 + A_2 k^2 - \frac{A_3}{k^2}, \quad (26)$$

$$\beta = B_1 + B_2 k^2 - \frac{B_3}{k^2}.$$

Plotting a leading-order approximation to Eq. (25) as a function of  $b'$  shows that for any value of  $a'$  when  $b'$  becomes sufficiently large there is a limiting domain size. This is a manifestation of the competition between the desire to collapse because the chain (on average) prefers one solvent and the desire to segregate the A- and B-type segments because of preferential solvation. The limiting domain size is

the scale below which collapse cannot occur without destroying the microphase ordering. If  $b'$  is sufficiently large, as temperature decreases near the critical point for solvent demixing, the domain size first decreases and then acquires a limiting value beyond which it cannot decrease because of the competition between the desires to collapse and microphase segregate and the constraints imposed by chain connectivity and the sequence disorder. The existence of a limiting domain size is distinct from the behavior exhibited by homopolymers in mixed solvents near criticality (*vide supra*). As is obvious, this picture obtained in the disordered phase will get further complicated immediately after the phase transition when the quartic terms that reflect the quenched fluctuations in the RHP sequence begin to play an important role (*vide infra*). Furthermore, considering heteropolymers with correlated sequence fluctuations (e.g., statistically blocky heteropolymers) will lead to interesting variations of the domain size above which the system is collapsed and microphase ordered.

The phase transition is driven by concentration fluctuations described by the unstable eigenvector that belongs to the smaller eigenvalue, and is given by

$$\frac{m}{\rho} = \left( -\frac{\Gamma_{12}}{\Gamma_{11}} \right)_{k=k^*}, \quad (27)$$

where  $\Gamma_{ij}$  are the elements of the  $2 \times 2$  matrix that constitutes the quadratic coefficient of the free-energy functional ( $1 \equiv m, 2 \equiv \rho$ ). Substituting for these matrix elements and the value of  $k^*$ , I find that the unstable mode satisfies the condition

$$\rho a' (A + k^{*2}) + m b' (A - (M/b'^2) k^{*2}) = 0, \quad (28)$$

where  $M = 4(b+1) - b'^2 \rho_0$ . For further physical insight, it is instructive to consider the nature of this unstable eigenmode in the limit where the driving force for microphase ordering due to the disparity in segment-solvent interactions greatly exceeds the propensity for microphase ordering due to the bare intersegment interactions [ $b'^2 > 4(b+1)$ ]. In this limit, the unstable mode satisfies  $\rho a' + m b' = 0$ . This says that the instability that drives the phase transition is one where the concentration fluctuations are such that the two order parameters  $\rho$  and  $m$  fluctuate with weights proportional to the parameters that drive collapse and microphase ordering, respectively. A result that is consistent with intuition.

As I have noted before, linear RHPs in a single solvent do not exhibit a scattering peak in the disordered state because the sequence does not impose a natural length scale. The same is true for linear RHPs in mixed solvents far from the critical temperature. However, near criticality, due to selective segmental solvation and long-range correlated solvent density fluctuations, a preferred length scale emerges. This should manifest itself as a scattering peak in the disordered state. Consider the following experiment. A long linear RHP (made up of A- and B-type segments) immersed in a mixture of short-A and -B homopolymers. By selective deuteration, one could carry out neutron-scattering experiments that measure the elements of the structure factor matrix which de-

scribes the correlations between the fluctuations in the densities of the RHP segments.<sup>29</sup> At temperatures sufficiently above the critical temperature for demixing of the homopolymer blend, no scattering peak should be observed. However, as the critical temperature is approached more closely, even in the disordered state, a peak should be observed. This peak is trivially related to the structure factor.

The structure factor matrix ( $\mathbf{S}$ ), which describes the correlations between the density fluctuations of different types of RHP segments, can be easily obtained from Eq. (20). A simple rotation of the  $2 \times 2$  matrix of quadratic coefficients ( $\mathbf{\Gamma}$ ) of the free-energy functional in terms of  $\rho$  and  $m$  yields the inverse of  $\mathbf{S}$ . The structure factor matrix can be easily translated to neutron-scattering intensities if the scattering lengths and segment sizes of the chemical units that make up the RHP are known. I obtain the structure factor matrix to be

$$S = \frac{1}{\beta} \begin{pmatrix} \gamma_{22} & \gamma_{12} \\ \gamma_{21} & \gamma_{11} \end{pmatrix}. \quad (29)$$

Elements of the matrix  $\gamma$  are the quadratic coefficients of the free-energy functional in terms of  $\rho_A$  and  $\rho_B$  (with  $1 \equiv A$ ,  $2 \equiv B$ ), and are given by

$$\begin{aligned} \gamma_{11} &= \frac{1}{8} \left[ (4a - a'^2 \rho_0) + 4(b+1) - b'^2 \rho_0 - 2a'b'\rho_0 \right. \\ &\quad \left. + (2l^2 + 8c^2)k^2 - \frac{(a'+b')^2 A}{k^2} \right], \\ \gamma_{12} &= \frac{1}{8} \left[ (4a - a'^2 \rho_0) - 4(b+1) + b'^2 \rho_0 + (2l^2 - 8c^2)k^2 \right. \\ &\quad \left. + \frac{(b'^2 - a'^2)A}{k^2} \right], \quad (30) \\ \gamma_{22} &= \frac{1}{8} \left[ (4a - a'^2 \rho_0) + 4(b+1) - b'^2 \rho_0 + 2a'b'\rho_0 \right. \\ &\quad \left. + (2l^2 + 8c^2)k^2 - \frac{(a'-b')^2 A}{k^2} \right]. \end{aligned}$$

Equations (29) and (30) also show the long-range attractions between like segments and repulsions between segments of the opposite type that are induced by solvent density fluctuations near the critical point. These equations allow one to plot the structure factor for the  $AA$ ,  $BB$ , or  $AB$  density fluctuations. In Fig. 2, I plot the shape of the structure factor that describes the correlations between the fluctuations in the density of A-type RHP segments. The parameters chosen to construct this plot are arbitrary except that they lead to a peak.

