Integral Equation Theory of Random Copolymer Melts

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ABSTRACT: An integral equation theory is developed for the structure and thermodynamics of melts of random copolymers. The molecules are modeled as flexible chains with a random sequence of two types of sites, with square well potentials between sites. The polymer reference interaction site model (PRISM) integral equation theory is extended to random copolymers and used to calculate the static correlations and spinodal lines. For threadlike chains and with the incompressible random phase approximation (IRPA), the PRISM theory reduces to a replica field theory or Landau-type theory presented earlier by others. In this limit the theory predicts a macrophase separation for values of the monomer correlation strength, λ, greater than a critical value. For smaller values of λ a microphase separation is predicted with strong concentration fluctuations at finite wave vectors. With the hard-core interactions included, however, the predictions of the theory with different closure approximations are qualitatively different from each other. With atomic closure approximations the nature of the spinodal diagram is similar to the IRPA, although fluctuations are predicted to promote microphase separation. With molecular closure approximations the theory predicts that no microphase separation occurs in these systems and that there is a macrophase separation for all values of λ.

I. Introduction

The alloying of polymers to make new materials with tunable properties is of considerable interest. However, since the entropy of mixing of polymers is small, different species of high molecular weight polymers generally do not mix. Alloying polymers on a molecular level, where each polymer molecule consists of more than one type of monomer, has therefore been pursued extensively. This paper is concerned with random copolymers, where each molecule is composed of two types of monomers, and the sequence of monomers is random, though correlated. There are many commercially important random copolymers,[1−3] and the phase behavior of these materials has been a subject of recent interest.[4−19] We present an integral equation theory for the structure and thermodynamics of random copolymers.

The possibility of a microphase separation in random copolymers was suggested by considering the growth of concentration fluctuations on characteristic length scales manifested by a peak in the static structure factor at finite (nonzero) wave vectors.[20,21] The phase behavior can be discussed in terms of a monomer correlation length, λ, which represents the degree of blockiness in the average distribution of monomers along the backbone: $\lambda = 1$ corresponds to a blend of homopolymers, and $\lambda = -1$ corresponds to alternating A−B copolymers. Note that only macrophase separation is possible for $\lambda = 1$. If a microphase separation occurs (with decreasing temperature) for other values of λ, there must be a transition line between microphase-separated and macrophase-separated states, which implies the existence of a tricritical Lifshitz point.

Fredrickson and Milner (FM)[5] presented a replica field theory for the phase behavior of random copolymer melts with two types of monomers (denoted A and B). Using a mean-field approximation, they obtained the phase diagram of random copolymer melts from the limit of stability (spinodal line) of the mixed state. They predicted that for $\lambda > -0.28$ decreasing the temperature resulted in the growth of concentration fluctuations at zero wave vector and therefore a macrophase separation. For smaller values of λ there was a growth of concentration fluctuations at finite wave vectors with decreasing temperature, therfore resulting in a microphase separation. They therefore located a tricritical Lifshitz point for $\lambda = -0.28$. The Landau theory of Fredrickson et al.[6] makes similar predictions.

A microphase separation is expected to be a first-order phase transition similar to crystallization, and the spinodal condition corresponding to a divergence in the susceptibility at fixed wave vectors is an artifact of a mean-field approximation. Angerman et al.[14] presented a Landau theory for the microphase separation in random copolymers in the $\lambda \rightarrow 1$ limit. They predicted a third-order transition into a bcc phase and first-order transitions into hexagonal and lamellar phases. The importance of fluctuations in the theory of heteropolymers has been emphasized.[7,8,16,18,19,21−23] Angerman et al.[16] included the effect of fluctuations within the Hartree approximation. They showed that fluctuations stabilized the disordered state, but the qualitative features of the phase diagram were not significantly altered.

Microphase separation has not been observed (to our knowledge) in experiments or simulations of melts of random copolymers. Experiments have shown that melts of random block copolymers,[2,3] where each molecule consists of blocks of monomers in a random sequence, display a microphase-separated state, although the morphology of these microphase-separated states is not well established. Recently, Houdayer and Müller (HM)[18,19] presented fluctuating bond lattice simulations or random copolymers. For large values of λ they observed a macrophase separation with decreasing temperature. As the temperature was decreased further, however, they observed a transition to a mixed

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"sponge" phase. For values of λ lower than some critical value they did not observe any phase separation. The value of λ for which the system showed no phase transition became larger with increasing degree of polymerization, going from about $\lambda = 0.54$ for a chain length of $N = 5$ to $\lambda = 0.8$ for $N = 20$. They attributed this failure of mean-field theory to the importance of fluctuations. In fact, they showed, from an application of the Ginzburg criterion, that the size of the critical region *increased* with increasing degree of polymerization, emphasizing that mean-field theory became *worse* as the chain length was increased, contrary to expectations arising from conventional wisdom obtained from the study of polymer blends and diblock copolymers. A theoretical approach that can treat short chains and can also incorporate fluctuations on all length scales is therefore of considerable interest.

In this paper, we generalize the polymer reference interaction site model (PRISM) integral equation theory[25−29] to two-letter random copolymer melts. The PRISM theory has been successful in studying homopolymer melts, polymer blends, and block copolymers, providing physical insights on many problems, often with quantitative accuracy.[25,26,30] We generalize this approach to random coplymer melts by starting with an infinite component system and assuming that the correlation functions are only a function of the monomer identity. The resulting equations are identical to the PRISM equations for, e.g., diblock copolymers,[27,28] but with the appropriate intramolecular correlations calculated for random copolymers. For two-letter random copolymers this results in a set of four coupled nonlinear integral equations that can be solved iteratively. The advantage of the PRISM approach is that liquid state fluctuations on all lengths are naturally and easily incorporated. A disadvantage is that this is a theory of the *disordered* state, and the microphase separation is estimated from the growth of fluctuations at finite wave vector in the disordered liquid. First-order phase transitions are not directly obtained although, in princple, this is possible if PRISM is supplemented by, e.g., a density functional theory for ordered phases.

In the thread limit and with the incompressible random phase approximation,[26] the predictions of the PRISM theory for the spinodal lines are identical to those of the replica field theory[5] and Landau-type density functional theory.[6] When a finite hard-core interaction is incorporated between sites, different closure approximations make qualitatively different predictions for the spinodal lines. The predictions of atomic closures are qualitatively similar to the thread limit, but molecular closures[29] predict no growth of concentration fluctuations at finite wave vector, and therefore no microphase separation under any conditions, before a macrophase separation occurs. This demonstrates that not only are fluctuations important in these systems, but that their incorporation into theory is subtle. The effect of interaction between monomers, density, chain stiffness on structure, and phase transitions are also investigated.

The rest of the paper is organized as follows. The model and theory are described in section II, results are presented and discussed in section III, and summary and conclusions are presented in section IV.

II. Model and Theory

A. Molecular Model. We study a model of monodisperse two-letter (A and B) random copolymer melts considered by Fredrickson and co-workers.[5,6] Each polymer molecule is freely jointed, with a bond length of σ, has exactly N monomers each of which is either of type A or of type B. The sequence of monomers in each molecule is different and the distribution of sequences is determined by a set of bimolecular reaction rate constants, $k_{MM'}$, for the combination of a species of type M with a monomer of type M' (M, $M' \in$A, B).

