Analytic PRISM Theory of Structurally Asymmetric Polymer Blends and Copolymers

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ABSTRACT: Analytic PRISM theory with the new molecular closures is applied to determine the effective chi-parameters and spinodal instability curves for structurally asymmetric polymer alloys. Compressibility effects are found to be very important, and the use of a literal incompressible RPA-like approximation is shown to incur qualitative errors in most cases. A rich and nonadditive dependence of phase transition temperatures and apparent SANS chi-parameters on backbone stiffness asymmetry, attractive interaction potential asymmetry, and thermodynamic variables is found for binary homopolymer blends. A novel strategy for designing miscible mixtures based on a cancellation, or "compensation", of the relevant asymmetries is identified. The influence of chain stiffness asymmetry in blends characterized by specific interactions is also studied. Generalization of the analytic PRISM theory to mixtures of random copolymers and periodic block copolymer melts is presented. All the rich behavior predicted for phase-separating homopolymer mixtures is again found for these systems, plus additional non mean field effects associated with random copolymer composition and block architecture. The theory is applied semiquantitatively to interpret recent experiments on polyolefin blends, diblock copolymers, and random copolymer alloys. Theoretical predictions are made which qualitatively account for recent experimental observations of a strong influence of stiffness asymmetry on phase separation temperatures, and the breakdown of the mean field random copolymer approach. Anomalous behavior is also predicted for deuterated mixtures due to an interference between the consequences of stiffness asymmetry and enthalpic interactions. The physical mechanism for the many non-Flory–Huggins effects predicted by the compressible PRISM theory is local, scalar density correlations, which appears to be different than the "nematic fluctuation" mechanism suggested by recent field theoretic work.

I. Introduction

Real polymer blends generally do not satisfy the "symmetric" criteria with regard to the intramolecular structure of the different components nor the attractive intermolecular potentials. The *literal* use of an incompressible RPA approximation[1] to compute thermodynamics and phase diagrams is expected to represent a poor approximation due to the importance of "compressibility" and local density correlation effects associated with the structural and interaction potential asymmetries. A rigorous analysis of the binary homopolymer blend leads to three independent partial structure factors, $\hat{S}_{MM'}(k)$, and three distinct measures of mean interactions, the direct correlation parameters $\hat{C}_{MM'}(0) \equiv C_{MM'}$, not a single chi-parameter.[2] The exact spinodal condition is given by[2]

$$1 - \rho_A N_A C_{AA} - \rho_B N_B C_{BB} + \rho_A \rho_B N_A N_B (C_{AA} C_{BB} - C_{AB}^2) = 0 \quad (1.1)$$

Deviations between the spinodal boundary predicted by the *literal* incompressible RPA approximation and eq 1.1 reflect the explicit influence of density and coupled density/concentration fluctuations. If one insists on expressing the spinodal boundary in terms of a single "effective chi-parameter", χ_{EFF}, *defined* by the incompressible spinodal condition

$$2\chi_{EFF}\phi_A\phi_B \frac{N_A N_B}{\phi_A N_A + \phi_B N_B} \equiv 1 \quad (1.2)$$

then by comparison of eqs 1.1 and 1.2 the effective chi-parameter is

$$2\chi_{EFF} = \frac{\rho[C_{AA}C_{BB} - C_{AB}^2][\phi_A N_A + \phi_B N_B]}{\phi_A N_A C_{AA} + \phi_B N_B C_{BB}} \quad (1.3)$$

where the relations $\phi_M = \rho_M/\rho$ and $\rho \equiv \rho_A + \rho_B$ have been employed which is appropriate when the elementary sites of the model chain are of the *same volume.* (Note that this effective chi-parameter is generally *not* the same as the apparent SANS chi-parameter χ_s.) Since the species-dependent direct correlation parameters consist of an athermal packing part plus an enthalpic contribution[3] (see eq I.3.8 of paper I[3]), the effective chi-parameter *cannot generally be decomposed into additive contributions from different physical effects nor potentials.* Note also that eq 1.3 is *non*perturbative in inverse temperature and attractive potential strength. This contrasts strongly with the form of the effective χ parameter deduced from a literal incompressible approximation (see eq I.2.11).

The primary focus of this paper is to establish the role of asymmetries on the spinodal phase boundary of simple model polymer alloys using analytic PRISM theory with the R-MMSA and/or R-MPY/HTA closures.[4,5] For a binary blend of Gaussian thread homopolymers the structure of each chain is specified by its statistical segment length, σ_M, segmental hard core diameter, $d_M \equiv d$, degree of polymerization, N_M, and the attractive "tail" potentials, $v_{MM'}(r)$, of eq I.3.3. The blend is also characterized by the thermodynamic variables: total segmental density $\rho = \rho_A + \rho_B$, or equivalently a dimensionless total packing fraction $\eta = \pi\rho d^3/6$, volume fraction of A segments, $\phi = \rho_A/\rho$, and temperature T.

The remainder of the paper is structured as follows. In section II the analytical predictions for the reference athermal blend are reviewed and discussed. The effect of stiffness asymmetry on the spinodal of symmetric attractive blends is determined in section III. Section IV derives spinodal instability conditions for blends characterized by both stiffness and attractive potential asymmetries (of the Berthelot form), while specific attraction mixtures are treated in section V. Analytic predictions for the apparent SANS chi-parameter are derived in section VI. Generalization of the analytic PRISM theory to blends composed

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of random copolymers and periodic block copolymers are presented in sections VII and VIII, respectively. A comparison of the theoretical results with experimental studies on polyolefins is presented in section IX. The PRISM theory predictions are contrasted with recent phenomenological field theoretic work in section X. The paper concludes with a summary and discussion in section XI. The present paper has been written under the assumption that the reader is familiar with the preceding paper[3] which is referred to as paper I. Equations from paper I will be quoted using the prefix notation I.

II. Athermal Reference Blend

The "athermal reference blend" is defined[6,7] as the *hypothetical* limit of vanishing interchain attractive potentials, i.e. $\beta v_{MM'}(r) = 0$. Contrary to recent statements,[8] in the $d \rightarrow 0$ thread limit the properties of the athermal reference blend predicted by PRISM theory have been analytically determined in the long chain limit.[7] In three dimensions for Gaussian chains the results are

$$C^{(0)}_{BB} = \gamma^4 C^{(0)}_{AA} \quad \text{and} \quad C^{(0)}_{AB} = \gamma^2 C^{(0)}_{AA} \tag{2.1}$$

$$\begin{aligned}\sigma_A^{-3} C^{(0)}_{AA} &= -\frac{\pi^2}{108}\rho\sigma_A{}^3[\phi + \gamma^2(1-\phi)] \\ &= -\frac{\pi}{18}\eta\Gamma^3[\phi + \gamma^2(1-\phi)]\end{aligned} \tag{2.2}$$

where $\gamma = \sigma_B/\sigma_A$, and $\Gamma = \sigma_A/d$ is the aspect ratio of the A chain. Analogous results have been obtained as a general function of polymeric fractal and spatial dimensionalities.[9] The "scaling" form of eq 2.1 for the repulsive force direct correlation parameters arises from the simultaneous influence of a pointlike hard core impenetrability condition plus the connectivity-induced power law correlations of long Gaussian chains. The factor of γ^2 could be thought of as a "segmental surface area" ratio as suggested by empirical approaches,[10] but in PRISM theory it arises from the fact that random walks are characterized by a mass fractal dimension of 2.

The intermolecular site–site pair correlations are[7,9]

$$g^{(0)}_{MM'}(r) = 1 - \xi_{EFF}\frac{1 - \exp(-r/\xi_{EFF})}{r} \equiv G_0(r) \tag{2.3}$$

where ξ_{EFF} is a concentration-, total density-, and stiffness asymmetry-dependent effective screening length given by[11]

$$\xi_{EFF} = \frac{\sigma_A}{2\eta\Gamma^3[\phi + \gamma^2(1-\phi)]} = \frac{36\sigma_A}{-\pi\sigma_A{}^{-3}C^{(0)}_{AA}} \tag{2.4}$$

Note that for the *constant volume* athermal thread blend the intermolecular packing correlations are independent of species label M,M′, which is reminiscent of the "van der Waals I" conformal solution model.[12]

Several features of the athermal reference blend need to be emphasized. Within the context of incompressible Flory–Huggins theory a purely athermal blend is taken to be an ideal mixture, i.e. the mean field enthalpic chi-parameter vanishes $\chi_0 = 0$. However, if one adopts the *incompressible* RPA idealization of eq I.2.11, in conjunction with the PRISM results for the athermal direct correlation functions of eqs 2.1 and 2.2, then as previously shown by Curro and Schweizer[7,9] a *negative* effective chi-parameter is obtained

$$\chi^{(0)}_{INC} = -\frac{\eta^2\Gamma^6}{6}(\gamma^2 - 1)^2[\phi + \gamma^2(1-\phi)] \tag{2.5}$$

This result implies that structural asymmetry ($\gamma \neq 1$) always stabilizes the constant volume *athermal* blend *in the sense* that *pure* concentration fluctuations are reduced relative to the $\gamma = 1$ melt. Moreover, within this *incompressible description* and the R-MMSA and/or R-MPY/HTA closure the effective chi-parameter in the presence of attractive potentials is given from eq I.2.11 as the sum of the (negative) athermal and (positive) mean field enthalpic contributions

$$\chi_{INC} = \chi^{(0)}_{INC} + \chi_0 \tag{2.6}$$

Equation 2.6 predicts that statistical segment length asymmetry will *always decrease the effective chi-parameter and help solubilize the blend.* Such an interpretation of the PRISM theory predictions was recently employed by Bates et al.[13] Unfortunately, as emphasized by both Dudowicz and Freed,[14] and Curro and Schweizer,[7,9] the athermal reference blend is not an adequate *model* of any real phase separating system (since $\beta v_{MM'}(r) = 0$). Prior comparisons by Curro and Schweizer of the PRISM theory predictions for this model with experiment were deliberately limited to *negative* chi-parameter mixtures. Moreover, an incompressible idealization, and hence a single chi-parameter, for an inherently miscible blend is a quantitatively poor approximation since concentration fluctuations are small. This point was numerically demonstrated by Curro and Schweizer for the asymmetric stiffness blend where the individual *compressible* partial structure factors at $k = 0$ were found to be *much larger* than their incompressible RPA counterpart.[7]

An analytic demonstration of the inadequacy of the literal incompressible RPA follows from a comparison of the long wavelength partial structure factors of the blend relative to the melt behavior. The concentration fluctuations of the latter are describable by the RPA formula with a *zero* chi-parameter, i.e. $\hat{S}_{RPA}(0) = N\phi(1 - \phi)$. Introducing the ratio

$$R_{MM} \equiv \frac{[\hat{S}_{MM}(k{=}0)]_{BLEND}}{[\hat{S}_{MM}(k{=}0)]_{MELT}} \tag{2.7}$$

and using the "effectively incompressible" relation $-\rho N_M C_{MM'} \gg 1$, eqs I.2.3, and the analytical results of eqs 2.1 and 2.2 yields in the large N limit

$$R_{AA} = \frac{\gamma^4}{\phi + \gamma^2(1-\phi)} \qquad R_{BB} = \frac{1}{\phi + \gamma^2(1-\phi)} \tag{2.8}$$

Alternatively, if the literal expression for the melt structure factor is employed (with a presumed statistical segment length of σ_A), one obtains

$$R_{AA} = 1 + \frac{(\gamma^2 - 1)\phi}{\phi + \gamma^2(1-\phi)} \qquad R_{BB} = 1 - \frac{(\gamma^2 - 1)(1-\phi)}{\phi + \gamma^2(1-\phi)} \tag{2.9}$$

From either perspective, the correct conclusion from PRISM theory when compressibility effects are included is that the more flexible component will exhibit larger long wavelength fluctuations (less stable) in the blend *relative to the melt*, while the stiffer polymer will behave in the opposite manner. Hence, although the constant volume reference athermal blend is completely miscible, conclusions for real phase-separating blends based on a *literal* incompressible approximation incur qualitative errors in the sense that the prediction of eq 2.6 that stiffness asymmetry will always stabilize the mixture is not valid. This is *not* a failing of the PRISM theory, but rather only the RPA definition of an incompressible chi-parameter. The predictions of PRISM theory for athermal, structurally asymmetric blends at constant pressure, not constant volume, remain to be determined.

III. Structurally Asymmetric Blends with Symmetric Attractions

Although not directly relevant to real materials, polymer alloy models which assume the interchain attractive potentials are "symmetric" [as defined in eq I.3.9] have been the subject of considerable study by computer simulations.[15–17] phenomenological field theories, and prior PRISM theory.[2,5,7] In the thread limit the direct correlations for this model binary mixture in the presence of stiffness asymmetry are given in their most general form by[18]

$$C_{MM} = C_{MM}^{(0)} - q\beta\tilde{H}_{AA}$$

$$C_{AB} = C_{AB}^{(0)} - z\beta\tilde{H}_{AA} \tag{3.1}$$

where z and q are numerical constants, and the attractive energy scale variable $\tilde{H}_{AA}$ is given by

$$|\tilde{H}_{AA}| = |\hat{v}_{AA}(0)| \quad \text{R-MMSA} \tag{3.2a}$$

$$= |\hat{v}_{AA}(0)|\frac{a}{a + \xi_{EFF}} \quad \text{R-MPY/HTA} \tag{3.2b}$$

for the R-MMSA and R-MPY/HTA closures of present interest. A positive (negative) "bare" enthalpic chi-parameter corresponds to $q > z$ ($q < z$). Substituting eq 3.1 in the general spinodal eq 1.1, and using eq 2.1, yields

$$\frac{k_B T_S}{\rho|\tilde{H}_{AA}|} = N\phi(1-\phi)\frac{(1+\gamma^4)q - 2z\gamma^2}{\phi + \gamma^4(1-\phi)} \tag{3.3}$$

where the "effectively incompressible" limit has been invoked since it is essentially exact for the symmetric blend problem.[5,7] For simplicity I have considered the equal degree of polymerization case. The above result should be contrasted with the Flory–Huggins-like result (i.e., $\gamma = 1$) and the *literal* incompressible description based on eqs 2.5 and 2.6:

$$\frac{k_B T_{FH}}{\rho|\tilde{H}_{AA}(\gamma{=}1)|} = 2N\phi(1-\phi)(q-z) \tag{3.4}$$

$$\frac{k_B T_{S,INC}}{\rho|\tilde{H}_{AA}|} = \frac{2N\phi(1-\phi)(q-z)}{1 + [\eta^2\Gamma^6/6](\gamma^2-1)^2[\phi + \gamma^2(1-\phi)])} \tag{3.5}$$

The incompressible theory predicts stiffness asymmetry strongly promotes miscibility relative to the structurally symmetric case. This result is very different than the "correct" compressible result of eq 3.3 which predicts that the influence of stiffness asymmetry is a nonuniversal question. For the R-MMSA closure the ratio of the compressible PRISM and Flory–Huggins spinodal temperatures is

$$\frac{T_S}{T_{FH}} = \frac{(1+\gamma^4)q - 2z\gamma^2}{2(q-z)\{\phi + \gamma^4(1-\phi)\}} \tag{3.6}$$

while for the R-MPY/HTA closure one obtains using eqs 2.4 and 3.2:

$$\frac{T_S}{T_{FH}} = \frac{(1+\gamma^4)q - 2z\gamma^2}{2(q-z)\{\phi + \gamma^4(1-\phi)\}}\left[\frac{a + \xi_{EFF}(\gamma{=}1)}{a + \xi_{EFF}(\gamma,\phi)}\right] \tag{3.7}$$

where a is the spatial range parameter of the attractive Yukawa potential defined in eq I.3.3. The above spinodal temperature ratios can be either greater or less than unity depending on the detailed values of the structural asymmetry ratio, attractive interaction potential parameters, blend composition, aspect ratio, and packing fraction. Thus the literal incompressible RPA based analysis is not generally reliable.