It is worth remarking on the shape of the structure factor displayed in Fig. 2 since it announces the nature of the ordered phase immediately after the phase transition. It decays much faster at small  $k$  than for large  $k$ . The competition between the propensity for collapse and microphase ordering leads to a preferred length scale over which segment density fluctuations are correlated. On scales larger than this length ( $k < k^*$ ), the correlations between like-type segments decays

sharply since this is the scale above which we have microphase ordering. The same physics leads to a gradual decay of these correlations on scales shorter than this preferred length ( $k > k^*$ ).

The collapsed and microphase ordered morphology that I have described above will not persist arbitrarily close to the critical point of the solvent mixture. As in the homopolymer case, once the solvent density fluctuations exceed chain dimensions the chain will reexpand and lose the microphase ordered pattern. The experimental consequence of this is that the peak in the structure factor (scattering intensity) will disappear once the critical point is approached too closely. Microphase ordering may happen again at lower temperatures driven by the bare intersegment interactions. The ordering at lower temperature may occur with a pattern opposite to that observed at higher temperatures if the parameter  $b$  is positive. The appearance of a peak in the scattering intensity as the system is cooled followed by its disappearance and possible reappearance may be amusing to observe and have practical consequences.

## CONCLUDING REMARKS

I have studied some aspects of the behavior of disordered heteropolymers with a random sequence distribution in mixed solvents near the critical point of the solvent mixture. This physical situation can perhaps be conveniently examined by experiments carried out using RHPs immersed in a binary blend of shorter homopolymers. My major finding is that the long-range correlations between solvent density fluctuations near criticality induce effective intersegment interactions that lead to a phase transition wherein partial chain collapse is accompanied by microphase ordering. On scales larger than a certain preferred length, the chain is collapsed and microphase ordered, and it is disordered on smaller scales. This is shown schematically in Fig. 1. This preferred scale manifests itself even in the disordered state. In many circumstances, the preferred domain size cannot decrease below a limiting value that is set by the competition between the desire to collapse and that to microphase segregate. I predict that as the system is cooled toward the critical point, a peak should appear in the scattering intensity. This is in stark contrast to linear RHPs in a single solvent. In this case, there is no scattering peak with a finite-wave vector in the disordered state. I also predict that the peak will disappear once the system is brought too close to criticality and the solvent density fluctuations are correlated over scales larger than coil dimensions. The unstable mode at the phase transition provides some insight into the nature of the concentration fluctuations that drive the phase transition.

Although I have not explicitly derived the quartic terms of the free-energy functional, my equations can be used to obtain these terms in a straightforward manner. In fact, their form is already clear. For example, Eqs. (17) and (18) make clear that the quartic terms proportional to the strength of the quenched fluctuations in the sequence will lead to terms that  $\sim 1/(k_1^2 + k_2^2)$ . Such quartic terms must be explicitly considered in order to study the morphology of the ordered phase and the way in which the domain size varies with tempera-

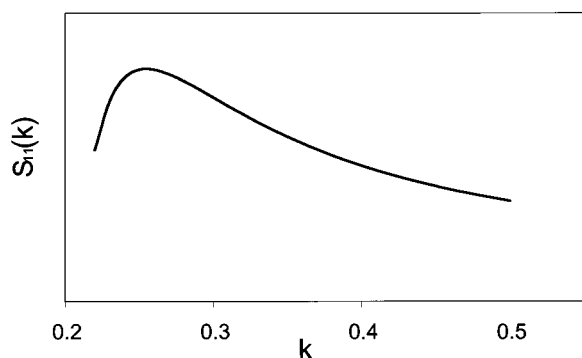


FIG. 2. Structure factor for the density fluctuations of A-type RHP segments in the disordered phase at temperatures near the critical point. The parameters used to draw this curve are:  $M = -2.5$ ,  $R = (4a - a'^2\rho_0) = 2.5$ ,  $a' = 1$ ,  $b' = -0.1$ ,  $c = 2$ ,  $1 = \rho_0 = 1$ , and  $A = 0.04$ . The units on the ordinate are arbitrary. The peak in the structure factor (scattering intensity) is predicted to be absent at high temperatures, and to disappear when the critical point is approached arbitrarily closely. A reappearance of the peak at lower temperatures is also possible due to the bare interactions.

ture (and other parameters) immediately after the phase transition. It is already clear, however, that terms  $\sim 1/(k_1^2 + k_2^2)$  will lead to strong temperature dependence of the dominant wave vector immediately after the transition. These effects will be fruitful to explore in conjunction with scattering experiments or (at the very least) simulation studies. It is my hope that such experimental and simulation studies will be carried out in the near future.

Other issues that are worth considering include the changes in the mechanical response of the solution as it is brought near the critical point, goes through the phase transition that I have described, and then becomes disordered again. Also, the dynamics of the ordering transition and fluctuation corrections are worth studying.

I have considered only the possibility of microphase ordering in this paper. Another issue that may be worth considering in the future concerns the possibility that the RHPs could undergo a phase transition wherein only a few dominant conformations determine the thermodynamics. In particular, the possibility of such freezing on scales commensurate with the domain size needs to be considered in light of the work done for correlated RHP sequences in a single solvent.<sup>30</sup> However, it is possible that this type of ordering is precluded in this case because of the long-range interactions induced by the solvent density fluctuations.

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