In the case of two-letter AB random copolymers, this Markov step growth process is characterized by the average copolymer composition f, i.e., fraction of A monomers, and a correlation parameter λ.[5,6,18] The latter is defined as the nontrivial eigenvalue of the 2 × 2 matrix, $\mathbf{p}$, of transitional probabilities, where the element p_{AB} is the conditional probability that a monomer of type B is followed by a monomer of type A. In the steady-state approximation, p_{AB} is independent of the monomer position along the chain. The conservation of probability requires that

$$p_{\mathrm{AA}} + p_{\mathrm{BA}} = 1 \tag{1}$$

$$p_{\mathrm{AB}} + p_{\mathrm{BB}} = 1 \tag{2}$$

$$f p_{\mathrm{AA}} + (1 - f) p_{\mathrm{AB}} = f \tag{3}$$

and therefore the $\mathbf{p}$ matrix has only one degree of freedom that can be specified by λ, defined as $\lambda = p_{\mathrm{AA}} + p_{\mathrm{BB}} - 1$. Note that $-1 \le \lambda \le 1$, where the limits $\lambda = 1$ and -1 correspond respectively to a blend of homopolymers ($p_{\mathrm{AA}} = p_{\mathrm{BB}} = 1$) and a melt of alternating copolymers ($p_{\mathrm{AA}} = p_{\mathrm{BB}} = 0$). In the former case a monomer of type A (B) is always followed by another monomer of type A (B), and in the latter case a monomer is always followed by a monomer of the other type. When $\lambda = 0$, all elements of $\mathbf{p}$ are equal to 0.5. This happens when the product of two relative reactivity ratios, $r_1 = k_{\mathrm{AA}}/k_{\mathrm{BA}}$ and $r_2 = k_{\mathrm{BB}}/k_{\mathrm{AB}}$, is close to one and is referred to as an ideal random copolymer. As λ decreases, the degree of "blockiness" decreases. Note that this model does not reduce to a diblock copolymer in any limit.

A square-well interaction potential is used between all pairs of monomers. The interaction potential $V_{MM'}(r)$ between monomers of type M and M' is given by

$$\begin{aligned} \beta V_{MM'}(r) &= \infty, \quad 0 < r < d \\ \beta V_{MM'}(r) &= \beta \epsilon_{MM'}, \quad d < r < 2\sigma \\ \beta V_{MM'}(r) &= 0, \quad r > 2\sigma \end{aligned} \tag{4}$$

where M and M' denote types of monomers, A and B, d is the hard sphere diameter of a monomer, 2σ is the well width, and β is $1/k_{\mathrm{B}}T$, where k_{B} is Boltzmann's constant and T is the temperature. For all numerical calculations we set $d = \sigma$. The exception is studies of the so-called thread model where $d \to 0$, but the well width is still σ. We set our length scale by choosing $\sigma = 1$. We choose ϵ_{AB} ($=\epsilon_{\mathrm{BA}}$) to be positive and ϵ_{AA} ($=\epsilon_{\mathrm{BB}}$) to be negative so that like monomers attract each other and unlike monomers repel each other. We characterize the strength of the interaction using the parameter $\epsilon \equiv -(\epsilon_{\mathrm{AA}} + \epsilon_{\mathrm{BB}} - 2\epsilon_{\mathrm{AB}})/2$ (note that $\epsilon > 0$). For most studies in this work, we use the set $\{\epsilon_{\mathrm{AA}}, \epsilon_{\mathrm{AB}}, \epsilon_{\mathrm{BB}}\} = \{0, 1, 0\}$.

B. Integral Equation Theory. It is important to note that there is no quenched disorder in the system in the thermodynamic limit (when the number of molecules tends to infinity). Although the sequence in each chain is fixed, in the thermodynamic limit each possible species is present a macroscopic number of times in the mixture. Since the polymers are free to move, no local property is frozen and there is no quenched disorder, as has been noted previously.[4,18,19] The melt of random copolymers can therefore be conveniently treated as a mixture of many species by specifying their compositions. One complication is that when the degree of polymerizations of chains is very large, the number of possible sequences can be much larger than Avogadro's number, N_{av}, e.g., $N_{\mathrm{av}} \ll 2^N$ for $N \geq 100$. In this case, every sequence is not present many times even in a macroscopic system, and the system may be considered to be quenched in this respect. From a practical standpoint, if this type of quenchedness were important, then results for experimental observables would vary from sample to sample. Such a variation is expected to be small and is certainly not reported in experiments. This is not important from the standpoint of liquid state theory because integral equations are derived from the partition function in the grand canonical ensemble, and the above issue does not arise.

From a theoretical standpoint, it appears that the microphase separation predicted in conditions where the spinodal condition points to a macrophase separation does not depend on whether the system is treated as quenched or annealed.[14] At the level of second correlators, theories that perform quenched averages using the replica trick[5,8] give identical results to those that perform annealed averages.[6,14] It has also been pointed out[31] that annealed averaging for multicomponent systems is equivalent to replica quenched averaging at the level of fourth correlators. The qualitative phase behavior is therefore expected to be independent of whether the system is treated as quenched or annealed.

To derive the integral equations for a random copolymer melt, we start with the PRISM equation for a multicomponent mixture of 2^N components, obtained by each choice (A or B) for each monomer. Of course, not all of these sequences are distinct. In fact, there are $2^{N-1} + 2^{[N/2]-1}$ distinct sequences, where $[x]$ is the smallest integer greater than or equal to x. Given two parameters, f and λ, however, the set of number densities of each species, $\{\rho^m, m = 1, ..., 2^N\}$ can be obtained. For this mixture, the set of PRISM equations can be written as (in Fourier space)

$$\hat{h}^{ij}_{\alpha\beta}(k) = \sum_{n=1}^{N}\sum_{l=1}^{N}\hat{\omega}^{i}_{\alpha n}(k)\hat{C}^{ij}_{nl}(k)\hat{\omega}^{j}_{l\beta}(k) + \sum_{m=1}^{2^N}\sum_{n=1}^{N}\sum_{l=1}^{N}\rho^m\hat{\omega}^{i}_{\alpha n}(k)\hat{C}^{im}_{nl}(k)\hat{h}^{mj}_{l\beta}(k) \quad (5)$$

where the carets denote Fourier transforms, k is the momentum transfer variable, $C^{ij}_{kl}(r)$ and $h^{ij}_{\alpha\beta}(r)$ are the site–site direct and total correlation functions, respectively, between a site α of the ith molecule and a site β of the jth molecule, and $\omega^{i}_{\alpha\beta}(r)$ is the normalized intramolecular probability distribution function between site α and site β on molecule i. The above set of equations includes the usual PRISM approximations, such as the neglect of end effects. This is a set of coupled nonlinear equations of order N^2, and it is technically intractable to solve analytically or numerically.