Prior numerical and analytical PRISM studies which employed the atomic "mean spherical approximation" (MSA) closure[2,7,9,19] have considered the special attractive potential case of $q = 0$ and $z = 1$. For the R-MMSA molecular closure one obtains from eq 3.6 for this potential choice:

$$\frac{T_S}{T_{FH}} = \frac{\gamma^2}{\phi + \gamma^4(1-\phi)} \tag{3.8}$$

For $\phi = {}^1/_2$ blends this ratio is slightly less than unity for modest values of stiffness asymmetry ratio. For example, if $\gamma = 1.1$, then one obtains a value of 0.982. Recent studies by Binder and co-workers[15] of structurally symmetric blends using lattice Monte Carlo simulations have focused primarily on two specific symmetric choices: ($q = 1$, $z = 0$) and ($q = 1$, $z = -1$). If such studies were generalized to include stiffness asymmetry then eq 3.6 predicts

$$\frac{T_S}{T_{FH}} = \frac{(1+\gamma^4) - 2z\gamma^2}{2(1-z)\{\phi + \gamma^4(1-\phi)\}} \tag{3.9}$$

which again implies a weak stabilization of the blend by the stiffness asymmetry. At high densities where the effective density correlation length, ξ_{EFF}, is small compared with the spatial range parameter of the attractive Yukawa potential, a, the R-MPY/HTA predictions based on eq I.3.7 would be very similar to the above results.

I now consider the more physically realistic case of attractive potentials obeying the Berthelot scaling relations. The consequences of stiffness asymmetry on phase behavior are found to be dramatically different.

IV. Structural and Interaction Potential Asymmetric Blends

The statistical segment length asymmetry enters via the ratio $\gamma = \sigma_B/\sigma_A$, with the Berthelot attractive potential scaling defined in eq I.4.2. The density and asymmetry ratio are treated as if they were independent of temperature. In reality there are (generally small) corrections to this assumption, and hence one can view the equations derived below as transcendental equations for the spinodal temperature. For structurally asymmetric mixtures characterized by monomer shape differences, the Berthelot asymmetry parameter λ contains (in a crude average sense) information concerning the influence of monomer level packing correlations on the local attractive energy.

A. Liquid–Liquid Phase Separation. Generalization of the compressible PRISM/R-MMSA and/or R-MPY/HTA analysis to include stiffness asymmetry is straightforward on the basis of the analysis of Appendix A of paper I. For the $N_A = N_B = N$ case the spinodal is given by[18]

$$k_BT_S = \rho|\tilde{H}_{AA}|N(\lambda-\gamma^2)^2\frac{\phi(1-\phi)}{\phi+\gamma^4(1-\phi)}\left\{1+\frac{\phi+\lambda^2(1-\phi)}{(-N\rho C_{AA}^{(0)})(\lambda-\gamma^2)^2\phi(1-\phi)}\right\} \quad (4.1)$$

$$= \frac{\rho|\tilde{H}_{AA}|}{\phi+\gamma^4(1-\phi)}\left\{N(\lambda-\gamma^2)^2\phi(1-\phi)+\frac{\phi+\lambda^2(1-\phi)}{-\rho C_{AA}^{(0)}}\right\} \quad (4.2)$$

where the "attractive energy scale" variable $\tilde{H}_{AA}$ is given by eq 3.2. Note that the only difference between the R-MMSA and the R-MPY/HTA closure predictions is the presence of the *temperature-independent, but density, composition-, and aspect ratio-dependent*, length scale ratio $a/(a+\xi_{EFF})$. Since this ratio is always less than unity, the R-MPY closure is predicted to *decrease* the spinodal temperature relative to the value obtained using the cruder R-MMSA approximation. The reduction is larger for lower polymer densities (or shorter tail potential range) due to the deeper local correlation hole.[11] The shape of the spinodal envelope is also not of the classic symmetric inverted parabola form due to both stiffness asymmetry and explicit compressibility corrections. The composition-dependent effective chi-parameter deduced from the spinodal condition using eq 1.3 is

$$2\chi_{EFF} = \rho\beta|\tilde{H}_{AA}|\frac{(\lambda-\gamma^2)^2}{\phi+\gamma^4(1-\phi)}\left\{1+\frac{\phi+\lambda^2(1-\phi)}{(-N\rho C_{AA}^{(0)})(\lambda-\gamma^2)^2\phi(1-\phi)}\right\} \quad (4.3)$$

Note that the effective chi-parameter is of an "enthalpic" nature but with multiple correlation corrections. The "collapse" of the independent asymmetry variables λ and γ into the positive difference variable $(\lambda-\gamma^2)^2$ is a mathematical consequence of the precise "scaling relations" of eqs 2.1 and I.4.2. The second, "explicit compressibility correction" term in the braces of eqs 4.1 and 4.3 is positive definite and hence will *always destabilize the blend.* Its dependence on polymer density is in general *very different* than the leading "concentration fluctuation" contribution. The latter monotonically increases with polymer density, while the former decreases with density since the fluid becomes less compressible. This aspect may often result in a complex and subtle dependence on polymer density of the critical temperature of binary blends diluted by a nonselective solvent.

If the explicit compressibility contribution is ignored, then simpler expressions are obtained

$$k_BT_S \cong \rho|\tilde{H}_{AA}|N(\lambda-\gamma^2)^2\frac{\phi(1-\phi)}{\phi+\gamma^4(1-\phi)}$$
$$\text{if} \quad (-N\rho C_{AA}^{(0)})(\lambda-\gamma^2)^2\phi(1-\phi) \gg 1 \quad (4.4)$$

$$2\chi_{EFF} = \rho\beta|\tilde{H}_{AA}|\frac{(\lambda-\gamma^2)^2}{\phi+\gamma^4(1-\phi)} \quad (4.5)$$

Equations 4.4 and 4.5 can be viewed as enforcing an "effective incompressibility" constraint *in a thermodynamically post facto manner.* It differs enormously from the spinodal predicted on the basis of the *literal RPA incompressibility* approach of eqs I.2.11 and 2.7 which is given by

$$k_BT_{S,INC} = \rho|\tilde{H}_{AA}|(\lambda-1)^2N\phi(1-\phi)\{1+(\eta^2\Gamma^6/6)(\gamma^2-1)^2 \times N\phi(1-\phi)[\phi+\gamma^2(1-\phi)]\}^{-1} \quad (4.6)$$

This result *incorrectly* predicts that increasing stiffness asymmetry monotonically stabilizes the mixture.

For the high N and density conditions of primary interest the inequality in eq 4.4 will be violated only for the very special case of $\lambda \approx \gamma^2$. However, if one does have this "accidental cancellation", or "compensation", of the attractive potential and structural asymmetry factors, then a large stabilization of the blend is predicted since the spinodal temperature from eq 4.1 now obeys the law $T_S \propto N^0$. This suggests an interesting and novel "strategy" for molecular engineering of miscible polymer blends or increasing the interfacial region in phase-separated alloys. The calculation of the critical volume fraction for such a "compensated blend" is straightforward but results in algebraically complex formulas which are not particularly illuminating and hence will not be presented here. It has also been suggested by one of the reviewers that for real experimental blends the "unusual" $T_S \propto N^0$ behavior may occur due to the fact that polymer blends tend to exhibit a much wider "critical regime" than expected from the incompressible RPA.

The difference between the PRISM plus literal incompressible approach and the more general compressible PRISM analysis becomes particularly striking in the limit that the intermolecular attractive potentials become identical, i.e. $\lambda \rightarrow 1$. Such a situation might be realized in blends of polymers of different tacticities. From eq 4.6 one sees the incompressible prediction is that the spinodal temperature vanishes! That is, the blend behaves as a purely miscible athermal system. Moreover, for the thread model eq 2.3 implies that at the R-MPY/HTA level the constant volume heat of mixing also vanishes. However, in the presence of compressibility effects phase separation is predicted by eq 4.4 which is driven by the stiffness asymmetry factor $(\gamma^2-1)^2$, even though there is no "pure enthalpic driving force" (i.e. $\chi_0 = 0$). The monotonic nature of the destabilization of the miscible phase by stiffness asymmetry for this case occurs since there is no energetic bias between like and unlike contacts.

Returning to the more general, but effectively incompressible, case of eq 4.4, the critical composition, ϕ_c, can be determined by maximizing the spinodal temperature. For the simpler R-MMSA closure the analytical result is

$$\phi_C = \frac{\gamma^2}{1+\gamma^2} \quad (4.7)$$

which implies that the blend composition at criticality is rich in the more flexible chain to a degree which increases with stiffness asymmetry. Substituting this result into eq 4.4 yields the critical temperature

$$k_BT_C = \rho|\hat{v}_{AA}(0)|N\frac{(\lambda-\gamma^2)^2}{(1+\gamma^2)^2} \quad (4.8)$$

which becomes extremely high if $\gamma^2 \gg \lambda$ but does approach a limiting value. This prediction is consistent with the physical expectation that blends of chains of greatly disparate aspect ratios (e.g. "rods and coils") will phase separate at very high temperatures, very low N, and/or very low total polymer densities, due to packing-induced "frustration". Of course, the present theory is not strictly applicable to the rod–coil mixture due to the use of a

Gaussian chain model and the neglect of possible liquid crystalline nematic order. Note that even if the "chemical energetic" effects are dominant, i.e. $\gamma \ll \lambda$, structural asymmetry can still significantly influence both the critical temperature and volume fractions. Moreover, if the energetic and structural asymmetries are comparable, then their consequences *are never separable* since the "cross terms" are always significant.

The asymmetry of the spinodal envelope can be quantified by computing, for a fixed value of reduced temperature $\Theta \equiv T_S/T_c \leq 1$, the ratio of the corresponding compositions minus the critical value, i.e.

$$R_\phi \equiv \frac{\phi_+ - \phi_c}{\phi_c - \phi_-} \tag{4.9}$$

Here, ϕ_+ (ϕ_-) denotes the composition greater (less) than the critical value, ϕ_c, which defines the spinodal curve at a subcritical temperature T_S. For $N_A = N_B = N$ *symmetric* blends, or for Flory–Huggins mean field theory, this ratio is unity for all values of Θ. Within the PRISM/R-MMSA theory in the effectively incompressible limit eqs 4.4 and 4.7 predict

$$R_\phi \equiv \frac{1+\delta}{1-\delta} \qquad \delta = \frac{(1-\gamma^2)(1-\Theta)}{\sqrt{[1-\Theta+(1+\Theta)\gamma^2]^2 - 4\Theta\gamma^4}} \tag{4.10}$$

The spinodal curve is broader toward the direction of larger concentration of flexible chains. Typical results for R_ϕ and a value of $\Theta = 0.8$ are 1.22, 1.93, 4.59, and 21.55 for $\gamma^{-1} = 1.25$, 2, 4, and 10, respectively. Two limiting cases are of interest: (a) weak segment length asymmetry, $|1-\gamma| \ll 1$, where $\delta \cong (1-\gamma)(1-\Theta)^{1/2}$, and (b) small "undercooling", $(1-\Theta) \ll 1$, where $\delta \cong [(1-\gamma^2)/2\gamma^2](1-\Theta)^{1/2}$. Such asymmetries in the spinodal curve may be very important for the kinetics of phase separation and in determining the morphology (e.g. droplets, percolating bicontinuous structure) of the phase separating structurally asymmetric blend.

For most of the λ,γ parameter space the correlation effects result in a critical temperature *higher* than predicted by the simple $\gamma = 1$ Flory–Huggins theory. However, there are "windows" of parameter space where stiffness asymmetry stabilizes the blend. The criteria for such stabilization are

$$\gamma^2 > \left[\lambda - \frac{|\lambda-1|}{2}\right] \Big/ \left[1 + \frac{|\lambda-1|}{2}\right] \quad \text{if} \quad \lambda > \gamma^2$$

$$\gamma^2 < \left[\lambda + \frac{|\lambda-1|}{2}\right] \Big/ \left[1 - \frac{|\lambda-1|}{2}\right] \quad \text{if} \quad \lambda < \gamma^2 \tag{4.11}$$

Whether the theory predicts *relative* stabilization or destabilization due to an increase of the stiffness asymmetry depends crucially on the sign of the quantity $\gamma - \lambda^{1/2}$. Since for many amorphous blends the asymmetry parameters may not deviate from unity by large amounts, the latter quantity may be close to zero in many polymer mixtures of interest.

By integrating the partial structure factors, one may also determine the free energy of mixing and thereby the binodal curve. For simplicity, I consider here only the R-MMSA closure and invoke an *effectively* incompressible approximation whence the osmotic compressibility is given by

$$\hat{S}^{-1}(0) = \frac{1}{N\phi(1-\phi)} - 2\chi_{\text{EFF}} = \frac{\partial^2 \beta F}{\partial \phi^2} \tag{4.12}$$

where the effective chi-parameter is given by eq 4.5. Use of the latter in eq 4.12 is exact at the spinodal (within the incompressibility approximation) but represents an approximation in the one-phase region. Integrating eq 4.12 and subtracting off the appropriate pure component limits yields the free energy of mixing

$$N\beta\Delta F_M = \phi \ln(\phi) + (1-\phi)\ln(1-\phi) + \frac{T_c}{T}\Psi \tag{4.13}$$

$$\Psi \equiv 2\frac{\gamma^2+1}{\gamma^2-1}\{(\gamma^{-4}-1)^{-1}\ln[1+(1-\gamma^{-4})\phi] + \phi[\ln\{(\phi + (1-\gamma^{-4})^{-1})/(1+(1-\gamma^{-4})^{-1})\} - (1+\gamma^{-4})^{-1}\ln(2-\gamma^{-4})]$$

Note that the nonideal part of the free energy does have the mean field temperature dependence but depends on both the enthalpic interactions and structural asymmetry and is an "infinite-order" (not bilinear) function of blend composition. Hence, it contains features which are both enthalpic and entropic like. This point re-emphasizes the *nonseparability* of energetic and athermal structural asymmetry effects. By equating the above nonideal contribution to the standard mean field Flory–Huggins form, an empirical effective "thermodynamic" chi-parameter can be defined

$$\chi_{\text{thermo}} = \frac{T_c}{T}\frac{\Psi(\phi)}{\phi(1-\phi)} \tag{4.14}$$

which is strongly composition-dependent. Note that this thermodynamic chi-parameter is *not the same* as either the effective chi-parameter of eqs 4.3 and 4.5, or the apparent SANS chi-parameter discussed in section V of paper I and section VI below. The binodal can be easily constructed from eq 4.13, and as noted above, its shape and relation to the spinodal will play an important role in determining the nature of the phase separation dynamics and morphologies. Generalization of the above results to the case of the R-MPY/HTA can also be done analytically but the formulas are considerably more complex and will not be presented here.