To make RISM integral equations feasible, we invoke the approximation that site–site direct and total correlation functions are independent of sites and sequences and depend only on the chemical identity of the monomers, i.e.

$$C^{ij}_{kl}(r) = C_{MM'}(r) \quad (6)$$

$$h^{ij}_{kl}(r) = h_{MM'}(r) \quad (7)$$

where M is the type of the kth monomer of molecule i and M' is the type of the lth monomer of molecule j. Averaging the PRISM equations over all the species then gives us a set of simplified integral equations.

The first step is to sum the PRISM equation over all monomers of the same type. To illustrate the procedure, we first sum the first term of the right-hand side of the RISM equation over the same types of monomers along the chain. If $\alpha \in M$, $\beta \in M'$, and P^i_M is the number of monomers of type M in the ith sequence, then

$$\sum_{\alpha=1}^{P^i_M}\sum_{\beta=1}^{P^j_{M'}}\sum_{k=1}^{N}\sum_{l=1}^{N}\hat{\omega}^{i}_{\alpha k}\,\hat{C}^{ij}_{kl}\,\hat{\omega}^{j}_{l\beta} = \frac{1}{\rho^i\rho^j}\sum_{X,Y\in\{A,B\}}\hat{\Omega}^{i}_{MX}\,\hat{C}_{XY}\hat{\Omega}^{j}_{YM'} \quad (8)$$

where

$$\hat{\Omega}^{i}_{MM'} = \rho^i\sum_{\alpha=1}^{P^i_M}\sum_{\beta=1}^{P^j_{M'}}\hat{\omega}^{i}_{\alpha\beta} \quad (9)$$

is the single chain structure function of polymers of ith sequence averaged over monomers. A similar manipulation of the second term gives

$$\sum_{\alpha=1}^{P^i_M}\sum_{\beta=1}^{P^j_{M'}}\sum_{m=1}^{2^N}\sum_{k=1}^{N}\sum_{l=1}^{N}\rho^m\hat{\omega}^{i}_{\alpha k}\,\hat{C}^{im}_{kl}\,\hat{h}^{mj}_{l\beta} = \frac{1}{\rho^i}\sum_{m=1}^{2^N}\rho^m\sum_{X,Y\in\{A,B\}}\hat{\Omega}^{i}_{MX}\hat{C}_{XY}\hat{h}^{j}_{YM'}P^{j}_{M'}P^{m}_{Y} \quad (10)$$

The left-hand term of the PRISM equation becomes

$$\sum_{\alpha=1}^{P^i_M}\sum_{\beta=1}^{P^j_{M'}}\hat{h}^{ij}_{\alpha\beta} = P^i_M\,P^j_{M'}\hat{h}_{MM'} \quad (11)$$

We now average over all the sequences, $i = 1, ..., 2^N$, with each weighted according to its statistical weight. This gives

$$\sum_{i}^{2^N}\sum_{j}^{2^N}\rho^i\rho^jP^i_M\,P^j_{M'}\hat{h}_{MM'} = \rho_M\rho_{M'}\hat{h}_{MM'} = \sum_{X,Y\in\{A,B\}}(\hat{\Omega}_{MX}\hat{C}_{XY}\hat{\Omega}_{YM'} + \rho_M\rho_{M'}\hat{\Omega}_{MX}\hat{C}_{XY}\hat{h}_{MM'}) \quad (12)$$

where $\rho_M = \sum_i^{2^N}\rho^iP^i_M$ is the number density of monomers of type M and

$$\hat{\Omega}_{MM'} = \sum_{i}\rho^i\sum_{\alpha=1}^{P^i_M}\sum_{\beta=1}^{P^j_{M'}}\hat{\omega}^{i}_{\alpha\beta} \quad (13)$$

is single chain structure function averaged over all pairs of monomers and all sequences.

The PRISM equations can be written compactly in matrix form as

$$\hat{\mathbf{H}} = \hat{\mathbf{\Omega}}\hat{\mathbf{C}}\hat{\mathbf{\Omega}} + \hat{\mathbf{\Omega}}\hat{\mathbf{C}}\hat{\mathbf{H}} = [\mathbf{I} - \hat{\mathbf{\Omega}}\hat{\mathbf{C}}]^{-1}\hat{\mathbf{\Omega}}\hat{\mathbf{C}}\hat{\mathbf{\Omega}} \qquad (14)$$

where $\hat{\mathbf{H}}$, $\hat{\mathbf{C}}$, and $\hat{\mathbf{\Omega}}$ are matrices of Fourier transforms of the total, direct, and intramolecular correlation functions, respectively, with the elements of the $\hat{\mathbf{H}}$ matrix given by $\hat{H}_{MM'}(k) = \rho_M\rho_{M'}\hat{h}_{MM'}(k)$. Equation 14 takes the same form as the PRISM equations for blends and diblock copolymers.[25,27,28] Given expressions for $\hat{\Omega}_{MM'}(k)$, and another closure relation between the total and direct correlation functions, the PRISM equations can be solved for the pair correlation functions and hence the thermodynamic properties. The static structure factor matrix $\hat{\mathbf{S}} = [\mathbf{I} - \hat{\mathbf{\Omega}}\hat{\mathbf{C}}]^{-1}\hat{\mathbf{\Omega}}$ is a 2 × 2 matrix whose elements are partial static structure factors, $\hat{S}_{MM'}(k)$.

C. Intramolecular Correlations. The elements of the $\hat{\mathbf{\Omega}}$ matrix can be written as

$$\hat{\Omega}_{MM'}(k) = \rho_{\mathrm{pol}}\langle\sum_{\alpha\in M}\sum_{\beta\in M'}\hat{\omega}^{m}_{\alpha\beta}(k)\rangle \qquad (15)$$

where $\langle\cdots\rangle$ denotes averaging over possible sequences and ρ_{pol} is the total number density of polymer molecules. To calculate $\hat{\Omega}_{MM'}(k)$, we first estimate the probability that two sites α and β on a chain are of type M and M', multiply this by the single chain structure factor for two sites a distance $\tau = |\alpha - \beta|$ apart along the chain backbone, and then sum over all α and β. The probability that a site α and a site β are of species M and M', respectively, is denoted $P_{MM'}(\tau)$ and is equal to the corresponding element of the 2 × 2 matrix $\mathbf{P}(\tau)$, where

$$\mathbf{P}(\tau) = \mathbf{p}^{\tau}\begin{pmatrix} f & 0 \\ 0 & 1-f \end{pmatrix}$$

Therefore, for a given chain, the probability that two monomers of type M and M' are at a distance τ along the backbone is equal to $2(N-\tau)P_{MM'}(\tau)$.

The elements of the single chain structure factor matrix can therefore be written as

$$\hat{\Omega}_{MM'} = 2\rho_{\mathrm{pol}}\sum_{\tau=1}^{N-1}\hat{s}_{\tau}(k)(N-\tau)P_{MM'}(\tau) + \rho_{\mathrm{pol}}NP_{MM'}(\tau=0) \qquad (16)$$

where $\hat{s}_{\tau}(k)$ is the Fourier transform of the intramolecular distribution between monomers separated by τ along the chain backbone. Note that $\hat{\mathbf{\Omega}}$ can be exactly evaluated using the three parameters ρ_{pol}, f, and λ. After some manipulation we obtain

$$\rho_{\mathrm{pol}}^{-1}\hat{\mathbf{\Omega}} = 2\sum_{\tau=1}^{N-1}(N-\tau)\hat{s}_{\tau}\hat{\mathbf{N}}\begin{pmatrix} \lambda^{\tau} & 0 \\ 0 & 1 \end{pmatrix}\hat{\mathbf{N}}^{-1}\begin{pmatrix} f & 0 \\ 0 & 1-f \end{pmatrix} + N\begin{pmatrix} f & 0 \\ 0 & 1-f \end{pmatrix} \qquad (17)$$

where $\hat{\mathbf{N}}$ is the normalized eigenmatrix of $\mathbf{p}$.

In this work, we invoke the ideality hypothesis and obtain the intramolecular distribution function, $\hat{s}_{\tau}(k)$, from a model of an isolated chain without excluded-volume interactions. We consider two such models: a Gaussian chain and via the discrete Koyama distribution for the semiflexible chain.[32] In the Gaussian chain model $\hat{s}_{\tau}(k) = \exp(-k^2\tau^2/6)$. In the semiflexible chain model, there is a bending energy on each bond given by $E_{\mathrm{B}} = \epsilon_{\mathrm{bend}}(1 + \cos\theta)$ where θ is the bond angle. As ϵ_{bend} is increased, the chains become stiffer. The single chain structure $\hat{s}_{\tau}(k)$ can be conveniently calculated using the discrete Koyama distribution,[32] with the intramolecular distribution calculated exactly for $\tau = 2$. For $\epsilon_{\mathrm{bend}} = 0$, this model provides an accurate estimate for the intramolecular structure of flexible freely jointed chains.

D. Closure Relations. For a fluid interacting via only a hard-core potential, the Percus–Yevick (PY) closure is known to be accurate for the pair correlation functions, when tested by comparison to simulation results. In this approximation, the exact core condition, $g^{(0)}_{MM'}(r) = 0$, for $r < d$ is supplemented with the approximation $C^{(0)}_{MM'}(r) = 0$, for $r > d$, where the superscript (0) denotes hard core, and $g_{MM'}(r) = 1 + h_{MM'}(r)$. In the mean spherical approximation (MSA), the exact condition $g_{MM'}(r) = 0$, for $r < d$ is supplemented with the approximation $C_{MM'}(r) = -\beta V_{MM'}(r)$, for $r > d$. Note that for hard chain polymers the MSA is identical to the PY closure. The MSA is accurate for the structure and thermodynamics of homopolymer melts and simple liquids but has been shown to be in qualitative error for the structure of polymer blends and for the thermodynamics of polymer blends when the compressibility route is used to calculate the thermodynamic properties.

To overcome the shortcomings of atomic closures such as the MSA, Schweizer and Yethiraj[29] developed molecular closure approximations which have been shown to be accurate for the thermodynamics of polymer blends and copolymers. All molecular closures take the form

$$[\mathbf{\Omega}^*\mathbf{C}^*\mathbf{\Omega}]_{MM'}(r) = [\mathbf{\Omega}^*\mathbf{C}^{(0)}{}^*\mathbf{\Omega}]_{MM'}(r) + [\mathbf{\Omega}^*\Delta\mathbf{C}^*\mathbf{\Omega}]_{MM'}(r), \quad r > d$$

where the asterisks denote matrix multiplications and convolutions in r-space. The hard-chain correlation functions $C^{(0)}_{MM'}(r)$ and $h^{(0)}_{MM'}(r)$ are obtained by solving the PRISM equations with the PY closure. Different molecular closures result from different choices for $\Delta\mathbf{C}$. The molecular closure for $r > d$ is combined with the exact hard-core condition, $g_{MM'}(r < d) = 0$.

We investigate three molecular closure approximations in this work: the reference molecular mean spherical approximation (R-MMSA), the linearized reference molecular Percus–Yevick (linearized R-MPY), and the linearized R-MPY with the high-temperature approximation (linearized R-MPY/HTA). The R-MMSA is the natural extension of the mean spherical approximation (MSA) to molecular liquids. This closure is given by

$$\Delta C_{MM'}(r) = -\beta V_{MM'}(r) \qquad (18)$$

A similar extension of the PY closure would result in

$$\Delta C_{MM'}(r) = [1 - \mathrm{e}^{\beta V_{MM'}(r)}]g_{MM'}(r) \qquad (19)$$

and this closure is referred to as the reference molecular Percus–Yevick closure (R-MPY). The R-MPY closure has convergence problems at low temperatures and is difficult to implement. The linearized R-MPY closure is given by

$$\Delta C_{MM'}(r) = -\beta V_{MM'}(r)g_{MM'}(r) \qquad (20)$$

where the exponent has been linearized. The high-temperature approximation to the linearized R-MPY closure is obtained by setting $g_{MM'}(r) \approx g^{(0)}_{MM'}(r)$ which results in the linearized R-MPY/HTA closure

$$\Delta C_{MM'}(r) = -\beta V_{MM'}(r) g^{(0)}_{MM'}(r) \tag{21}$$

E. Numerical Implementation. The PRISM equations with MSA and molecular closures are solved via Picard iteration using the fast Fourier transform (FFT). The correlation functions are discretized in r-space. We use 4096 points and a spacing in r-space of 0.02 or 0.04. To check our calculations, we also use 2048 and 8192 points in the FFT for some cases. In the case of the MSA closure, we first obtain initial guesses for functions $\gamma_{MM'}(r) = h_{MM'}(r) - C_{MM'}(r)$ and calculate $C_{MM'}(r)$ using the closure relation. The Fourier transforms $\hat{C}_{MM'}(k)$ are obtained using the FFT, and new estimates for $\hat{\gamma}_{MM'}(k)$ are obtained using the PRISM equations. The next guess for $\gamma_{MM'}(r)$ is then obtained via an inverse FFT. To ensure convergence, it is sometimes necessary to mix the new γ functions with old values. The procedure for the molecular closures is similar, except that we iterate over the functions $\Gamma_{MM'}(r) = h_{MM'}(r) - [\mathbf{\Omega}^*\mathbf{C}^*\mathbf{\Omega}]_{MM'}(r)$ and calculate $[\mathbf{\Omega}^*\mathbf{C}^*\mathbf{\Omega}]_{MM'}(r)$ from the closure relations. Note that for the thread model with the R-MMSA the closure gives the direct correlation $C_{MM'}(r) = C^{(0)}_{MM'}(r) - \beta V_{MM'}(r)$. This $C_{MM'}(r)$ is inserted into PRISM equations to obtain the static structure factor matrix $\hat{\mathbf{S}}$; i.e., no iteration is necessary.