Another question particularly relevant to SANS experiments is how deuteration of one component changes the critical temperature.[20] Let the B-component be the deuterated species (which will experience a lowering of the effective dispersion interaction). On the basis of eq 4.8, there are three general cases depending on the values of the asymmetry ratios of the fully hydrogenated mixture. (i) T_c will *increase* if $\lambda < 1$ and $\gamma > 1$ [i.e., the deuterated species is stiffer but more weakly interacting]. (ii) T_c will *decrease* if $\lambda > 1$ and $\gamma < 1$ [i.e., the deuterated species is more flexible but stronger interacting]. (iii) The effect of deuteration on the critical temperature depends on the "sign" of $1 - \gamma^2$ when $\lambda > 1$ and $\gamma > 1$, or $\lambda < 1$ and $\gamma < 1$ [i.e., the deuterated species is both the stronger (weaker) interacting and stiffer (more flexible) chain]. These situations are directly relevant to recent "deuteration swap" experiments on polyolefins[21,22] which appear to display the type of nonintuitive complexity described above (see sections VI and VII for more a detailed discussion). Note that only for the case of $\gamma = 1$ corresponding to the structurally symmetric, isotopic-like blend does the energetically repulsive deuteration procedure invariably lead to a less stable mixture.

In summary, the above results show that the influence of statistical segment disparity on phase separation predicted by PRISM/R-MMSA theory is *not separable from the enthalpic interactions* and is a manifestly *non*universal process. Moreover, predictions of phase behavior based on the literal incompressible aproximation produce qualitatively incorrect results. Thus suggestions that phase behavior can be described in terms of a single chi-parameter which includes different physical effects in an independent, additive manner are not generally valid.

Incorporation of degree of polymerization asymmetry, $N_A \neq N_B$, is straightforward. The result for the spinodal temperature is

$$k_BT_S = \rho|\tilde{H}_{AA}|\frac{\phi(1-\phi)(\lambda-\gamma^2)^2(-\rho C_{AA}^{(0)})N_AN_B + \phi N_A + (1-\phi)\lambda^2 N_B}{(-\rho C_{AA}^{(0)})[\phi N_A + (1-\phi)\gamma^4 N_B]} \tag{4.15}$$

In the effective incompressible limit [as employed when passing from eq 4.1 to 4.4] this expression simplifies to

$$k_BT_S = \rho|\tilde{H}_{AA}|\phi(1-\phi)(\lambda-\gamma^2)^2\frac{N_AN_B}{\phi N_A + \gamma^4(1-\phi)N_B} \tag{4.16}$$

The literal Flory–Huggins theory predicts

$$k_BT_{FH} = \rho|\hat{v}_{AA}(0)|\phi(1-\phi)(\lambda-1)^2\frac{N_AN_B}{\phi N_A + (1-\phi)N_B} \tag{4.17}$$

which displays a different dependence on the chain degrees of polymerization due to the segment length asymmetry. Hence, the apparent molecular weight dependence is influenced by the chain stiffness difference even in the effectively incompressible limit. The effective chi-parameter deduced from the spinodal of eq 4.15 via the definition $2\chi_{EFF} = (\phi N_A)^{-1} + ([1-\phi]N_B)^{-1}$ is given by

$$2\chi_{EFF} = \rho\beta|\tilde{H}_{AA}|(\gamma^2-\lambda)^2\left[\frac{\phi N_A + (1-\phi)N_B}{\phi N_A + \gamma^4(1-\phi)N_B}\right]\{1 + (-\rho C_{AA}^{(0)}\phi(1-\phi)(\gamma^2-\lambda)^2)^{-1}[\phi N_A^{-1} + (1-\phi)N_B^{-1}]\} \tag{4.18}$$

Note that in this degree of polymerization asymmetric case the effective chi-parameter is molecular weight-dependent. The second term in curly braces vanishes in the effective incompressible limit.

The critical properties in the effective incompressible limit for the R-MMSA closure are given by

$$\phi_c = \frac{\gamma^2}{\gamma^2 + \sqrt{N_A/N_B}} \tag{4.19a}$$

$$k_BT_C = \rho|\hat{v}_{AA}(0)|(\gamma^2-\lambda)^2\frac{N_AN_B}{(\sqrt{N_A} + \gamma^2\sqrt{N_B})(\sqrt{N_B} + \gamma^2\sqrt{N_A})} \tag{4.19b}$$

$$\text{if} \quad \phi N_A^{-1} + (1-\phi)N_B^{-1} \ll -\rho C_{AA}^{(0)}\phi(1-\phi)(\gamma^2-\lambda)^2$$

Note that the critical composition can be close to the symmetric value of $^1/_2$ by an accidental compensation of the structural and molecular weight asymmetries. For the "solvent limit", defined as $N_A \gg N_B$, eqs 4.19 reduce to

$$\phi_c \cong \gamma^2\sqrt{N_B/N_A} \qquad k_BT_c \cong \rho|\hat{v}_{AA}(0)|(\gamma - \lambda\gamma^{-1})^2 N_B \tag{4.20}$$

In the limits $\gamma = N_B \rightarrow 1$, mean field Flory–Huggins predictions are obtained from the PRISM/R-MMSA theory.

In the presence of explicit compressibility corrections, and/or for the R-MPY/HTA closure of eq 3.2b, closed form analytic expressions for the critical properties cannot be obtained although numerical analysis is trivial. For moderate and long chains at meltlike densities, the corrections associated with explicit compressibility effects or local density correlations contained in the R-MPY/HTA closure are relatively small [since $\xi_{EFF} \ll a$ and $-N\rho C_{AA}^{(0)}(1-\gamma^2)^2 \gg 1$], and hence the critical properties and shape of the spinodal envelope are expected to be weakly modified from the above R-MMSA results.

As a minor caveat note that in all the analytic calculations of this section the total site number density, ρ, has been treated as a constant. For constant pressure conditions of relevance to most experiments, the total density is (weakly) temperature and composition dependent due to "equation-of-state" effects. However, the qualitative trends with regards to the influence of composition, N, interaction potential asymmetry, and stiffness asymmetry on the spinodal and effective chi-parameter are generally not expected to be significantly changed. On the other hand, the persistence length of polymers is temperature-dependent and, possibly, composition-dependent due to "nonideality" effects. In some cases this feature could significantly influence in a complex manner the effective χ parameter and spinodal temperatures via the γ parameter.

The predictions of analytic PRISM for the spinodal temperatures and effective chi-parameter derived in this and the preceding section display a very rich dependence on the single chain structural asymmetry variables (γ, Γ, and $R_N = N_B/N_A$), the interchain attractive potential asymmetry variable λ, the ratio of interaction potential length scales, a/d, and the thermodynamic state variables η and ϕ. Moreover, *these dependences are intimately coupled*. Hence, the answer to a question such as "does chain stiffness asymmetry favor or disfavor miscibility" *cannot be generally given independent of the values of the other system variables*. This coupling or "nonadditivity" aspect mathematically arises within the compressible PRISM theory from "cross terms" between the repulsive (athermal) and attractive potential contributions to the $k = 0$ direct correlations in the instability condition of eq 1.1. The effective chi-parameter deduced from the spinodal is *fundamentally enthalpic in origin* (it vanishes if $v_{AA} \rightarrow 0$) but contains multiple correlation corrections. Moreover, within a compressible theory *local* density and coupled density–concentration fluctuations strongly modify the long wavelength concentration fluctuation correlation length, ξ_ϕ, due to the influence of enthalpic interactions on packing and vice-a-versa. Such correlation effects are *not* entirely embodied in the heat of mixing.

B. Low Temperature Liquid–Gas Transition. The isothermal compressibility, κ_T, of a binary homopolymer blend is given by eq I.2.6. Employing this equation for the equal degree of polymerization case, plus the analytic results of the previous sections for the $k = 0$ direct correlation functions, yields the explicit result

$$S \equiv \rho k_BT\kappa_T = \{N^{-1} + [(-\rho C_{AA}^{(0)})(\phi + \gamma^2(1-\phi))^2 + \rho\beta|\tilde{H}_{AA}|(\phi + \lambda(1-\phi))^2]\}^{-1} \tag{4.21}$$

and its large N, athermal reference system analog

$$S_0 = \{[(-\rho C_{AA}^{(0)})(\phi + \gamma^2(1-\phi))^2]\}^{-1} \tag{4.22}$$

I define a liquid–gas spinodal temperature, T_{LG}, by the divergence of κ_T, which yields[23]

$$k_B T_{LG} = \rho|\tilde{H}_{AA}|\frac{[\phi + \lambda(1-\phi)]^2}{(-\rho C_{AA}^{(0)})[\phi + \gamma^2(1-\phi)]^2 + N^{-1}} \qquad (4.23)$$

The liquid–liquid spinodal temperature, T_S, for the same model is given by eq 4.4 in the effective incompressible limit. In the large N regime the ratio of these two spinodal temperatures is

$$\frac{T_S}{T_{LG}} = N\phi(1-\phi)(\lambda - \gamma^2)^2(-\rho C_{AA}^{(0)})[\phi + \gamma^4(1-\phi)]^{-1}\left[\frac{\phi + \gamma^2(1-\phi)}{\phi + \lambda(1-\phi)}\right]^2 \qquad (4.24)$$

Since $T_S \propto N$ for dense, high polymer blends, one clearly has the inequality $T_S \gg T_{LG}$ *unless* the quantity $N(\lambda - \gamma^2)^2$ is of order unity. If the latter condition holds, then the *explicit* influence of density fluctuations on liquid–liquid phase separation and the explicit compressibility-related errors incurred by Flory–Huggins theory will be maximized.

In the limit that $\gamma = \lambda^{1/2}$, so that $(\lambda - \gamma^2)^2 = 0$ precisely, eq 4.24 does not hold since terms of order N^{-1} in eqs 4.1 and 4.23 cannot be ignored. Simple algebraic analysis yields the qualitative result that $T_S \propto N^0$ and

$$\rho|\tilde{H}_{AA}|\frac{T_S - T_{LG}}{k_B T_S T_{LG}} = N^{-1}\frac{(\gamma^2 - 1)^2\phi(1-\phi)}{[\phi + \gamma^2(1-\phi)]^2[\phi + \gamma^4(1-\phi)]} \qquad (4.25)$$

Hence, in this very special case liquid–liquid phase separation still precedes the liquid–gas transition but is suppressed to much lower temperatures. In the asymptotic $N \rightarrow \infty$ limit the liquid–liquid and liquid–gas spinodal temperatures become identical.

Returning to the large N regime, and excluding the very special $N(\lambda - \gamma^2)^2 \leq 1$ case, eq 4.1 can be combined with eq 4.23 to yield

$$k_B T_S = N\phi(1-\phi)\rho|\tilde{H}_{AA}|(\lambda - \gamma^2)^2[\phi + \gamma^4(1-\phi)]^{-1} + k_B T_{LG}[\phi + \lambda^2(1-\phi)]\left[\frac{\phi + \gamma^2(1-\phi)}{\phi + \lambda(1-\phi)}\right]^2 \qquad (4.26)$$

which displays the N-independent contribution to the liquid–liquid spinodal temperature associated with density fluctuations. Generalization to the degree of polymerization asymmetric case is immediate.

V. Blends with Specific Interactions

Generalization of the structurally asymmetric analysis to the case of the interchain attractions consisting of a nonpolar part which obeys the Berthelot scaling relations plus an extra "specific" A–B *attraction* (characterized by a parameter $J = \Delta\tilde{H}/\tilde{H}_{AA} > 0$ as in eq I.5.6) is easily carried out on the basis of the results of section V and Appendix A of paper I. For simplicity, I consider a blend with $N_A = N_B$ and shall only briefly summarize the results in order to point out the influence of a $\gamma \neq 1$ structural asymmetry. The liquid–gas transition for this model is given by

$$k_B T_{LG} = \rho|\tilde{H}_{AA}|\frac{[\phi + \lambda(1-\phi)]^2 + 2J\phi(1-\phi)}{(-\rho C_{AA}^{(0)})[\phi + \gamma^2(1-\phi)]^2 + N^{-1}} \qquad (5.1)$$

Comparing eqs I.5.4 and 5.1, one sees that structural asymmetry only weakly influences the liquid–gas spinodaltemperature. As before, liquid–liquid phase separation due to concentration fluctuations divergence falls into two general cases. In the "effectively very strong" specific interaction case, defined as $2\gamma^2 J \gg (\lambda - \gamma^2)^2$, the analog of eq I.5.11 is

$$\frac{k_B T_S}{\rho|\tilde{H}_{AA}|} \cong (-\rho C_{AA}^{(0)})^{-1}\frac{J + 2\lambda}{2\gamma^2} \qquad (5.2)$$

This result implies an N-independent phase separation at very low temperatures. The presence of structural asymmetry can increase or decrease the phase separation temperature depending on blend density, composition, and the magnitude of γ relative to unity.

The second general case corresponds for moderate and large N to the inequality $2\gamma^2 J < (\lambda - \gamma^2)^2$. There are two extreme subcases depending on the size of the dimensionless quantity

$$Y \cong N\frac{(-\rho C_{AA}^{(0)})\phi(1-\phi)\,[(\lambda - \gamma^2)^2 - 2J\gamma^2]^2}{4J(J + 2\lambda)[\phi + \gamma^4(1-\phi)]} \qquad (5.3)$$

relative to unity. Obviously, for very large N one has $Y \gg 1$, and this is the most probable case even for moderate chain lengths. For this situation, a classic UCST process occurs and the analog of eq I.5.14 is

$$k_B T_S \cong \rho|\tilde{H}_{AA}|N\phi(1-\phi)\frac{[(\lambda - \gamma^2)^2 - 2J\gamma^2]}{\phi + \gamma^4(1-\phi)} \quad \text{if} \quad Y \gg 1 \qquad (5.4)$$

The presence of structural asymmetry can increase or decrease the phase separation temperature depending on the magnitude of γ relative to the intermolecular potential parameters and blend composition. The opposite subcase, $Y \ll 1$, is much less likely but might be realized for very strong specific interactions (large J) *and* a special choice of nonpolar attractive potentials and stiffness asymmetry (λ and γ) such that the factor $-2\gamma^2 J + (\lambda - \gamma^2)^2$ is small. For this situation the analog of eq I.5.15 is

$$\frac{k_B T_S}{\rho|\tilde{H}_{AA}|} \cong \sqrt{N\phi(1-\phi)\frac{J(J + 2\lambda)}{(-\rho C_{AA}^{(0)})[\phi + \gamma^4(1-\phi)]}} \qquad (5.5)$$

Since the predicted spinodal temperature goes to zero if either the compressibility vanishes or $J = 0$, this thermally-induced phase separation process is intimately related to the presence of a specific interaction and density fluctuations.

Generalization of the specific interaction blend calculation to the $J < 0$ case, and the LCST "toy model",[3] is easily carried out on the basis of the analysis of Appendix A and section VB of paper I but will not be presented here.

VI. SANS Chi-Parameters

In this section the apparent SANS chi-parameter for the Berthelot potential model is determined by following the analysis given in section VI of paper I.[3] Generalizations to treat the "purely athermal" blend and the "specific interaction" or "symmetric" potential cases are straightforward to derive but are not presented here.

Using eqs I.3.8 and I.4.2 in eq I.6.1 yields the empirical SANS chi-parameter based on a $k = 0$ extrapolation of the scattering intensity:

$$2\chi_S = \frac{T_1}{\phi N_A} + \frac{T_2}{(1-\phi)N_B} + T_3 \tag{6.1}$$

$$T_1 \equiv 1 + B_Q\{-\gamma^4 + \lambda^2(-\beta|\tilde{H}_{AA}|/C_{AA}^{(0)})\}$$

$$T_2 \equiv 1 + B_Q\{-1 + (-\beta|\tilde{H}_{AA}|/C_{AA}^{(0)})\}$$

$$T_3 \equiv B_Q\rho\beta|\tilde{H}_{AA}|(\gamma^2 - \lambda)^2 \tag{6.2}$$

The common B_Q factor is given by

$$B_Q \equiv \frac{(b_A - b_B)^2}{(\gamma^2 b_A - b_B)^2 + (\beta|\tilde{H}_{AA}|/C_{AA}^{(0)})[\lambda b_A - b_B]^2} \tag{6.3}$$

where b_M denotes the neutron scattering lengths. The above general result (within the Berthelot potential model) can be employed to compute the effective SANS chi-parameter for any values of temperature, composition, chain lengths, and microscopic parameters. However, further analytic simplification can be obtained for two limiting cases which are of particular interest: (i) $T \gg T_c$ corresponding to the high temperature limit; (ii) $(T - T_c)/T_c \ll 1$, corresponding to temperatures close to the critical point.

As discussed in paper I, straightforward algebra yields (in leading order) an effective chi-parameter of the standard empirical form:

$$\chi_S = \mathrm{A} + (B/T) \tag{6.4}$$

Introducing the positive parameters

$$b_1 \equiv \left(\frac{b_A - b_B}{\gamma^2 b_A - b_B}\right)^2 \qquad b_2 \equiv \left(\frac{\lambda b_A - b_B}{\gamma^2 b_A - b_B}\right)^2 \tag{6.5}$$

one obtains in the high temperature limit

$$A = \frac{1 - b_1\gamma^4}{2\phi N_A} + \frac{1 - b_1}{2(1-\phi)N_B} \tag{6.6}$$

$$B = \frac{\rho|\tilde{H}_{AA}|}{2}\left\{b_1(\gamma^2 - \lambda)^2 + (-\rho C_{AA}^{(0)})^{-1}\left[\frac{b_1(\lambda^2 - b_2\gamma^4)}{\phi N_A} + \frac{b_1(1 - b_2)}{(1-\phi)N_B}\right]\right\} \tag{6.7}$$

In general, the A and B factors are sensitive functions of molecular weight, composition, density, structural and potential asymmetry variables, and the neutron scattering lengths. The influence of stiffness and interaction potential asymmetries on the B factor of the apparent SANS chi-parameter is very similar to that predicted to occur for the spinodal temperatures (see section IV). Note that the qualitative nature of the apparent composition dependence, and even the sign of A and B, depend on all the system parameters. In the effective incompressible limit, the second explicit compressibility term in the braces of eq 6.7 vanishes.

A case of particular experimental interest is an isotopic mixture. This is just a special case of the present analysis corresponding to $\lambda \cong 1.02$. For a $\phi = {}^1/_2$ and equal degree of polymerization blend eq 6.6 yields

$$A = -\frac{(\gamma - \gamma^{-1})^2}{N} - \frac{(\Theta - 1)(\gamma^2 + \gamma^{-2})}{N} \cong \frac{4(\gamma - 1)}{N}\left[\frac{b_A + b_B}{b_A - b_B}\right] \tag{6.8}$$

where

$$\Theta \equiv \left(\frac{b_A - b_B}{\gamma b_A - \gamma^{-1} b_B}\right)^2$$

The second approximate equality in eq 6.8 applies for small stiffness asymmetry, $|\gamma - 1| \ll 1$. With the convention that component A is deuterated, and using values of the scattering lengths appropriate for polystyrene (see ref 2 of paper I), eq 6.8 predicts a value of the product AN which varies from -0.45 ($\gamma = 0.95$) to 0 ($\gamma = 1$) to 0.31 ($\gamma = 1.05$). Thus, for an isotopic blend composed of chains with $N = 1000$ statistical segments, with deuterated polymers having a statistical segment length roughly 5% *larger* than their hydrogenated analog, eq 6.8 predicts $A \cong -4.5 \times 10^{-4}$. Such a negative value is typical of many isotopic mixtures,[20,40,42] although the precise magnitude and sign predicted by eq 6.6 is sensitive to blend composition, molecular weight, neutron scattering lengths, and γ.

In the $(T - T_c)/T_c \ll 1$ low temperature case the analysis of paper I can be easily repeated. In the hypothetical effective incompressible limit, defined as $-C_{AA}^{(0)} \to \infty$, the high temperature forms of eqs 6.6–6.8 are recovered. More generally, the effective incompressibility limit will apply if the inequality in eq 4.4 or 4.19 is obeyed at the critical composition ϕ_c. In practice, this condition is much more likely to be obeyed for structurally asymmetric blends as compared with the isotopic-like mixtures considered in paper I, unless an accidental cancellation of asymmetry effects occurs, i.e. $(\gamma^2 - \lambda)^2 \approx 0$. Hence, the general algebraic analysis of the low temperature situation seems of less interest and will not be presented here.

It is also of interest to consider the alternative approach to calculating an apparent SANS chi-parameter based on fitting the k-dependent scattering profiles, i.e. eq I.2.22. In the effective incompressible regime one easily obtains for the stiffness asymmetric Berthelot thread model the result

$$2\chi_S = \rho\gamma^{-2}\beta|\tilde{H}_{AA}|(\gamma^2 - \lambda)^2 + \frac{1 - \gamma^2}{N_A\phi} + \frac{1 - \gamma^{-2}}{N_B(1-\phi)} \tag{6.9}$$

Again, for the R-MMSA and R-MPY/HTA closures this prediction is of the general form found in many SANS experiments, i.e. $\chi_S = A + (B/T)$. Note that B is always positive for the Berthelot thread model, but the molecular weight dependent A factor can in general be positive or negative depending on the precise values of the stiffness asymmetry ratio, blend composition, and degrees of polymerization. Equation 6.9 predicts a rich variety of composition dependences.

VII. Random Copolymer Blends

Many polymers have some degree of randomness in their structure, such as atacticity, microstructure variations (e.g., 1–2 and 1–4 in polybutadiene), and random branching (e.g., polyolefins). Even "regular homopolymers" often consist of a monomeric structure which contains chemically distinct groups and hence, strictly speaking, is an alternating copolymer (e.g., polystyrene). In applying PRISM to these systems a "multisite" model is most realistic but results in a proliferation of nonlinear integral equations. An approximate alternative, which I adopt in this paper, is to "preaverage" the chemical inhomogeneities into a single site "effective homopolymer" description. Such an approach is routinely used by experimentalists when analyzing SANS data,[24] in random copolymer mean field theory[25] and Landau theory of liquid crystalline blends.[26]

This preaveraging should be adequate as a first approximation within a coarse-grained thread model for statistically random copolymers, or periodic copolymers when the "block size" is of the order the statistical segment length and microphase separation is not relevant. If these conditions do not hold, then an explicit accounting for the sequence quenched disorder is required.[27]

A. General Analysis for the Bertholet Potential Model. Consider a binary alloy of two thread copolymers. Copolymer no. 1 consists of elementary units A and B with N_1 total segments of which a fraction x are of type A. Copolymer no. 2 consists of elementary units C and D with N_2 total segments of which a fraction y are of type C. The volume fraction of type 1 molecules is denoted ϕ_1, and the total segmental density of the liquid is ρ. The chains are taken to be Gaussian with mean statistical segment lengths $\sigma_1(x)$ and $\sigma_2(y)$ and stiffness asymmetry ratio $\gamma_{\rm eff}(x,y)$, all of which in general depend on temperature.

The attractive potential contributions to the direct correlation parameters are taken to obey the Berthelot relations at the elementary unit level, i.e.

$$|\tilde{H}_{\rm MM'}| = \sqrt{\tilde{H}_{\rm MM}\tilde{H}_{\rm M'M'}} \qquad \rm M,M' = A,B,C,D \tag{7.1}$$

This immediately implies that at the effective segment level the Berthelot relation again applies, i.e.

$$|\tilde{H}_{11}| = \{x\sqrt{|\tilde{H}_{\rm AA}|} + (1-x)\sqrt{|\tilde{H}_{\rm BB}|}\}^2$$

$$|\tilde{H}_{22}| = \{y\sqrt{|\tilde{H}_{\rm CC}|} + (1-y)\sqrt{|\tilde{H}_{\rm DD}|}\}^2 \tag{7.2}$$

$$|\tilde{H}_{12}| = \sqrt{\tilde{H}_{11}\tilde{H}_{22}}$$

Within this model the copolymer alloy is treated as an effective homopolymer binary blend. Hence, all the analysis of the previous sections which employed the Berthelot attractive potential model is directly applicable once the appropriate mapping of variables is determined. The effective attractive potential asymmetry variable is

$$\lambda_{\rm EFF} = \frac{\tilde{H}_{12}}{\tilde{H}_{11}} = \lambda_{\rm CA}\frac{y + (1-y)\lambda_{\rm DC}}{x + (1-x)\lambda_{\rm BA}} \tag{7.3}$$

where the three independent attractive potential asymmetry variables associated with the elementary units are

$$\lambda_{\rm MM'} \equiv \sqrt{\tilde{H}_{\rm MM}/\tilde{H}_{\rm M'M'}} \tag{7.4}$$

The quantity $\tilde{H}_{\rm MM}$ and the effective screening length follow from eqs 3.2 and 2.4 as

$$|\tilde{H}_{\rm MM}| = |\hat{v}_{\rm MM}(0)| \qquad \text{R-MMSA} \tag{7.5a}$$

$$= |\hat{v}_{\rm MM}(0)|\frac{a}{a + \xi_{\rm EFF}} \qquad \text{R-MPY/HTA} \tag{7.5b}$$

$$\xi_{\rm EFF} = \frac{\sigma_1}{2\eta\Gamma^3[\phi_1 + \gamma_{\rm EFF}^2(1-\phi_1)]} = \frac{36\sigma_1}{-\pi{\sigma_1}^{-3}C_{11}^{(0)}} \tag{7.6}$$

With the notational identification that $A \rightarrow 1$ and $B \rightarrow 2$, the results of section IV for the spinodal temperature and effective chi-parameter directly apply to the random copolymer alloy. Equations 4.15 and 4.18 include degree of polymerization asymmetry and explicit compressibility contributions and are thus the most general results. Using equation 7.3 one obtains in the simpler effective incompressible limit

$$k_{\rm B}T_{\rm S} = \rho|\tilde{H}_{\rm AA}|\phi_1(1-\phi_1)\frac{N_1N_2}{\phi_1N_1 + {\gamma_{\rm EFF}}^4(1-\phi_1)N_2}\{\lambda_{\rm CA}[y + (1-y)\lambda_{\rm DC}] - {\gamma_{\rm EFF}}^2[x + (1-x)\lambda_{\rm BA}]\}^2 \tag{7.7}$$

$$2\chi_{\rm EFF} = \rho\beta|\tilde{H}_{\rm AA}|\frac{\phi_1N_1 + (1-\phi_1)N_2}{\phi_1N_1 + {\gamma_{\rm EFF}}^4(1-\phi_1)N_2}\{\lambda_{\rm CA}[y + (1-y)\lambda_{\rm DC}] - {\gamma_{\rm EFF}}^2[x + (1-x)\lambda_{\rm BA}]\}^2 \tag{7.8}$$

Of course, for modest degrees of polymerization, solutions, and/or asymmetry variables near unity *explicit* compressibility effects may be important in determining the phase boundary. The spinodal temperature and effective chi-parameter are then *increased* by amounts given by

$$k_{\rm B}T_{\rm S} \rightarrow k_{\rm B}T_{\rm S} + \rho|\tilde{H}_{\rm AA}|\frac{\phi_1N_1 + (1-\phi_1){\lambda_{\rm EFF}}^2N_2}{(-\rho C_{11}^{(0)})[\phi_1N_1 + (1-\phi_1){\gamma_{\rm EFF}}^4N_2]} \tag{7.9}$$

$$\chi_{\rm EFF} \rightarrow \chi_{\rm EFF}\{1 + (-\rho C_{11}^{(0)}\phi_1(1-\phi_1)({\gamma_{\rm EFF}}^2 - \lambda_{\rm EFF})^2)^{-1}[\phi_1{N_1}^{-1} + (1-\phi_1){N_2}^{-1}]\} \tag{7.10}$$

where C_{11} is given by eq 2.2 with the appropriate mapping of variables described above. If the explicit compressibility effects are not important and the R-MMSA closure is employed, then the critical volume fraction and temperature are given by the direct generalizations of eqs 4.19. Note also that if the structural asymmetry vanishes, i.e. $\gamma_{\rm eff} = 1$, then eqs 7.7 and 7.8 reduce to the well-known incompressible mean field random copolymer formulas,[25] except for the local density correlation correction embodied in $\tilde{H}_{\rm AA}$ for the R-MPY/HTA closure.

The ratio of the predicted spinodal temperature of eq 7.7 and its mean field $\gamma_{\rm eff} = 1$ analog can be greater or less than unity depending on the parameters characterizing the blend. Thus stiffness asymmetry, deuteration of one of the chains, and/or any other chemical or physical modification of microstructure can either promote or hinder miscibility depending on the subtle interplay of all the factors in eqs 7.7 and 7.9.

B. Special Cases. I briefly consider two special cases of particular experimental interest. The first is a random copolymer "composition" blend. For this system the elementary units on both chains are identical, but the relative proportion of the two monomers differs. Thus, assuming no deuteration, in my notation A = C and B = D. There is only one independent attractive potential asymmetry parameter, $\lambda_{\rm BA}$, associated with the energy of interaction differences of A and B units. For this case eq 7.7 becomes

$$k_{\rm B}T_{\rm S} = \rho|\tilde{H}_{\rm AA}|\phi_1(1-\phi_1)\frac{N_1N_2}{\phi_1N_1 + {\gamma_{\rm EFF}}^4(1-\phi_1)N_2}\{(\lambda_{\rm BA} - 1) \times (y-x) + ({\gamma_{\rm EFF}}^2 - 1)[x + \lambda_{\rm BA}(1-x)]\}^2 \tag{7.11}$$

The analog of eq 4.19, and also eqs 7.8–7.10, is easily obtained and not written down here. If the structural asymmetry vanishes then eq 7.11 reduces to

$$k_BT_S = \rho|\tilde{H}_{AA}|(\lambda_{AB} - 1)^2[x - y]^2\phi_1(1 - \phi_1) \times \frac{N_1N_2}{\phi_1N_1 + (1 - \phi_1)N_2} \quad (7.12)$$

which displays the classic mean field dependence,[25] i.e. the AB homopolymer blend result multiplied by the square of the difference composition variable, $x - y$. A *necessary* condition for this simple law to be accurately obeyed is

$$|y - x| \gg \left|\frac{(\gamma_{EFF}^2 - 1)[x + \lambda_{AB}(1 - x)]}{\lambda_{AB} - 1}\right| \quad (7.13)$$

Recall that since for random copolymers γ_{EFF} is generally a function of x and y (an also temperature and/or blend composition), the validity, or lack thereof, of the above inequality may depend strongly on the absolute values of the individual composition variables and not just their difference. More generally, the ratio of the predicted spinodal of eq 7.13 and the corresponding mean field random copolymer theory result is

$$\frac{T_S}{T_{MF}} = \frac{|\tilde{H}_{AA}|}{|\vartheta_{AA}|}\,\frac{\phi_1N_1 + (1 - \phi_1)N_2}{\phi_1N_1 + \gamma_{EFF}^4(1 - \phi_1)N_2}\left\{1 + \frac{\gamma_{EFF}^2 - 1}{(\lambda_{BA} - 1)(y - x)}[x + \lambda_{AB}(1 - x)]\right\}^2 \quad (7.14)$$

which clearly shows that deviations (*either* positive or negative) from random copolymer mean field theory can arise from three distinct factors (although the leading factor is unity in the R-MMSA closure; see eq 7.5a).