Two types of phase transitions are predicted by the theory, i.e., macrophase and microphase transitions. For the macrophase transition, we obtain the phase boundary from the spinodal condition, where the partial structure factors diverge, i.e., where $\det|\mathbf{I} - \hat{\mathbf{\Omega}}\hat{\mathbf{C}}| = 0$. In practice, $\det|\mathbf{I} - \hat{\mathbf{\Omega}}\hat{\mathbf{C}}|$ is calculated for a series of temperatures, and the temperature where it goes to zero is found by extrapolation. For the microphase transition boundary we use the empirical recipe suggested by Guenza and Schweizer.[22] In mean-field theory, the structure factors have a peak at finite wave vectors, k^*. The amplitude of this peak grows with decreasing temperature and diverges for $T \equiv T_{\mathrm{MF}}$. In the PRISM theory, fluctuations prevent this divergence in the scattering function. A first-order phase transition to a microphase-separated state might be present but cannot be predicted by a theory for the disordered state. Guenza and Schweizer suggested an empirical recipe that is depicted in Figure 1. The solid line is the prediction of PRISM with the MSA closure for $\hat{S}^{-1}_{\mathrm{AA}}(k^*)$ where k^* is the wave vector at which there is a peak in $\hat{S}_{\mathrm{AA}}(k)$). The dashed line is a tangent drawn at high temperatures and intercepts the abscissa at the inverse reduced temperature $\beta\epsilon_{\mathrm{MF}}$. The order−disorder temperature (ODT) is estimated by extrapolating a tangent drawn through the $\hat{S}^{-1}_{\mathrm{AA}}(k)$ curve at $\beta\epsilon_{\mathrm{MF}}$ to $\hat{S}^{-1}_{\mathrm{AA}}(k^*) = 0$. This definition of the ODT is arbitrary but reasonable and has been motivated in a convincing fashion previously.[22]

III. Results and Discussion

Unless otherwise noted, the energy parameters are chosen to be $\epsilon_{\mathrm{AA}} = \epsilon_{\mathrm{BB}} = 0$ and $\epsilon_{\mathrm{AB}} = \epsilon_{\mathrm{BA}} = \epsilon > 0$, $f = 1/2$, and the monomer density is fixed at $\rho_{\mathrm{mon}}\sigma^3 = 1$, where $\rho_{\mathrm{mon}} = N\rho_{\mathrm{pol}}$. For a given value of λ, as the temperature is decreased, i.e., $\beta\epsilon$ ($\sim 1/T$) is increased, the random copolymer melt can undergo a phase transition. This is manifested by a growth in the partial structure factors.

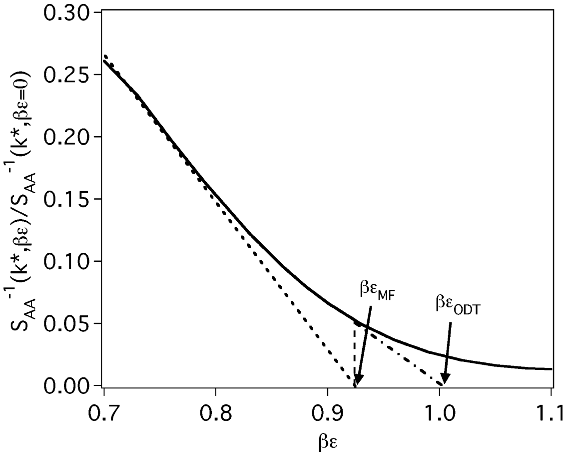

Figure 1. Example of inverse peak scattering function from the PRISM theory with the MSA closure with definitions of $\beta\epsilon_{\mathrm{MF}}$ and $\beta\epsilon_{\mathrm{ODT}}$.

When a macrophase separation is approached, the partial structure factors grow at zero wave vector, and when a microphase separation is approached, the partial structure factors grow at finite wave vector. We estimate the phase boundary from the compressibility route; i.e., we report spinodal lines.

In the $d \rightarrow 0$ thread limit, with post facto imposition of incompressibility, and with some other approximations that are exact in the $N \rightarrow \infty$ limit, the PRISM theory reduces to the replica field theory of Fredrickson and Milner (FM).[5] To derive this result, we first assume that the Gaussian approximation can be used for the intramolecular correlation functions and use the R-MMSA closure, which in the thread limit reduces to $C_{MM'}(r) = C^{(0)}_{MM'}(r) - \beta V_{MM'}(r)$. For the symmetric model, $C^{(0)}_{MM'}(r)$ is independent of species, i.e., $C^{(0)}_{MM'}(r) = C^{(0)}(r)$ for all M and M'. The spinodal condition, $\det|\mathbf{I} - \hat{\mathbf{\Omega}}\hat{\mathbf{C}}| = 0$, is

$$1 - \hat{\Omega}_{\mathrm{AA}}\hat{C}_{\mathrm{AA}} - (\hat{\Omega}_{\mathrm{AB}} + \hat{\Omega}_{\mathrm{BA}})\hat{C}_{\mathrm{AB}} - \hat{\Omega}_{\mathrm{BB}}\hat{C}_{\mathrm{BB}} + (\hat{\Omega}_{\mathrm{AB}}\hat{\Omega}_{\mathrm{BA}} - \hat{\Omega}_{\mathrm{AA}}\hat{\Omega}_{\mathrm{BB}})(\hat{C}_{\mathrm{AB}}\hat{C}_{\mathrm{BA}} - \hat{C}_{\mathrm{AA}}\hat{C}_{\mathrm{BB}}) = 0 \tag{22}$$

With the R-MMSA closure, $\hat{C}_{\mathrm{AA}} = \hat{C}_{\mathrm{BB}} = C_0$, where C_0 is independent of temperature, and $\hat{C}_{\mathrm{AB}} = \hat{C}_{\mathrm{BA}} = -\beta\hat{V}_{\mathrm{AB}}$. If we impose the incompressibility constraint, i.e., $-\rho_{\mathrm{mon}}C_0 \gg 1$, following David and Schweizer,[27] we obtain

$$\frac{\hat{\Omega}_{\mathrm{AA}} + \hat{\Omega}_{\mathrm{BB}} + \hat{\Omega}_{\mathrm{BA}} + \hat{\Omega}_{\mathrm{AB}}}{\hat{\Omega}_{\mathrm{AA}}\hat{\Omega}_{\mathrm{BB}} - \hat{\Omega}_{\mathrm{BA}}\hat{\Omega}_{\mathrm{AB}}} - 2\chi = 0 \tag{23}$$

where we have defined $\chi \equiv -\rho_{\mathrm{mon}}\hat{V}_{\mathrm{AB}}$. We refer to this approximation as the thread model with the incompressible random phase approximation (IRPA) as has been suggested previously.[22,27] For Gaussian chains, in the limit of large N and $k^2\sigma^2/\ll 1$, eq 23 reduces to

$$G_2^{-1}(k^2\sigma^2/6) - 2\chi = 0 \tag{24}$$

where

$$G_2(x) = f(1-f)\left(\frac{2(x - 1 + \mathrm{e}^{-x})}{x^2} + \frac{2\lambda(1 - \mathrm{e}^{-x})^2/x^2}{1 - \lambda\mathrm{e}^{-x}}\right) \tag{25}$$

This condition is identical to the result from the FM

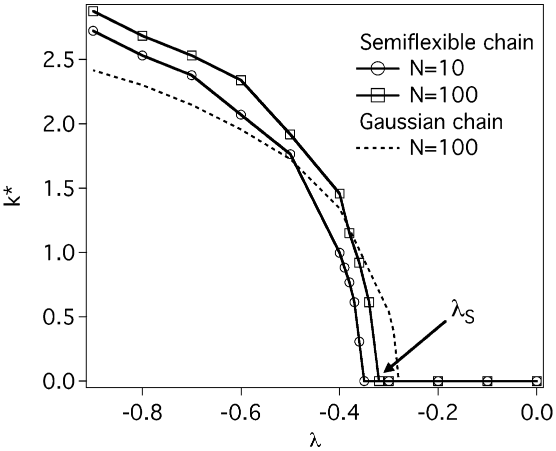

Figure 2. PRISM predictions for the position of the peak in the partial structure factors (denoted k^*) as a function of λ for various N with the single chain structure obtained using either the Gaussian chain model or the semiflexible chain model.