Generalization of the above formulas to explicitly treat deuteration swap experiments is straightforward. For concreteness, I adopt the labeling convention that copolymer no. 2 (with units C and D) is the deuterated species. With regards to the λ *ratio* quantities, I assume that if the two interacting species are *both* deuterated, then the corresponding λ parameter is the same as for the hydrogenerated case, i.e. $\lambda_{DC} = \lambda_{BA}$ in eqs 7.7–7.10. On the other hand, $\lambda_{CA} = 1/\lambda_O$, where $\lambda_O \cong 1.016$ is the standard isotopic parameter for the fully deuterated case.[20] For the partially deuterated case of fraction x_D one has

$$\lambda_{ISO} = \sqrt{\tilde{H}_{hh}/\tilde{H}_{dd}} = [x_D^2\lambda_O^{-2} + (1 - x_D)^2 + 2x_D(1 - x_D)\lambda_O^{-1}]^{-1/2} \quad (7.15)$$

where the standard Berthelot model for the isotope effect has been adopted. Assuming deuteration does not change polymer stiffness (an apparently controversial assumption at present[21,39]), then for fixed chain compositions, x and y, blend composition, ϕ_1, and degrees of polymerization, eq 7.7 predicts the change in the phase separation temperature in the effective incompressible limit is proportional to

$$k_BT_S/|\tilde{H}_{AA}| \propto \{\lambda_{ISO}^{-1}[y + (1 - y)\lambda_{BA}] - \gamma_{EFF}^2(x,y)[x + (1 - x)\lambda_{BA}]\}^2 \quad (7.16)$$

The opposite case corresponding to (partial) deuteration of copolymer no. 1 is simply given by

$$k_BT_S/|\tilde{H}_{AA}| \propto \lambda_{ISO}^{-2}\{\lambda_{ISO}[y + (1 - y)\lambda_{BA}] - \gamma_{EFF}^2(x,y)[x + (1 - x)\lambda_{BA}]\}^2 \quad (7.17)$$

Incorporation of the explicit compressibility contributions is straightforward but will not be given here.

The second special case of present interest is an alloy of an AB random copolymer and a homopolymer C. Equation 7.7 then reduces to

$$k_BT_S = \rho|\tilde{H}_{AA}|\phi_1(1 - \phi_1)\frac{N_1N_2}{\phi_1N_1 + \gamma_{EFF}^4(1 - \phi_1)N_2}\{\lambda_{CA} - \gamma_{EFF}^2[x + (1 - x)\lambda_{BA}]\}^2 \quad (7.18)$$

where the effective stiffness asymmetry ratio now depends only on the compositional variable x and there are two independent attractive potential asymmetry variables. The corresponding mean field result is

$$k_BT_{MF} = \rho|\vartheta_{AA}|\phi_1(1 - \phi_1)\frac{N_1N_2}{\phi_1N_1 + (1 - \phi_1)N_2}\{\lambda_{CA} - [x + (1 - x)\lambda_{BA}]\}^2 \quad (7.19)$$

There are many reports of the failure of eqs 7.12 and 7.19 for random copolymer blends.[28,29] Recent work has postulated that these deviations arise from a "sequence distribution effect", i.e. the interactions between two given monomer units are assumed to be dependent on the nature of respective intramolecular nearest neighbors.[30] This elaboration, even at the simple "triad" level, results in a proliferation of phenomenological χ parameters (e.g., five for an AB/C random copolymer/homopolymer mixture, and nine for a AB/CD blend where A = C and B = D are chemically identical). The present theory suggests deviations from mean field random copolymer theory may have an entirely different physical origin, i.e. stiffness asymmetry induced correlations and/or explicit compressibility effects.

The results of this section for random copolymer alloys display an even richer and more nonadditive range of phase diagram behavior than found for homopolymer blends. The extra nonuniversal complexity arises from both the additional attractive potential asymmetry variables associated with the single chain chemical inhomogeneities, and the microstructural dependence of the effective stiffness ratio. These features can give rise to windows of effective miscibility, nonlinear (and possibly nonmonotonic) dependence of the effective χ parameter on inverse temperature, and LCST type phase diagrams.

VIII. Block Copolymers

In this section I briefly consider a simple periodic class of "2M-block copolymers", $(A_xB_y)_M$, which consist of alternating sequences of A and B segments of length x and y, respectively. Generalization to treat an odd number of blocks (e.g. triblock copolymers) is immediate. The following variables are defined: concentration of A site $f = x/(x + y)$, $N = M(x + y)$ which is the total degree of polymerization, $N_A = xN$, $N_B = yN$, and ρ = number density of copolymer molecules. A detailed presentation of the formal theory and numerical and analytical predictions of PRISM for block copolymers is given elsewhere by David and Schweizer.[31]

A. General PRISM Theory for Block Copolymers. As for the homopolymer case, a tractable theory requires "preaveraging" chain end effects. In addition, an extra zeroth order approximation enters corresponding to neglecting "junction effects". That is, the direct correlation functions associated with a pair of sites of type M and M′ are assumed not to depend on the precise location of the M and M′ segments in the molecule. The resulting PRISM equations in Fourier space are given by[31,32]

$$\hat{\mathbf{H}}(k) = \hat{\Omega}(k)\hat{\mathbf{C}}(k)[\hat{\Omega}(k) + \hat{\mathbf{H}}(k)] \qquad (8.1)$$

where the intermolecular site–site pair correlation function matrix is defined as $\hat{H}_{\mathrm{MM}'}(k) \equiv \rho_{\mathrm{M}}\rho_{\mathrm{M}'}\hat{h}_{\mathrm{MM}'}(k)$, $\hat{C}_{\mathrm{MM}'}(k)$ is the site–site direct correlation function, and the intramolecular partial structure factor matrix is

$$\hat{\Omega}_{\mathrm{MM}'}(k) \equiv \rho \sum_{\alpha=1}^{N_{\mathrm{M}}} \sum_{\gamma=1}^{N_{\mathrm{M}'}} \hat{\omega}_{\alpha\mathrm{M}\gamma\mathrm{M}'}(k) \qquad (8.2)$$

where $\omega_{\alpha\mathrm{M}\gamma\mathrm{M}'}(r)$ is the normalized probability distribution function that a site α of type M is a distance r from site γ of type M′. It is convenient to introduce a related set of intramolecular correlation functions defined as

$$\hat{\omega}_{\mathrm{MM}}(k) \equiv N_{\mathrm{M}}^{-1} \sum_{\alpha,\gamma=1}^{N_{\mathrm{M}}} \hat{\omega}_{\alpha\mathrm{M}\gamma\mathrm{M}}(k)$$

$$\hat{\omega}_{\mathrm{AB}}(k) \equiv (N_{\mathrm{A}} + N_{\mathrm{B}})^{-1} \sum_{\alpha=1}^{N_{\mathrm{A}}} \sum_{\gamma=1}^{N_{\mathrm{B}}} \hat{\omega}_{\alpha\mathrm{A}\gamma\mathrm{B}}(k) \qquad (8.3)$$

The collective partial structure factors are given by

$$\hat{\mathbf{S}}(k) = \hat{\Omega}(k) + \hat{\mathbf{H}}(k) = [1 - \hat{\Omega}(k)\hat{\mathbf{C}}(k)]^{-1}\hat{\Omega}(k) \qquad (8.4)$$

In an approximate theory of block copolymers, finite length scale spinodal instabilities *may* be present corresponding to $\hat{S}_{\mathrm{MM}'}(k = k^*) = \infty$. From eq 8.4 this is equivalent to the condition

$$\Lambda \equiv \det\{1 - \hat{\Omega}(k)\hat{\mathbf{C}}(k)\} = 0 \quad \text{for} \quad k = k^* \qquad (8.5)$$

where the most unstable wavevector is determined by the requirement that $\Lambda(k^*)$ is a minimum. Using eqs 8.1–8.4 in this relation yields

$$1 - f\rho_{\mathrm{S}}\hat{\omega}_{\mathrm{AA}}(k^*)\hat{C}_{\mathrm{AA}}(k^*) - (1-f)\rho_{\mathrm{S}}\hat{\omega}_{\mathrm{BB}}(k^*)\hat{C}_{\mathrm{BB}}(k^*) - 2\rho_{\mathrm{S}}\hat{\omega}_{\mathrm{AB}}(k^*)C_{\mathrm{AB}}(k^*) + f(1-f)\rho_{\mathrm{S}}^{2}\delta\hat{\omega}(k^*)\delta\hat{C}(k^*) = 0 \qquad (8.6)$$

$$\delta\hat{\omega}(k) \equiv \hat{\omega}_{\mathrm{AA}}(k)\hat{\omega}_{\mathrm{BB}}(k) - f^{-1}(1-f)^{-1}\hat{\omega}_{\mathrm{AB}}^{2}(k)$$

$$\delta\hat{C}(k) \equiv \hat{C}_{\mathrm{AA}}(k)\hat{C}_{\mathrm{BB}}(k) - \hat{C}_{\mathrm{AB}}^{2}(k) \qquad (8.7)$$

where $\rho_{\mathrm{S}} = N\rho$ is the total site number density. Since microphase separation is a finite length scale ordering phenomena akin to crystallization, a critical point is not expected to exist in physical reality.

B. Connection with the Leibler Mean Field Theory. The mean field Landau theory of block copolymers developed by Leibler[33] is based on an incompressible RPA treatment of the liquid correlations. PRISM theory, however, includes both density and concentration fluctuations and the incompressibility constraint cannot be rigorously enforced. However, Schweizer and Curro have previously shown for polymer blends that contact can be made with the RPA approach by implementing the incompressibility constraint in a post facto manner using a straightforward free energy functional expansion method.[2] The identical procedure can be applied to the copolymer problem. The result for an AB block copolymer for which the A and B site volumes are equal ($=V$) is[31]

$$\hat{S}_{\mathrm{RPA}}^{-1}(k) = (\eta/V)[\hat{S}_{\mathrm{AA}}^{-1}(k) + \hat{S}_{\mathrm{BB}}^{-1}(k) - 2\hat{S}_{\mathrm{AB}}^{-1}(k)] \qquad (8.8)$$

which is of the identical *form* as for a binary homopolymer blend. Using eqs 8.2–8.4 in (8.8) yields

$$\hat{S}_{\mathrm{RPA}}^{-1}(k) = \frac{f\hat{\omega}_{\mathrm{AA}}(k) + (1-f)\hat{\omega}_{\mathrm{BB}}(k) + 2\hat{\omega}_{\mathrm{AB}}(k)}{f(1-f)\hat{\omega}_{\mathrm{AA}}(k)\hat{\omega}_{\mathrm{BB}}(k) - \hat{\omega}_{\mathrm{AB}}^{2}(k)} - 2\hat{\chi}_{\mathrm{INC}}(k) \qquad (8.9)$$

where the effective chi-parameter is given by k-dependent generalization of eq I.2.11.

If a small angle approximation that $\hat{\chi}_{\mathrm{INC}}(k)$ is a constant is invoked, then eq 8.9 is *identical in form* with Leibler's RPA result. In this case the spinodal condition is far simpler than eq 8.6. For example, for a fully symmetric ($x = y$) Gaussian diblock copolymer the well-known RPA result[33] is $\chi_{\mathrm{INC}}N = 10.495$. However, the "RPA-like" result of eq 8.9 is more general than the conditions associated with the standard derivation, since only post facto incompressibility has been assumed within the PRISM formalism and not any "weak segregation" restrictions. Since the true chi-parameter is a wavevector-dependent correlation function, not a phenomenological number, it is *functionally* related to all the other intramolecular and intermolecular pair correlations in the system. This results in k^* becoming a collective, many chain property.[31,36] Finally, except for the highly idealized symmetric (both structurally and attractive interaction potential) copolymer case, eq 8.9 is expected to incur significant errors since explicit compressibility effects are neglected.[34]

C. Molecular Closures and Analytic Predictions. The same molecular closures proposed for homopolymer blends[4,5] apply to copolymers but the nondiagonality of the intramolecular structure factor matrix introduces additional complexities. Equation I.2.27 becomes

$$[\Omega^*\mathbf{C}^*\Omega(r)]_{\mathrm{MM}'} \cong [\Omega^*\mathbf{C}^{(0)*}\Omega(r)]_{\mathrm{MM}'} + [\Omega^*\Delta\mathbf{C}^*\Omega(r)]_{\mathrm{MM}'} \qquad r > d_{\mathrm{MM}'} \qquad (8.10)$$

In this paper we consider only the analytically tractable thread polymer model. Since the hard core exclusion region reduces to a point of measure zero the R-MMSA and R-MPY/HTA closure equations entirely determine the direct correlation functions, i.e., they are not functionally related to the interchain pair correlations $g_{\mathrm{MM}'}(r)$ of the fully interacting copolymer melt.[3,5] For long chains the direct correlation function parameters are precisely the same as found for a polymer blend, i.e. eq I.3.5 for the R-MMSA closure and eq I.3.7 for the R-MPY/HTA approximation.

For the *symmetric* block copolymer all the reference direct correlations are identical, which immediately implies that the effective chi-parameter is identical to that found for symmetric blends in eqs I.3.16 and I.3.17. Hence, for the R-MMSA closure the mean field result $\chi_{\mathrm{INC}} = \chi_0$ holds, and thus *within the incompressible approximation of eq 8.9 one obtains precisely Leibler theory for all compositions and block architectures.* It appears that the combination of the R-MMSA or R-MPY/HTA closure, the symmetric model, and the idealized thread limit correspond to the conditions required within the PRISM integral equation formalism to obtain a RPA-like mean field theory.