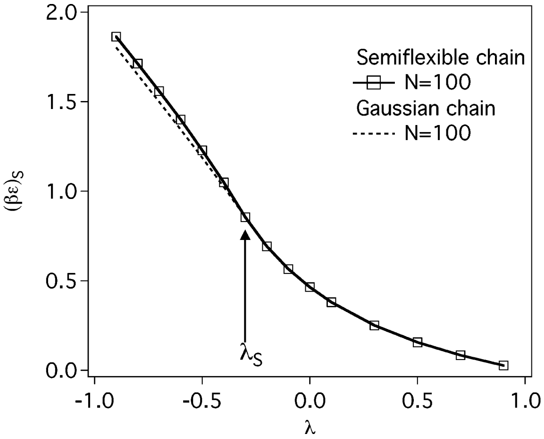

Figure 3. PRISM predictions for the spinodal lines as a function of λ for threadlike polymers with the IRPA. Single chain structure factors are calculated using semiflexible chain (with zero bending energy) or the Gaussian chain model.

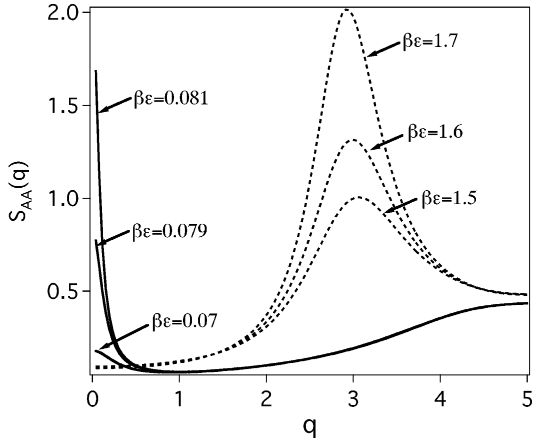

Figure 4. PRISM predictions for the partial structure factor as a function of inverse reduced temperature for $\lambda = -0.9$ with the MSA (dashed lines) and linearized R-MPY (solid lines) closure. Note the growth in concentration fluctuations at finite wave vector with the MSA closure that is absent with the linearized R-MPY closure.

mean-field theory.[5] This result is analogous to previous PRISM results for blends[25] and diblock copolymers.[22,27,28] Interestingly, eq 24 can also be derived by invoking the literal random phase approximation, i.e., $C_{MM'}(r) = -\beta V_{MM'}(r)$.

Numerical results using the incompressible R-MMSA in the thread limit, i.e., eq 23, show that PRISM predictions in this limit are very similar to those of FM,[5] with small differences. Figure 2 depicts the position of the peak in $\hat{S}_{AA}(k)$ (denoted k^*) as a function of λ for two chain models (Gaussian chain and semiflexible chain with zero bending energy) and various chain lengths. For λ greater than some value, which we call λ_S, $k^* = 0$, i.e., the partial structure factors show a prominent peak at zero wave vector corresponding to macrophase separation. For $\lambda < \lambda_S$, k^* increases monotonically as λ is decreased, suggesting that fluctuations grow on shorter and shorter length scales. The chain length dependence is quite weak, and results for $N = 1000$ are almost identical to those shown for $N = 100$. The qualitative behavior is similar for semiflexible and Gaussian chains. For $N = 100$, the value of λ_S is slightly higher for Gaussian chains (where $\lambda_S = -0.28$) when compared to semiflexible chains (where $\lambda_S = -0.3$). These values may be compared to the value of $\lambda_S = -0.268$ predicted by FM,[5] i.e., eq 24. Furthermore, the value of k^* increases less rapidly for Gaussian chains than for semiflexible chains. The predictions are quite similar for both models and similar to the predictions of FM.[5]

Figure 3 depicts the inverse spinodal temperature, $(\beta\epsilon)_S$, as a function of λ for $N = 100$ and for Gaussian and semiflexible chains. When λ is very close to 1, individual chains are similar to homopolymers, and the copolymer melt is similar to a blend of homopolymers. The system undergoes a macrophase separation into two phases at quite high temperature (low $\beta\epsilon$). As λ decreases from 1, a random copolymer melt shows a macrophase separation at lower temperature, which means that at the same temperature random copolymer chains with smaller λ are mixed better and more compatible with other chains. When a melt with $\lambda < \lambda_S$ reaches $(\beta\epsilon)_S$, it undergoes a microphase separation as described earlier. The phase diagram is similar for semiflexible chains and Gaussian chains. For the thread model with the IRPA, the χ parameter is given by $\chi = -\rho_{\text{mon}}(4\pi/3)\beta\epsilon$, and $\chi_S = 1.94$ for $\lambda = 0$. This is very close to the prediction of the Landau density functional theory of Fredrickson et al.[6] Note that the point at λ_S is expected to be a tricritical (Lifshitz) point because one expects a line of transitions separating the microphase-separated states for $\lambda < \lambda_S$ from the macrophase-separated states for $\lambda > \lambda_S$. Since PRISM does not converge for temperatures below the spinodal temperature, it cannot shed light on the existence of this tricritical point.

The predictions of the theory for the spinodal lines are drastically different with different closure approximations. Atomic closures predict both macrophase and microphase separation, but molecular closures predict only macrophase separation for all values of λ. In fact, with the molecular closures, there is no growth in scattering at nonzero wave vectors for any value of λ. (There is, of course, a hard sphere peak at $2\pi/d$.) We compare theoretical predictions for semiflexible chains with excluded volume, i.e., $d = \sigma$ and $N = 100$. Figure 4 depicts the partial structure factor as a function of inverse reduced temperature for $\lambda = -0.9$ with the (atomic) MSA and (molecular) linearized R-MPY closures. With the MSA closure, there is a peak in $\hat{S}_{AA}(k)$ at finite wave vectors with decreasing temperature (increasing $\beta\epsilon$). With the linearized R-MPY closure,