I consider only the simple Berthelot potential model and the present goal is solely to demonstrate that the rich nature of the predictions for blends derived in section IV also apply to block copolymers. Substituting eqs I.3.8, I.4.2, and 2.1 into (8.6) yields the spinodal temperature

$$\frac{k_B T_S}{\rho_S|\tilde{H}_{AA}|} = f(1-f)N(\gamma^2-\lambda)^2\tilde{F}(k^*,f,\gamma) + [-\rho_S C_{AA}^{(0)}]^{-1}\tilde{G}(k^*,f,\gamma,\lambda) \quad (8.11)$$

where the block architecture-dependent (x and y variables) functions F and G are given by

$$\tilde{F} \equiv N^{-1}\frac{\hat{\omega}_{AA}(k^*)\hat{\omega}_{BB}(k^*) - [f(1-f)]^{-1}\hat{\omega}_{AB}{}^2(k^*)}{f\hat{\omega}_{AA}(k^*) + \gamma^4(1-f)\hat{\omega}_{BB}(k^*) + 2\gamma^2\hat{\omega}_{AB}(k^*)} \quad (8.12)$$

$$\tilde{G} \equiv \frac{f\hat{\omega}_{AA}(k^*) + \lambda^2(1-f)\hat{\omega}_{BB}(k^*) + 2\lambda\hat{\omega}_{AB}(k^*)}{f\hat{\omega}_{AA}(k^*) + \gamma^4(1-f)\hat{\omega}_{BB}(k^*) + 2\gamma^2\hat{\omega}_{AB}(k^*)} \quad (8.13)$$

The functions F and G are both independent of N in the long chain limit. For stiffness symmetric $f = 1/2$ diblock copolymers in the $N \gg 1$ limit the quantity $F = 2/10.495$. The ordering wavevector, k^*, is (numerically) determined by maximizing the right hand side of eq 8.11 and is a function of all the variables in the problem. In the effective incompressible limit the second contribution on the right hand side of eq 8.11 vanishes, although one expects in general its magnitude will be very similar to what is found for the analogous binary blend. Note that the mathematical structure of eq 8.11 is qualitatively identical to the blend case of eq 4.1. Thus, for example, statistical segment asymmetry is predicted to strongly increase the asymmetry of the spinodal boundary of diblock copolymers. Another point is that since the concentration fluctuation driving force for phase separation in block copolymers is weaker than in blends (e.g. the critical value of $\chi_{EFF}N$ is larger), the N-independent explicit compressibility, or equation-of-state, contributions to the spinodal temperature are expected to be *relatively more important*.

Application of the PRISM theory of block copolymers to compute effective SANS chi-parameters, the properties of nonthread models, and the predictions of the full R-MPY closure is discussed elsewhere.[31] However, there are some features of this work which are important to briefly mention here. For the R-MMSA and R-MPY/HTA closures taking the thread limit results in a theory where the hard core exclusion condition is not relevant (except for determining the reference fluid $C_{MM'}^{(0)}$). *This great simplification does not occur for any nonzero hard core diameter.* Numerical calculations by David and Schweizer[31] for symmetric diblocks have shown that PRISM with the R-MMSA closure for nonthread symmetric diblocks *does not exhibit a critical point or spinodal instabilities if either the temperature or inverse degree of polymerization are nonzero.* The destruction of the critical point is a "finite size" fluctuation effect, as in the Brazovski–Fredrickson–Helfand theory,[35] but the mechanism is entirely different. A host of "fluctuation effects" with regard to the dependence of the scattering maximum and intensity on T and N are also found. There remains the question of whether "fluctuation phenomena" in diblock copolymers are a critical-like finite size effect, or an intrinsic process which survives in the $N \to \infty$ limit as suggested recently by several workers.[36,37] Numerical PRISM calculations for the *symmetric* diblock model based on the most sophisticated R-MPY closure[31] support an approximate "intrinsic" behavior for low and intermediate values of N. However, in the long chain limit global concentration fluctuation effects appear to become irrelevant in a manner which is qualitatively consistent with the Brazovski mechanism although the physical origin of the finite-size fluctuation process is very different.[31]

IX. Experimental Comparisons

Several groups have recently carried out SANS and/or cloud point studies of the phase behavior of nonpolar polyolefin alloys. These materials include blends and/or diblock copolymers[13] of polyethylene (PE), poly(ethylethylene) (PEE; which is structurally equivalent to atactic polybutene-1), poly(ethylenepropylene) (PEP), and compositional blends[21,22,38–40] of random copolymers of ethylene and butene-1 (PE/PEE random copolymers). In this section analytic PRISM theory is applied to semiquantitatively interpret many of the intriguing observations seen in these hydrocarbon alloys.

A subtle theoretical question is what is an adequate, but tractable, molecular model for these polymers. The explicit treatment of the chain branching aspect is difficult and certainly not directly describable within the thread or similar[8] coarse-grained models. *One consequence* of branching is variations in the effective backbone stiffness of different polyolefins. This aspect is naturally contained in the thread model via the parameter γ. However, one must keep in mind that the direct consequences of *disimliar monomer shape* may be even more important, both with regard to noncombinatorial entropy considerations and shape-dependent packing influences on the effective enthalpic interactions between the hydrocarbon units. In addition, the dispersion interactions between CH_x groups, where x = 1, 2, or 3, are not exactly equivalent,[41] and hence there are small differences in the bare attractive interaction potentials between polyolefins of different microstructures. Such differences are not necessarily negligible since all the "asymmetries" in polyolefins are quite small. These latter aspects enter the analytic PRISM theory only indirectly (or in an average sense) via the attractive contribution to the species-dependent direct correlation functions. Within the simple Berthelot approximation such effects are described solely by an effective value of the scaling parameter λ.

A. Compositional Blends of Polyolefin Random Copolymers. The analytic PRISM predictions for this system were derived in section VII. In order to semiquantitatively apply these formulas to the experimental alloys the parameters of the thread model must be determined in terms of the properties of the real molecules. This is an inherently nonunique problem due to the many ways a statistical segment can be defined. I adopt the common choice of a C_4H_8 group as the elementary repeat unit. This group has an effective volume of roughly 107 Å^3 for the PE–PEE copolymers of interest,[42] corresponding to an effective segmental hard sphere diameter of $d \cong 6$ Å. Calculation of an effective statistical segment length based on an equal volume criterion is essentially required by the nature of the present analytic thread model which cannot realistically describe monomer shape and space-filling volume. The attractive dispersion interactions between methylene groups can be described by a Lennard–Jones 6–12 potential with a well depth[43] $\epsilon \cong 40$ K and associated hard core diameter[44] of $d_{CH_2} \cong 3.9$ Å. For the Yukawa potential employed in the analytical analysis, the appropriate spatial range parameter is $a \cong 0.465 d_{CH_2}$.[19] The characteristic ratios and temperature derivatives as measured by SANS are given by[45] C_∞ = 8.3 (PE) and 5.2 (PEE) at T = 298 K; $d(\ln C_\infty)/dT \cong -0.0012$ (PE) and 0.0004 (PEE) at T = 298 K, although there is considerable uncertainty in the latter number. The statistical segment length of species M is $\sigma_M = 2L_{CC}C_\infty{}^{1/2}$, where $L_{CC} \cong 1.5$

Å is the carbon–carbon bond length. At $T = 373$ K these numbers imply the stiffness asymmetry ratio ratio of PE relative to PEE is $\gamma \cong 1.19$. At the segmental level, the total packing fraction is taken to be the typical dense liquid value of $\eta = 0.5$.

With the above numerical information, the attractive potential Berthelot scaling parameter for PE and PEE can be determined within the R-MPY/HTA closure from the ratio of the cohesive energies of the respective melts. Using eqs I.3.3, I.3.20, and 3.2b, one obtains in the long chain limit

$$\lambda^2 = \frac{\epsilon_{\mathrm{PE,PE}}}{\epsilon_{\mathrm{PEE,PEE}}} \frac{a + \sigma_{\mathrm{PEE}}[\pi\rho\sigma_{\mathrm{PEE}}^3]^{-1}}{a + \sigma_{\mathrm{PE}}[\pi\rho\sigma_{\mathrm{PE}}^3]^{-1}} \equiv \lambda_0^2 \frac{1 + \sigma_{\mathrm{PEE}}[2a\eta\Gamma_{\mathrm{PEE}}^3]^{-1}}{1 + \sigma_{\mathrm{PE}}[2a\eta\Gamma_{\mathrm{PE}}^3]^{-1}} \tag{9.1}$$

where $\Gamma = \sigma/d$ denotes the aspect ratio. The leading factor is the ratio of Lennard–Jones energy parameters. In empirical group additivity schemes this quantity can be identified with the ratio of solubility parameters squared. According to either the Small or van Krevelen parameterizations,[41] $\lambda_0 \cong 1.06$. The second ratio factor in eq 9.1 arises from the local density correlations in the polymer melt and is greater than unity since PE is a stiffer chain (as defined on an equal volume segment basis) than PEE, and hence will display a larger value of the intermolecular pair correlation function, $g(r)$, near contact. This conclusion is qualitatively expected on physical grounds since at the chemically realistic level chain branching (especially if it is random) will tend to frustrate efficient local packing of carbon centers.[46]

Equation 9.1 can be explicitly evaluated using the numerical information described in the preceding two paragraphs. At $T = 373$ K one obtains $\lambda_{\mathrm{PE,PEE}} \cong 1.20$, and the combination asymmetry variable of prime importance to phase separation is given by $(\gamma^2 - \lambda) \cong 1.41 - 1.20 = 0.2$ for a blend of PE and PEE.[47] Interestingly, recent equation-of-state studies by Walsh et al.[48] find that the analogous quantity in empirical theories is approximately 0.1. The latter number corresponds to the percent difference in empirical solubility parameters, or $[P_{\mathrm{PE}}/P_{\mathrm{PEE}}]^{1/2} - 1$ in the enthalpic equation-of-state description. Given the sensitivity of our estimate to uncertainties in the required quantities, and the ambiguity in choice of mapping of the real polymer onto the thread model, such agreement is encouraging.

1. Breakdown of Mean Field Random Copolymer Theory. Compositional blends of random copolymers of PE and PEE have been studied over essentially the entire range of PE content by Crist and co-workers[21,38,39] and Balsara, Graessley, Lohse, and co-workers.[22,28,40] A striking feature of the experimental results is that mean field random copolymer theory fails.[28] Let PE–PEE copolymer no. 1 (no. 2) contain a fraction x (y) of PEE groups. Random copolymer theory[25] predicts that chi and the spinodal temperature are proportional to the squared compositional difference only, i.e. $(y-x)^2$. Experimentally, the value of the SANS chi *at fixed compositional difference*, monotonically *decreases* by a factor of order 4–6 as the PEE content is *reduced* from near unity to zero.[28,38,40]

To address this phenomenon we apply eq 7.11. Direct experimental measurements of the compositionally-dependent segment lengths have not been published. Thus we shall employ a simple "mean field" approximation which linearly interpolates between the two limiting cases of PE and PEE homopolymers.

$$\gamma_{\mathrm{EFF}}^2 \cong \frac{y\sigma_{\mathrm{PEE}}^2 + (1-y)\sigma_{\mathrm{PE}}^2}{x\sigma_{\mathrm{PEE}}^2 + (1-x)\sigma_{\mathrm{PE}}^2} \tag{9.2}$$

Experimentally, the compositional differences considered are generally small, e.g. $|y - x| \leq 0.1$–0.2. Under this condition eq 9.2 can be simplified as

$$\gamma_{\mathrm{EFF}}^2 \cong 1 + (y - x)\frac{(1 - \gamma_0^2)}{x + (1-x)\gamma_0^2} \tag{9.3a}$$

where

$$\gamma_0^2 \equiv (\sigma_{\mathrm{PE}}/\sigma_{\mathrm{PEE}})^2 = C_{\infty,\mathrm{PE}}/C_{\infty,\mathrm{PEE}} \tag{9.3b}$$

Substituting eq 9.3a into eq 7.11 yields

$$k_{\mathrm{B}}T_{\mathrm{S}} = \rho|\tilde{H}_{\mathrm{AA}}|(\lambda_{\mathrm{PE,PEE}} - 1)^2\phi_1(1 - \phi_1) \times \frac{N_1N_2}{\phi_1N_1 + \gamma_{\mathrm{EFF}}^4(1 - \phi_1)N_2}(y - x)^2\Omega^2 \tag{9.4}$$

$$\Omega \equiv 1 + \left[\frac{1 - \gamma_0^2}{\lambda_{\mathrm{PE,PEE}} - 1}\right]\frac{x + (1-x)\lambda_{\mathrm{PE,PEE}}}{x + (1-x)\gamma_0^2} \tag{9.5}$$

Since γ_{EFF} is close to unity for the compositional alloys of interest, essentially all the deviation from random copolymer mean field theory in eq 9.4 is contained in the factor Ω due to the nonequality of the statistical segment lengths of PE and PEE. Moreover, as the branching content is varied from near unity to near zero the change in this factor is

$$\frac{\Omega(x{=}1)}{\Omega(x{=}0)} = \gamma_0^2 \tag{9.6}$$

which is *independent* of the attractive interaction asymmetry parameter. Using eq 9.3b, the square of the above ratio (which from eq 9.4 is the relevant factor for the phase separation temperature) is approximately 2.0 at $T = 373$ K and 2.5 at $T = 298$ K. Alternatively, if the equal segmental volume scheme employed recently by Bates et al.[13] for determining the effective statistical segment lengths of PE and PEE is adopted, then the corresponding ratio for 298 K is $(8.8/5.0)^4 \cong 10$ and roughly 6.5 for $T = 373$ K. As discussed above, the corresponding experimental ratio is in the range 4–6. For the modest compositional differences of experimental relevance these numerical estimates do not significantly change if the approximation of eq 9.3a is not employed, but rather eq 9.2 plus (7.11) are literally applied. However, the quantitative sensitivity of the theoretical predictions to statistical segment length definition is clearly demonstrated by the above estimates. Summarizing, PRISM theory does predict that as the mean branch content of the polymers is reduced (at constant compositional difference, blend composition, and degrees of polymerization), the alloy becomes *increasingly stable* by an amount that seems to be in rough accord with experiments.

2. Anomalous Deuteration Effects. The second "anomalous" experimental observation by both Crist and Rhee[21] and Graessley et al.[22] is the very large effect on the SANS chi-parameter and cloud point of *partial* (typically 35%) deuteration of one of the random copolymers. Besides the surprisingly large magnitude of the deuteration effect, its "sign" depends on whether the deuterons are on the more heavily or lightly branched chain. For example,[22] for 50/50 blends of $x = 0.52$ and $y = 0.66$ copolymers the critical temperatures from SANS are 95 °C if the $x = 0.52$ chain is partially deuterated and 180 °C if the $x = 0.66$ chain is partially deuterated. The fully hydrogenous alloy has a critical temperature roughly in the middle of these two values. Hence, although deuteration *in isolation* (i.e. isotopic blends) is always a repulsive effect,[20] for the present case it can either stabilize or destabilize the blend. In all cases studied so far *the effective chi-parameter is larger when the more highly branched component is deuterated.*

A simple enthalpic-based empirical solubility parameter approach has been suggested by Graessley et al.[22] to qualitatively account for the above observations. Rhee and Crist have offered an alternative explanation based on deuteration-induced segmental volume changes.[21] A potential complication is that some recent SANS experiments[39,40] on partially deuterated polyolefins find "elevated" values of the statistical segment lengths relative to values extracted from prior isotopic blend[42] and Θ solvent measurements.[49] The suggestion has been made[39] that partial deuteration significantly changes the local polymer stiffness (possibly in a molecular weight-dependent fashion), which if true could qualitatively influence the deuteration swap experiments and my analysis given below. The one model-independent conclusion that can be unambiguously drawn from these experiments is that all the asymmetries in the problem (enthalpic, stiffness, deuteration effect) are of comparable magnitude and thus "cross terms" are very important. This would seem to render inadequate any incompressible-based theory which represents the effective chi-parameter as a sum of independent contributions from different physical effects.