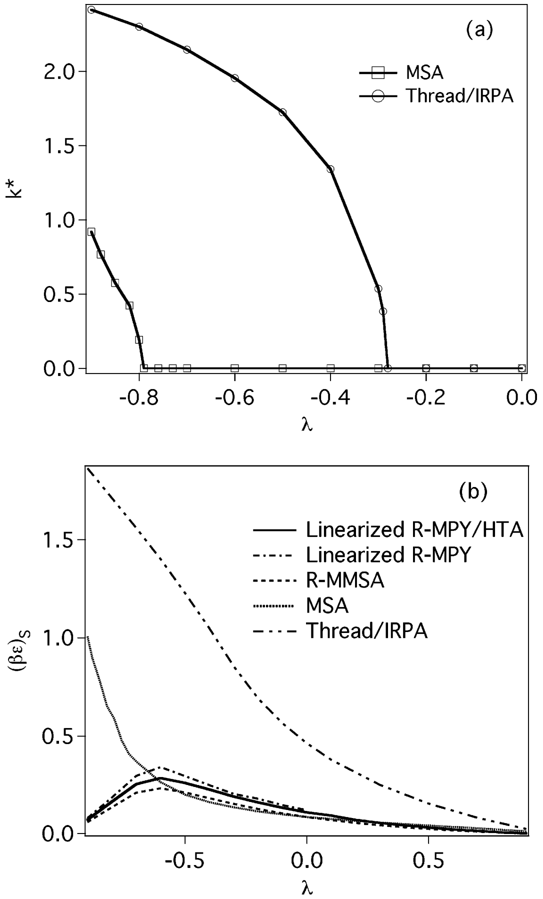

Figure 5. PRISM predictions for the (a) peak wave vector and (b) spinodal lines as a function of λ for molecular closures (R-MMSA, linearized R-MPY, and linearized R-MPY/HTA) and an atomic closure (MSA), for $N = 100$ and $\rho_{\mathrm{mon}}\sigma^3 = 1$. Also shown are the predictions of the thread model with the IRPA.

however, there is no peak in $\hat{S}_{\mathrm{AA}}(k)$ at finite wave vectors at all.

Parts a and b of Figure 5 depict predictions of the atomic MSA and three molecular (R-MMSA, linearized R-MPY, and linearized R-MPY/HTA) closures for the peak wavevector and spinodal temperature, respectively, as a function of λ. For comparison, the predictions of the theory in the thread limit with the IRPA are also shown. The most striking result is that $k^* = 0$ for molecular closures for all values of λ. The molecular closures predict that there is no microphase separation in random copolymers melts and that macrophase separation occurs for all values of λ! The atomic closure makes predictions that are qualitatively similar to the thread/IRPA model; i.e., there is a macrophase separation for $\lambda > \lambda_{\mathrm{S}}$ and a microphase separation for $\lambda < \lambda_{\mathrm{S}}$, but the value of λ_{S} is very different; $\lambda_{\mathrm{S}} = -0.8$ for the atomic closure whereas $\lambda = -0.3$ for the thread model with the IRPA. The domain period is also much larger in the atomic closures than for the thread (i.e., value of k^* is smaller for a given λ).

An intriguing prediction of the molecular closures is that the spinodal value of $\beta\epsilon$ actually shows a maximum as a function of λ. We verify that this maximum for $\lambda = \lambda_{\max}$ is not an artifact of the particular state points considered and that this is not a liquid−vapor spindoal condition. The predictions of the closures for a reduced density of $\rho_{\mathrm{mon}}\sigma^3 = 0.57$ are almost identical to those of Figure 5b if $\rho_{\mathrm{mon}}(\beta\epsilon)$ is plotted against λ. In addition, the predictions of the theory for $\{\epsilon_{\mathrm{AA}}, \epsilon_{\mathrm{AB}}, \epsilon_{\mathrm{BB}}\} = \{-0.5, 0.5, -0.5\}$ and $\{\epsilon_{\mathrm{AA}}, \epsilon_{\mathrm{AB}}, \epsilon_{\mathrm{BB}}\} = \{-1, 0, -1\}$ are virtually identical to those shown in Figure 5b. We also verify that the spinodal does not correspond to a liquid−vapor transition; i.e., in all cases the compressibility remains finite and small. The phase diagram is also insensitive to N for $N \geq 100$. It therefore appears that this phase diagram is a robust prediction of the theory.

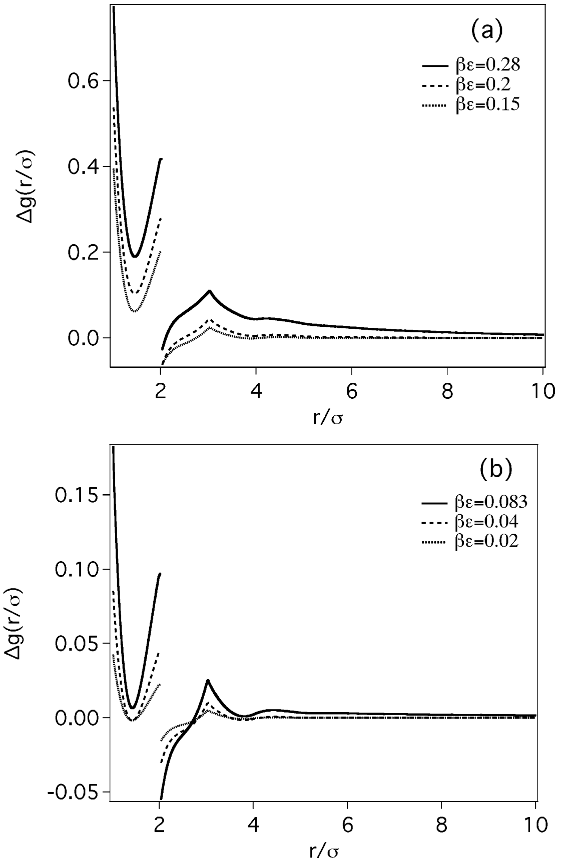

Figure 6. PRISM predictions with the linearized R-MPY closure for the concentration fluctuation pair correlation function, $\Delta g(r) \equiv g_{\mathrm{AA}}(r) + g_{\mathrm{BB}}(r) - 2g_{\mathrm{AB}}(r)$, for $N = 100$, $\rho_{\mathrm{mon}}\sigma^3 = 1$, and various values of $\beta\epsilon$ (as marked): (a) $\lambda = -0.5$ and (b) $\lambda = -0.9$.

The nature of the phase transition is different for $\lambda < \lambda_{\max}$ than it is for $\lambda > \lambda_{\max}$. Parts a and b of Figure 6 depict the concentration fluctuation pair correlation function, $\Delta g(r) \equiv g_{\mathrm{AA}}(r) + g_{\mathrm{BB}}(r) - 2g_{\mathrm{AB}}(r)$, for $N = 100$, $\rho_{\mathrm{mon}}\sigma^3 = 1$, and various values of $\beta\epsilon$ and for $\lambda = -0.5$ and -0.9, respectively. For $\lambda = -0.5$, the variation of $\Delta g(r)$ with increasing $\beta\epsilon$ is as one expects near a macrophase separation; i.e., $\Delta g(r)$ develops a long tail that becomes more prominent and of longer range as the spinodal temperature is reached. This phase transition is similar to what one would see, for example, in symmetric polymer blends. While the qualitative behavior of $\Delta g(r)$ is similar for $\lambda = -0.9$, the structure at short distances is different. In particular, for $r \approx 2\sigma$, $\Delta g(r)$ decreases as the spinodal temperature is approached (more A−B contacts) whereas $\Delta g(r)$ increases as the spinodal temperature is approached for $\lambda > \lambda_{\mathrm{S}}$. The behavior on short length scales is what one would expect in melts of alternating copolymers.

We interpret the phase transition for $\lambda < \lambda_{\max}$ in terms of a polymer−solvent phase separation. For large negative values of λ most of the polymer molecules are very close to being alternating copolymers. There are some molecules, however, that have a more blocky sequence.

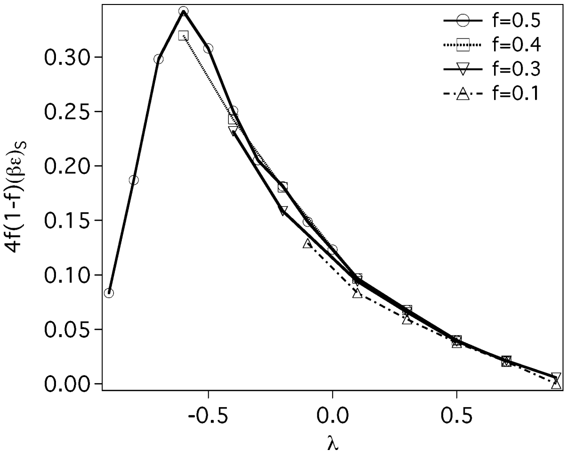

Figure 7. PRISM predictions with the linearized R-MPY closure for the spinodal lines as a function of λ for different compositions, *f*.

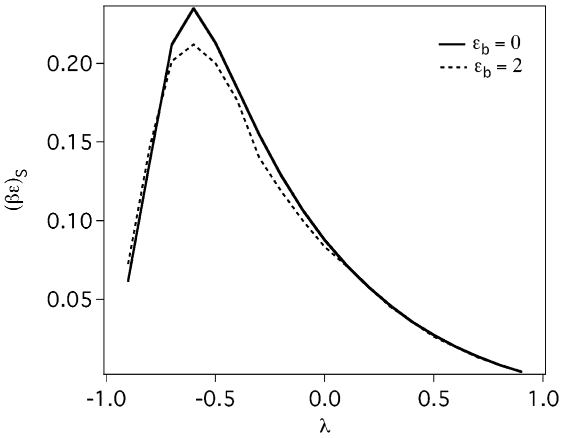

Figure 8. Effect of stiffness on the spinodal line $\rho_{\mathrm{mon}}(\beta\epsilon)_{\mathrm{S}}$ as a function of λ.

If one thinks of the majority of polymers as the "solvent", one can imagine a phase separation of the dilute blocky phase into an A-rich and a B-rich phase, with the solvent present in equal concentrations in both phases. Note that such a phase transition might be difficult to observe in simulations because of the finite size of the simulation cell and therefore a small number of molecules in any given realization.

Figure 7 compares the spinodal diagram for different compositions, *f*. Since the elements of the matrix **p** are greater than or equal to zero, there is a lower limit of λ for different values of *f*, i.e., $\lambda \geq -|f/(1-f)|$. In Figure 7, the spinodal lines for several compositions are plotted for the appropriate range of λ. The spinodal lines for all *f* collapse onto a single curve, as predicted by FM,[5] and the maximum in $4f(1-f)(\beta\epsilon)_{\mathrm{S}}$ near $\lambda \approx -0.6$ is observed for both $f = 0.4$ and 0.5.

Figure 8 compares the spinodal diagram for $N = 100$, $\rho_{\mathrm{mon}}\sigma^3 = 1$, and the linearized R-MPY closure for two values of stiffness, $\epsilon_{\mathrm{bend}} = 0$ and 2. Stiffer chains phase separate at slightly higher temperatures when $\lambda > -0.6$. But when $\lambda < -0.6$, the spinodal temperatures seem independent of stiffness and even show the opposite trend. This might be because there are more pairs of unlike monomers in alternating copolymers than in homopolymers, and as temperature is decreased, alternating polymer chains gets effectively stiffer.

IV. Summary and Conclusions

We extend the PRISM integral equation theory to study the structure and thermodynamics of random copolymer melts. In addition to the usual approximations, such as neglect of end effects, etc., we assume that the pair correlation functions depend only on the species identity and not on the location along the chain backbone. The resulting integral equations are identical in structure to integral equations for diblock copolymers, except that the intramolecular structure is averaged over all sites as well as sequences. In the thread limit, with the incompressible random phase approximation and certain other approximations, the theory reduces to the replica field theory of Fredrickson and Milner[5] and the Landau theory of Fredrickson et al.[6] In this limit, the theory predicts a macrophase separation with decreasing temperature for values of the monomer correlation length, λ, greater than a critical value (denoted λ_{S}) and a microphase separation for $\lambda < \lambda_{\mathrm{S}}$.

For chains with excluded volume, i.e., finite hard-core diameter, the PRISM predictions are qualitatively different with atomic and molecular closure approximations. Atomic closures such as the MSA closure predict a phase diagram qualitatively similar to the thread model with the IRPA although λ_{S} is shifted to -0.8, and the domain period is also larger. However, molecular closures such as R-MMSA and linearized R-MPY closures predict only a macrophase separation for all values of λ. The molecular closure approximations predict that the inverse spinodal temperature displays a maximum as a function of λ, with phase separations of different character for values of λ greater than and smaller than the maximum. The spinodal temperatures for different densities and interactions fall onto one universal line when $\rho_{\mathrm{mon}}(\beta\epsilon)_{\mathrm{S}}$ is plotted vs λ.

The microphase separation predicted in the limit of threads disappears when molecular closures are employed for polymers with finite excluded volume. Angerman et al.[14,16] found microphase separation for various *f* in the $\lambda \to 1$ limit, for large enough degree of polymerization such that each chain contains many blocks. The other difference between the PRISM approach is that, although the theory includes fluctuations to all orders, the phase diagram is estimated from the properties of the disordered state and not from a comparison of the free energy of the disordered state to that of an ordered microphase-separated state. It is possible that there is, in reality, a microphase separation for these conditions but that this is not manifested in the partial structure factors of the disordered state. The only way to incorporate this effect into the theory would be to make the intermolecular correlation functions depend on the sequence of the polymers. This would make the theory complicated enough to be intractable from the practical standpoint.

The specific predictions of the molecular closures (and previous theories) are not in agreement with available simulations. In particular, in the simulations the phase diagram is a strong function of *N* whereas in the theory the phase diagram becomes independent of *N* for large *N*. In addition, for small values of λ no phase transition is observed in the simulations, while a macrophase separation is predicted for all values of λ by the molecular closures. This phase transition of dilute polymers in an alternative copolymer "solution" might be difficult to observe in simulations because of the small number of molecules and finite size effects. It is also important to note that the (lattice) model employed in the simulations is very different from that employed in the theory, and it is clear that concentration fluctuations on a monomer correlation length scale are important in this problem. In fact, preliminary results suggest PRISM does predict microphase separation for random block copolymers, and the spinodal line might be different if intramolecular and intermolecular correlations are treated in a self-consistent fashion. Off-lattice simulations, self-consistent implementation of the theory (where intramolecular and intermolecular correlations are calculated in a self-consistent fashion), and elimination of the primary approximation (that the correlation functions are functions only of species identity), at least for short chains, would go a long way into resolving these issues.

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