The deuteration swap phenomenon was considered in section VII and predictions *based on the assumption* that deuteration only modifies enthalpic interactions are given by eqs 7.16 and 7.17. Defining copolymer no. 2 as the deuterated species, then eq 7.16 predicts that since the parameter $\lambda_{\mathrm{ISO}} > 1$ (see eq 7.15) the critical temperature will be *raised* if

$$Q \equiv \frac{\gamma_{\mathrm{EFF}}^{2}(x,y)[x + (1-x)\lambda_{\mathrm{PE,PEE}}]}{y + (1-y)\lambda_{\mathrm{PE,PEE}}} > 1 \qquad (9.7)$$

and lowered if $Q < 1$. The actual value of Q is subtle because if the more highly branched polymer is deuterated then $y > x$ and $\gamma_{\mathrm{EFF}} < 1$ which implies the enthalpic and stiffness asymmetry factors compete since $\lambda_{\mathrm{PE,PEE}} > 1$. The preferable approach to evaluating Q would be to employ highly accurate experimentally determined values of the stiffness asymmetry ratio. We proceed by *assuming* the linear interpolative approximation of eq 9.3, whence eq 9.7 can be written as

$$(y - x)\left[\frac{\lambda_{\mathrm{PE,PEE}} - 1}{y + (1-y)\lambda_{\mathrm{PE,PEE}}} - \frac{{\gamma_0}^2 - 1}{x + (1-x){\gamma_0}^2}\right] > 0 \qquad (9.8)$$

The sign of the factor in square braces is determined by the sign of $\lambda - {\gamma_0}^2$. With the mapping of the real chain onto the thread model chosen in this section the above factor is negative and of order −0.2. This conclusion also holds for the alternative parameter choices.[47] Hence, deuteration of the more branched chain is predicted to *lower* the critical temperature, in disagreement with the experimental observations. The critical temperature of eq 7.16 can be written for fixed degrees of polymerization and blend composition as

$$\frac{k_{\mathrm{B}}T_{\mathrm{S}}}{|\tilde{H}_{\mathrm{AA}}|} \propto \left\{(y-x)(\lambda_{\mathrm{PE,PEE}} - 1)\left[1 - \left(\frac{{\gamma_0}^2 - 1}{\lambda_{\mathrm{PE,PEE}} - 1}\right)\frac{x + (1-x)\lambda_{\mathrm{PE,PEE}}}{x + (1-x){\gamma_0}^2}\right] + (1 - {\lambda_{\mathrm{ISO}}}^{-1})[y + (1-y)\lambda_{\mathrm{PE,PEE}}]\right\}^2 \qquad (9.9)$$

The second term is always positive since the parameter λ_{ISO} is roughly 1.006 for a 35% partially deuterated chain (see eq 7.15). Thus, for $y - x = 0.15$, and the parameters employed throughout this section, the leading term is in the range [−0.03, −0.06] and the second term is approximately 0.006. Hence, deuteration is predicted to change the critical temperature by a factor of order 1.2–1.6, which is unexpectedly large and is at least of the correct *absolute* magnitude as observed in the experiments.

It is important to note that the analytic thread model PRISM predictions which do *agree* with the experiments would *not* change if the attractive interaction asymmetry variable was larger and of the order 1.6. However, such a value would reverse the sign of the factor $\lambda - \gamma^2$ and result in a prediction for the deuteration swap problem in qualitative agreement with experiments. Alternatively, if the mapping of the real chain onto the thread model emphasized only *backbone* stiffness (not the equal segment volume approach), then the more branched chain would be stiffer. This would imply the relevant γ parameters would then be less than unity, and the stiffness and attractive potential asymmetry parameters would "reinforce" each other rather than "compete" (both greater than unity). For such a model the theoretical PRISM prediction for the deuteration swap problem would also qualitatively agree with experiment. Definitive resolution of these issues must await both theoretical and experimental advances, i.e. a more chemically realistic treatment of the influence of monomer shape and local packing on the enthalpic interactions in the blend, and highly accurate measurements of the statistical segment lengths of random polyolefin copolymer blends as a function of temperature, degree of polymerization, blend composition, and level of deuteration.

B. Polyolefin Homopolymer Blends and Diblock Copolymer Melts. Recent experiments by Bates et al.[13] on blends and diblock copolymers of PE, PEE, and PEP have been interpreted as demonstrating a strong correlation of miscibility with chain stiffness. These data are not reproduced here, and the reader is referred to the original paper. Such an interpretation, however, is not unique. The only model-independent conclusion which can be unambiguously drawn is that *miscibility is decreased as the difference in amount of chain branching between the two species increases.* Moreover, the interpretative assumption[13] that the athermal entropic consequences of chain stiffness is the dominant physical factor, and enthalpic effects are of minor significance, does *not* seem consistent with either the deuteration swap experiments[21,22] nor the enthalpic-based interpretations of Walsh et al. for polyolefin equation-of-state data.[48]

If I do adopt the Bates et al. interpretation,[13] then application of the analytic PRISM theory to these experiments is straightforward on the basis of the results of sections IV (homopolymer blends, eq 4.4), VII (homopolymer + random copolymer blend, eq 7.18), and VIII (diblock copolymers, eq 8.11). Inspection of these equations immediately shows that under the assumption of small, roughly monomer-independent, enthalpic differences among the polyolefins (i.e. λ parameters near unity), the phase transition temperatures are predicted to increase very strongly with increasing disparity in statistical segment lengths. Thus at this crude, qualitative level the analytic PRISM theory is consistent with all of the measurements of ref 13. The physical origin of the PRISM theory miscibility predictions is local scalar density correlations, which is distinct from the "nematic fluctuation" mechanism suggested by Liu and Fredrickson.[8] It must be emphasized that yet another alternative physical mechanism might be the non mean field influence of chain microstructure and monomer shape on chain packing and enthalpic interactions.

It is important to determine whether analytic PRISM theory predicts critical temperatures of the correct order of magnitude. Consider the most extreme case of structural asymmetry studied by Bates et al. corresponding to a $f = {}^1/_2$ PE–PEE diblock copolymer melt with $N = 410$.[13] Using the R-MPY/HTA closure in eq 8.11 with $F \cong 2/10.5$ and eqs 2.4 and 3.2b, one obtains

$$k_BT_S = \rho_S|\hat{v}_{AA}(0)|\frac{19.52}{1 + [\sigma_{PEE}/(\eta\Gamma_{PEE}{}^3(1 + \gamma^2))]}(\gamma^2 - \lambda)^2 \tag{9.10}$$

where the explicit compressibility contribution has been ignored. Using the same parameters for PE and PEE employed in the previous section (the $T = 373$ K values for segment lengths) this reduces to

$$\begin{aligned} k_BT_S &\cong 0.18\rho_S|\hat{v}_{AA}(0)| \\ &= 0.18[\rho_{CH_2}d_{CH_2}{}^3(20\pi/9)\epsilon_{CH_2}n] \end{aligned} \tag{9.11}$$

where the second line follows from using the Lennard–Jones potential for methylene groups and n is the number of methylene-like groups per segment (4 in this case). Substituting the appropriate numerical values[43,44] of $\rho_{CH_2}d_{CH_2}{}^3 = 2$ and $\epsilon_{CH_2} \cong 40$ K yields a very rough estimate of 400 K for the critical temperature compared to the experimental value of 393 K. The nearly exact agreement is *certainly fortuitous* given the uncertainties in the required parameters, the sensitivity of the theoretical formulas to these parameters, and the simplicity of the thread polymer model. Nevertheless, such order-of-magnitude agreement is encouraging and would seem to imply that the analytic PRISM theory and our mapping of parameters are reasonable.

Finally, the data of Bates et al.[13] do reveal another interesting feature not commented on by the authors. For alloys where the two species have relatively large differences in statistical segment lengths (PE/PEE, PEP/PEE) the phase transition temperatures increase roughly linearly, or slightly faster, with an increasing degree of polymerization. Such mean field behavior is consistent with the analytic PRISM predictions for the case where the explicit compressibility contributions to the spinodal temperature, which scale as N^0, are relatively small. However, for the cases where the statistical segment lengths are rather similar (PE–PEE random copolymer blended with PEP, and PEP/PE blends and copolymers), the phase separation temperature was observed to grow *much slower* than linearly with molecular weight. For example, 50/50 blends of PE–PEE random copolymer with PEP phase separated at 297 K for $N = 420$ and 359 K for $N \cong 1690$. Thus, a 4-fold increase of degree of polymerization induced only a 20% increase in T_c. Within PRISM theory such non-Flory–Huggins behavior may be due to a large explicit compressibility contribution (relative to the N-dependent concentration fluctuation term), and/or the fact that the effective asymmetry variable, $(\gamma^2 - \lambda)^2$, is close to zero but temperature dependent since $d(\ln C_\infty)/dT \neq 0$.

There exist many other polymer alloys where the structural and attractive potential asymmetries may play an important and competing role. Some of the recent SANS studies include d-polystyrene/*p*-methylpolystyrene blends and diblocks,[50] poly(dimethylsiloxane)/poly(diethylsiloxane) blends,[51] 1–2/1–4 polybutadiene diblock copolymers,[52] blends of polyisoprene and polybutadiene of variable microstructures,[53] tacticity blends (e.g. PMMA[54]), PMMA/poly(ethylene oxide) blends,[55] polyisoprene/poly(vinylethylene) blends,[56] and compositional blends of random copolymers of ethylene and its chlorinated analog.[29] All these systems exhibit intriguing non-Flory–Huggins aspects in their effective χ parameter and/or cloud point behavior. Detailed applications of PRISM theory to these alloys is desirable but in many cases is made difficult by an inaccurate or nonexistent knowledge of the relevant parameters such as the statistical segment lengths in the blend and the attractive potential parameters. I hope the present work provides some incentive to accurately determine these parameters.

X. Comparison with Incompressible Field Theory

Liu and Fredrickson have recently proposed a phenomenological Landau theory for the influence of stiffness asymmetry on blend miscibility.[8] Their approach presumes that nematic or orientational fluctuations, known to be of prime importance in liquid crystalline materials, are also significant in amorphous blends. This physical idea is distinct from the scalar packing correlation effects described by PRISM theory which are universally present for all dense liquids. Of course, both types of correlations presumably have a common physical origin, the intermolecular forces and chain connectivity, although only the PRISM theory attempts a microscopic description.

Liu and Fredrickson have employed an *incompressible* RPA approximation to obtain an effective chi-parameter of the form[8]

$$\chi_{EFF} = \chi_0 + \Delta\chi \tag{10.1}$$

Here, $\chi_0 \propto T^{-1} > 0$ represents the contribution of unfavorable "isotropic" enthalpic interactions and $\Delta\chi$ is the correction due to nematic fluctuations. The latter is computed using a phenomenological "Maier-Saupe" interaction with a strength characterized by an unknown parameter $w > 0$. The physical origin and magnitude of w are not specified (it could be due to anisotropic attractions and/or steric excluded volume forces), but it serves, by construction, to favor orientational alignment of chain segments. The nematic fluctuation component of χ_{EFF} is found to be[8]

$$\Delta\chi \propto \frac{B(cw - B)}{\rho(B - w)}\left[\frac{\gamma - 1}{\gamma + 1}\right]^2 \tag{10.2}$$

where c is a constant of order 2, ρ is a dimensionless monomer density, and $B > 0$ is inversely proportional to the compositionally weighted *mean* statistical segment length.

Curiously, the prediction of eq 10.2 can be of *either sign* depending on the magnitude of w relative to B, or effectively the proximity of the amorphous blend to a hypothetical isotropic–nematic phase transition. If $cw < B$, then the chi-parameter from orientational correlations is negative and the blend is stabilized. This prediction and the mathematical dependence of eq 10.2 on the stiffness difference parameter $\gamma - 1$ are in accord with the *purely athermal, incompressible PRISM chi-parameter* of eq 2.6. However, if $cw > B$ then the opposite conclusion is reached.

I have several comments.

(1) *Compressible* PRISM theory *does agree* with the statement that increasing stiffness asymmetry destabilizes *effectively athermal* blends, i.e. mixtures with $\lambda = 1$, $\chi_0 = 0$, but *nonzero* attractions (see eqs 4.4 and 4.5). However, the physical mechanism in PRISM theory is not nematic fluctuations but rather scalar density correlations or "packing effects". Moreover, the compressible nature of the fluid is essential, and the blend destabilization arises from an interference, or cross term, between the repulsive (entropic) and attractive (enthalpic) contributions to the direct correlation functions.

(2) Since the crucial Maier–Saupe parameter w is unknown, neither its magnitude nor its temperature dependence is unambiguously determinable. Thus, eq 10.2 cannot predict a critical temperature from the incompressible spinodal condition, $2\chi_{\mathrm{EFF}}N\phi(1-\phi) = 1$, without a more microscopic specification of the relevant forces. As a corrollary, if $\Delta\chi$ is entropic in origin [T-independent so χ_{EFF} is of the form $A + (B/T)$], then there may not exist a positive temperature solution to the spinodal condition if A is too large. Even if there is a solution, a linear scaling law between T_S and N will not be generally obtained unless $AN \ll 1$. The chi-parameter of eq 10.2 is also composition-independent. These features appear to be in strong contrast with the compressible PRISM predictions such as eq 4.1 and 4.4 where phase separation is driven by enthalpic effects strongly modified by stiffness-induced correlation corrections which generally depend on blend composition.

(3) As a general comment, any theory based on the literal incompressible approach of eq 10.1 cannot describe *nonadditive* asymmetry-induced phenomena.

Beyond the technical aspects discussed above, there is the fundamental question of the relevance of nematic fluctuations in blends composed of amorphous and/or crystallizable flexible polymers. This question has been intensely studied over the past two decades both experimentally,[57] and by chemically realistic computer simulations.[58–61] The consensus seems to be that equilibrium orientational order in flexible chain molecule liquids is very weak in magnitude and spatially short range. An equivalent statement is that amorphous polymers exist far away from a hypothetical isotropic–nematic phase transition. This conclusion appears to have been most strongly documented for alkanes and polyethylene. Moreover, among the group of polyolefin molecules recently studied by several groups, polyethylene is the *highest aspect ratio* polymer. Regularly and/or randomly branched polymers, such as PEE, PEP, and random copolymers of PE and PEE, have even smaller aspect ratios. From a physical perspective, the irregular space-filling nature of the their backbone contour would seem to inhibit even further the development of significant nematic-like order.

Thus, in my opinion, unless it can be demonstrated that the phenomenological parameter w required for a significant $\Delta\chi > 0$ is consistent with the extensive body of *equilibrium* simulational and experimental data on orientational order in hydrocarbon liquids, it seems unlikely that an incompressible liquid-crystalline-based description of amorphous flexible polymer mixtures captures the most important consequences of stiffness asymmetry on miscibility. On the other hand, for alloys composed of one or more large aspect ratio, mesogenic-like chain(s) the liquid-crystalline-based approach may be very good and more appropriate than PRISM theory. However, even for this case compressibility, or equation-of-state, effects[62] are expected to be important which may compromise somewhat a literally incompressible RPA-like approach.

XI. Discussion

The miscibility behavior predicted by analytic PRISM theory for simple threadlike polymers is extremely rich. The non mean field effects arise from the combined (often competing) influences of chain connectivity, stiffness, packing, and interchain attractions in a compressible macromolecular fluid. The nonuniversality and nonadditivity of the consequences of molecular structural and interaction potential asymmetries on phase stability can be viewed as a virtue in the sense that a great variety of phase behaviors are possible by rational chemical structure modification. At the same time, however, this complexity prevents the establishment of overly general "structure–property" or "cause-and-effect" rules for miscibility.

The present work does reinforce the conclusions of others[14,34,61,62] that a literal incompressible RPA approach to thermodynamics is highly inadequate. Ignoring finite compressibility or equation-of-state effects not only precludes description of LCST phase transitions but also misses all the nonadditive thermodynamic consequences of structural and interaction potential asymmetries on UCST phase separation. The inadequacy of an incompressible approximation generally increases strongly as the asymmetries between the molecular components increase.[14,34,62] The presence of phenomenological parameters of unclear relation to the real intermolecular forces is also a limitation of field theoretic approaches.

Most of the analysis of this paper has employed a Berthelot scaling simplification for the influence of attractive forces on the direct correlation functions. In reality there are deviations from such simple laws due to either the interchain potential functions themselves or the influence of packing correlations on the effective enthalpic interactions in the liquid. Such effects are straightforwardly incorporated in PRISM theory, either via numerical computation or within the general analytic thread model framework presented in Appendix A of paper I. Such corrections to Berthelot scaling will obviously result in even more complex and subtle relationships between chemical structure, thermodynamic state, and phase diagrams.

With regard to the "accuracy" of the analytic results derived in this paper there are three broad issues. The first is how accurate are the statistical mechanical approximations, i.e. the new molecular closures,[4,5] for polymer alloys. Extensive comparison[5] with lattice Monte Carlo simulations of simple symmetric blends[15] suggest the reformulated PRISM theory is quite accurate. Off-lattice simulations are in progress[16] to test the predictions of PRISM for simple symmetric and structurally asymmetric blend models which will shed more light on this question.

The second broad issue concerns the adequacy of the models employed for investigating non mean field effects. This is a general, and subtle, problem in the statistical mechanics of dense polymeric materials since a priori one expects thermodynamic properties are very sensitive to local chemical structure and packing. The *hope* is that for flexible macromolecules enough "self-averaging" of chemical details occurs such that relatively simple semiflexible models of chain structure are useful. Recent experimental diffraction measurements and atomistic PRISM calculations for polyethylene melts[44] provide support for the "self-averaging" idea since $g(r) < 1$ for all r and is rather featureless in qualitative agreement with PRISM results for Gaussian and thread polymer melts. Present research is attempting to address this question further by using numerical PRISM theory to investigate the influence of nonequal segmental volumes and/or nonspherical monomer shape on blend packing correlations, effective partial enthalpies, and phase stability. Recent work which employs atomistic models of hydrocarbon structure have documented the feasability and good accuracy of the PRISM-based theory for *quantitatively* determining the equation-of-state,[43,63] scattering patterns,[44] and crystallization[64] of alkane and polyethylene melts. Future research by Curro and co-workers will consider atomistic models of polyolefins and vinyl polymers.

The third general issue is whether the "thread" idealization yields analytic predictions for phase behavior which are representative of the numerical solutions of PRISM theory using finite hard core diameter semiflexible chain models. For simple symmetric blends Yethiraj and Schweizer have shown that the analytic thread predictions for the blend properties of thermodynamic importance are generally in excellent agreement with the numerical studies.[4,5] For blends of semiflexible chains of varying persistance length, but identical (nonzero) hard core diameter, preliminary studies again find the thread predictions are in excellent accord with the numerical calculations.[65] These studies are very encouraging with regard to the reliability (within the PRISM framework) of the thread-based analytical results, but more work on this question is desirable in order to establish the generality of such agreement. A "hybrid" or "intermediate" approach is also being developed where numerical solutions for a more chemically realistic *athermal reference system* are combined with the thread-based simple closure relations of eq I.3.8. Such an approach is computationally much easier to implement since the simple mathematical structure of the thread-based theory is retained, but chemically realistic models can be employed.

There are also several "higher order" and more subtle effects which deserve careful study. (1) Use of the full R-MPY closure[5] allows temperature-induced changes in interchain packing to be included in the determination of the attractive potential contribution to the direct correlations functions. Numerical studies using this most sophisticated level of PRISM theory may allow a microscopic description of LCST phase transitions in "specific attraction" and other polymer alloys. (2) The validity of conformational "ideality" in polymer alloys is unclear. Subtle changes in the relative stiffness of components in a blend relative to the melt, or as a function of temperature, density, blend composition, et cetera, may have major consequences on phase diagrams. Hence, a fully "self-consistent" approach to determining intramolecular and intermolecular pair correlations is desirable. "Self-consistent PRISM" theory has been recently developed[66] and applied to solutions and melts of linear[66,67] and star-branched[68] molecules and can also be implemented for polymer alloys. Nonideal conformational effects may also result in qualitatively new features such as the presence of both a LCST and UCST in the same system and unusual non mean field temperature dependences of the effective SANS χ parameter. (3) For blends composed of chains with significant structural asymmetries explicit equation-of-state effects are expected to be especially important. Hence, for some systems, particularly LCST blends, PRISM theory may need to be applied in a constant pressure formulation in order to account for temperature and composition-dependent volume changes.

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References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(2) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1989**, *91*, 5059.
(3) Schweizer, K. S. *Macromolecules*, preceding paper (referred to as paper I).
(4) Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.* **1992**, *97*, 5927.
(5) Schweizer, K. S.; Yethiraj, A. *J. Chem. Phys.* **1993**, *98*, 9053. Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.* **1993**, *98*, 9080. Yethiraj, A.; Schweizer, K. S. Manuscript in preparation.
(6) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1988**, *60*, 809.
(7) Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 1402; **1991**, *24*, 6736.
(8) Liu, A. J.; Fredrickson, G. H. *Macromolecules* **1992**, *25*, 5551.
(9) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1991**, *94*, 3986.
(10) Koningsveld, R.; Kleintjens, L. A.; Leblanc-Vinck, A. M. *J. Phys. Chem.* **1987**, *91*, 6423.
(11) The effective screening length in eq 2.4 diverges in the zero density limit since infinitely long chains have been assumed in the derivation. Thus, this formula should be employed only above the semidilute crossover density. For finite length chains the effective screening length becomes R_g in the dilute limit.
(12) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*; Butterworth Scientific: London, 1982.
(13) Bates, F. S.; Schulz, M. F.; Rosedale, J. H. *Macromolecules* **1992**, *25*, 5547.
(14) Dudowicz, J.; Freed, M. S.; Freed, K. F. *Macromolecules* **1991**, *24*, 5096.
(15) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711. Deutsch, H.-P.; Binder, K. *Macromolecules* **1992**, *25*, 6214.
(16) Kumar, S. Preprint, 1992. dePablo, J. Preprint, 1993. Elliot, R. J. private communication, 1993.
(17) Cifra, P.; Karasz, F. E.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2379.
(18) The $N \to \infty$ limit has been taken in order to derive analytic results for the athermal thread blend. Throughout this paper these results are employed for the large, but noninfinite, values of N of practical interest. Such an approach represents a very weak approximation since the athermal contribution to the direct correlation functions is determined by "local" packing effects which rapidly becomes insensitive to global coil size.
(19) Schweizer, K. S.; Curro, J. G. *Chem. Phys.* **1990**, *149*, 105.
(20) Bates, F. S.; Wignall, G. D.; Koehler, W. *Phys. Rev. Lett.* **1985**, *55*, 2425. Bates, F. S.; Wignall, G. D. *Phys. Rev. Lett.* **1986**, *57*, 1429.
(21) Rhee, J.; Crist, B. *J. Chem. Phys.*, submitted for publication.
(22) Graessley, W. W.; Krishnamoorti, R.; Balsara, N. P.; Lohse, D. J. *Macromolecules*, in press.
(23) In my analysis the athermal, hard core contribution to $\hat{S}(k=0) \equiv S_0$ is assumed to be temperature-independent. This is rigorously true for hard core repulsions. However, for soft core repulsions the corresponding *effective* hard core diameter will be weakly temperature-dependent (generally, but not always, increases with cooling) which would modify the conclusions in a quantitative manner.
(24) See, for example, refs. 21 and 22.
(25) Scott, R. L. *J. Polym. Sci.* **1952**, *9*, 423. tenBrinke, G.; Karacz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827. Kambour, R. P.; Bendler, J. T.; Bopp, B. C. *Macromolecules* **1983**, *16*, 753. Paul, D. R.; Barlow, J. *Polymer* **1984**, *25*, 487.

(26) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1990**, *23*, 531.

(27) Fredrickson, G. H.; Milner, S. T.; Leibler, L. *Macromolecules* **1992**, *25*, 6341.

(28) Balsara, N. P.; Lohse, D. J.; Sisseno, J.; Schulz, D. N.; Graessley, W. W.; Krishnamoorti, R. *ACS Polym. Mat. Sci. & Eng. Preprints* **1992**, *67*, 203.

(29) Zhikuan, C.; Ruona, S.; Karasz, F. E. *Macromolecules* **1992**, *25*, 6113 and references cited therein.

(30) Balacz, A. C.; Sanchez, I. C.; Epstein, I. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 2188.

(31) David, E. F.; Schweizer, K. S. *J. Chem. Phys.*, submitted for publication.

(32) Chandler, D. In *Studies in Statistical Mechanics VIII*; Montroll, E., Lebowitz, J., Eds.; North-Holland: Amsterdam, 1982; p 274 (see also references cited therein).

(33) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(34) Freed, K. F.; Dudowicz, J. *J. Chem. Phys.* **1992**, *97*, 2105; *Macromolecules* **1993**, *26*, 213.

(35) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697. Brazovski, S. A. *Sov. Phys. JETP* **1975**, *41*, 85.

(36) Freid, H.; Binder, K. *J. Chem. Phys.* **1991**, *94*, 8349.

(37) Tang, H.; Freed, K. F. *J. Chem. Phys.* **1992**, *96*, 862.

(38) Rhee, J.; Crist, B. *Macromolecules* **1991**, *24*, 5663. Nicholson, J. C.; Finerman, T. M.; Crist, B. *Polymer* **1990**, *31*, 2287.

(39) Crist, B.; Rhee, J. *Polymer*, submitted for publication.

(40) Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. *Macromolecules* **1992**, *25*, 6137.

(41) van Krevelin. *Properties of Polymers*; Elsevier: New York, 1972; p 55. van Krevelin. In *Computational Modeling of Polymers*; Bicerano, J., Ed.; Marcel Dekker: New York, 1992; Chapter 1.

(42) Bates, F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086.

(43) Curro, J. G.; Yethiraj, A.; Schweizer, K. S.; McCoy, J. D.; Honnell, K. G. *Macromolecules* **1993**, *26*, 2655 and references cited therein.

(44) Honnell, K. G.; McCoy, J. D.; Curro, J. G.; Schweizer, K. S.; Narten, A. H.; Habenshuss, A. *J. Chem. Phys.* **1991**, *94*, 4659. Narten, A. H.; Habenshuss, A.; Honnell, K. G.; McCoy, J. D.; Curro, J. G.; Schweizer, K. S. *J. Chem. Soc., Faraday Trans.* **1992**, *13*, 1791.

(45) Zirkel, A.; Urban, V.; Richter, D.; Fetters, L. J.; Huang, J. S.; Kampmann, R.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 6148.

(46) Theodorou, D. N.; Suter, U. W. *Macromolecules* **1985**, *18*, 1467.

(47) Using values of the statistical segment employed by either Bates et al. ($\sigma_{PE} \cong 8.4$ Å and $\sigma_{PEE} \cong 5.2$ Å at $T = 373$ K; see ref 13) or others ($\sigma_{PEE} \cong 6$ Å at $T = 373$ K; see refs 39 and 40) yields $\lambda_{PE,PEE} \cong 1.51$ or 1.36, respectively. The corresponding combination asymmetry variable is $(\gamma^2 - \lambda) \cong 1.1$ or 0.6, respectively. All the theoretical conclusions discussed in the text remain qualitatively the same if these parameters are employed.

(48) Walsh, D. J.; Graessley, W. W.; Datta, S.; Lohse, D. J.; Fetters, L. J. *Macromolecules* **1992**, *25*, 5236.

(49) Hattam, P.; Gauntlett, S.; Mays, J. W.; Hadjichristidis, N.; Young, R. N.; Fetters, L. J. *Macromolecules* **1991**, *24*, 6199.

(50) Jung, W. G.; Fischer, E. W. *Makromol. Chem. Makromol. Symp.* **1988**, *16*, 281.

(51) Meier, G.; Mompter, B.; Fischer, E. W. *J. Chem. Phys.* **1992**, *97*, 5884.

(52) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.

(53) See, for example: Sakurai, S.; Jinnai, H.; Hasegawa, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 4839.

(54) O'Reilly, J. M.; Yang, H.; Teegarden, D. *MRS Book of Abstracts, Fall 1989 Mtg.*; Materials Research Society: Pittsburgh, PA, 1989; paper J6.5, p 342; private communication, 1990.

(55) Ito, H.; Russell, T. P.; Wignall, G. D. *Macromolecules* **1987**, *20*, 2214.

(56) Tomlin, D. W.; Roland, C. M. *Macromolecules* **1992**, 25.

(57) See, for example: Flory, P. J. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 14. Fischer, E. W.; Strobl, G. R.; Dettenmaier, M.; Stamm, M.; Steidle, N. *Ibid.* **1979**, *68*, 26. Patterson, G. D.; Kennedy, A. P.; Latham, J. P. *Macromolecules* **1977**, *10*, 667.

(58) Rigby, D.; Roe, R. J. *J. Chem. Phys.* **1988**, *89*, 5280.

(59) Helfand, E.; Weber, T. A. *J. Chem. Phys.* **1979**, *71*, 4760.

(60) Vacatello, M.; Avitabile, G.; Corradini, P.; Tuzi, A. *J. Chem. Phys.* **1980**, *73*, 548. Avitabile, G.; Tuzi, A. *J. Polym. Sci., Polym. Phys.* **1983**, *21*, 2379.

(61) Dudowicz, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 1519. Tang, H.; Freed, K. F. *Macromolecules* **1991**, *24*, 958.

(62) Sanchez, I. C. *Macromolecules* **1991**, *24*, 908.

(63) Yethiraj, A.; Curro, J. G.; Schweizer, K. S.; McCoy, J. D. *J. Chem. Phys.* **1993**, *98*, 1635.

(64) McCoy, J. D.; Honnell, K. G.; Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1991**, *95*, 9348.

(65) Yethiraj, A.; Schweizer, K. S. *Bull. Am. Phys. Soc.* **1993**, *38* (1), 485; unpublished calculations.

(66) Schweizer, K. S.; Honnell, K. G.; Curro, J. G. *J. Chem. Phys.* **1992**, *96*, 3211.

(67) Melenkevitz, J.; Schweizer, K. S.; Curro, J. G. *Macromolecules*, in press. Grayce, C. J.; Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.*, submitted for publication.

(68) Grayce, C. J.; Schweizer, K. S. *Macromolecules*, to be submitted for publication.