

Analytic RISM Theory of Polymer Alloys: Molecular Closure Predictions for Structurally Symmetric Blends

Kenneth S. Schweizer

Departments of Materials Science & Engineering and Chemistry, University of Illinois, Urbana, Illinois 61801

Received April 28, 1993; Revised Manuscript Received July 26, 1993*

ABSTRACT: Polymer reference interaction site model (PRISM) theory with new molecular closure approximations is applied to analytically calculate the phase behavior and effective SANS χ parameter of binary blends composed of long threadlike chains. A general analysis of the validity of incompressible approaches to computing thermodynamics and scattering patterns is presented. The special case of structurally symmetric mixtures is then considered in depth, and the influence of density and coupled density/concentration fluctuations, or "compressibility effects", is investigated. Significant corrections to mean field Flory-Huggins theory are found for short and intermediate length polymers. The magnitude of these correlation corrections are strongly dependent on the precise nature of the interchain attractive potentials, blend composition, and molecular weight. Applications of the general formulas to isotopic blends are presented and qualitatively compared with experiments. The effect of strong "specific interactions" is also studied within the analytic PRISM framework. Under some circumstances such interactions merely quantitatively modify the upper critical solution temperature (UCST) process. However, depending on system-specific factors, different types of phase behavior are predicted to occur including lower critical solution temperature (LCST) phase separation. Within the present model the LCST phase transition is driven by thermally-induced local packing changes in the fluid.

I. Introduction

The structure and properties of phase-separating polymer alloys is a subject of intense scientific and technological interest.¹ With the advent of the small angle neutron scattering (SANS) technique much information concerning concentration fluctuations in polymer alloys has been accumulated and is commonly expressed in terms of an "apparent chi parameter", χ_s , which contains all nonideal mixing information.^{1,2} According to classical mean field ideas³ the chi-parameter is a purely energetic quantity which is inversely proportional to temperature and completely determined by the local chemical interactions between monomers embedded in a structureless fluid. In practice, chi-parameters and phase diagrams of real polymer alloy materials are far more complex and exhibit a host of "non mean field" features of both enthalpic and entropic origins. For example, χ_s often depends strongly on composition, pressure, global chain architecture, molecular weight, chain branching, and possibly the wavevector of observation.^{4,5} Even for the simplest polymer blend, the isotopic mixture, the SANS chi-parameter displays a significant, but apparently nonuniversal, composition dependence which is not well understood.⁵⁻⁷ Although a variety of novel theoretical and computer simulation⁸ approaches have been recently developed, fundamental understanding is in its early stages.

Over the past several years Curro, Schweizer, and co-workers have developed and widely applied an off-lattice, microscopic statistical mechanical approach for calculating the intermolecular structure, conformation, thermodynamics, and phase transitions of polymer liquids.⁹⁻¹⁸ The general methodology is known as the polymer reference interaction site model ("PRISM") theory and is based on the RISM approach for small, rigid molecular fluids developed by Chandler and co-workers.^{19,20} Using well-known closure approximations successfully employed for atomic and small molecule fluids, Curro and Schweizer have carried out several analytic^{13,21,22} and numerical

studies^{12,13} of model binary polymer blends. Their most provocative finding was that, for an isotopic-like symmetric blend, the PRISM theory with the atomic "mean spherical approximation" (MSA) closure leads to a nonclassical relation between the critical temperature, T_c , for phase separation (computed from the osmotic compressibility divergence) and the degree of polymerization, N , of the form $T_c \propto N^{1/2}$. This unexpected result corresponds to a massive stabilization of the mixed phase relative to Flory-Huggins mean field theory which predicts $T_c \propto N$.

Very recently, two studies have been performed on simple model binary blend systems in order to definitively investigate the critical temperature scaling question. Deutsch and Binder²³ have carried out a large scale lattice Monte Carlo simulation on a symmetric polymer mixture, and Gehlsen et al.²⁴ performed a SANS study on a family of specially-designed high molecular weight isotopic blends. The classical Flory-Huggins scaling law was found to a high degree of accuracy. Thus, at least for the idealized case of (nearly) symmetric polymer mixtures, Flory-Huggins scaling appears correct. This strongly suggests that the PRISM theory with the atomic-like MSA closure is in qualitative error. This led Yethiraj and Schweizer to re-examine the fundamental nature of closures for polyatomic fluids, and new "molecular" closure approximations were formulated which explicitly account for chain connectivity.²⁵⁻²⁷ The PRISM approach with these new molecular closures has been recently discussed in depth and agreement with Flory-Huggins scaling in the long chain limit is indeed found for the symmetric blend. Except for the Ising critical divergence aspect, the most sophisticated version of the new closures is in excellent accord²⁷ with all the non mean field aspects found in the lattice Monte Carlo simulations^{23,28} of symmetric model blends (e.g., quantitative renormalization of T_c , composition and density dependence of the effective chi-parameter).

It now appears that the reformulated PRISM integral equation theory of phase-separating fluids can be reliably employed to systematically explore, via numerical computation, the complex influences of chemical structure,

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

intermolecular forces, and thermodynamic state on polymer alloy thermodynamics, structure, and phase stability. However, it would be extremely useful from both a theoretical and experimental viewpoint to have a more approximate, but analytical, theory formulated at an intermediate level of chemical structure complexity. The foundation for such an analytic theory has been developed by Schweizer and Curro on the basis of the "polymer thread" idealization.^{21,22} Its essence is a coarse-graining of the real polymer structure to a level which allows the nonlinear PRISM integral equation(s) to be solved analytically in special cases. Despite the coarse-graining, non mean field influences of chain stiffness and aspect ratio, degree of polymerization, and the specific nature of the intermolecular attractive potentials on blend thermodynamics are retained. Moreover, the generally important consequences of density fluctuations ("compressibility or equation-of-state effects") are not ignored as commonly done in phenomenological statistical thermodynamic theories based on the "incompressible random phase approximation" (IRPA).²⁹

The purpose of the present and companion paper is to derive the spinodal phase diagram and effective chi-parameter predictions of the PRISM theory of polymer alloys with the new molecular closures at the thread model level. I anticipate the analytic results will be of value for both establishing general miscibility trends and for guiding numerical studies using PRISM theory. In addition, I believe the analytic analysis provides considerable physical insight into correlation effects in real polymer alloys, particularly within a homologous series of materials.

The remainder of this paper is structured as follows. The PRISM theory with the new molecular closures, and connections with the IRPA and the effective SANS chi-parameter, are discussed in section II. The general analytic thread model approach for the new closures is presented in section III along with specific results for the simplest case of "symmetric" polymer blends. In section IV spinodal phase diagrams are derived for nonpolar model blends which are "structurally symmetric" but which possess asymmetries in their intermolecular attractive potentials and/or chain length. Analytic results for model blends with strongly attractive or "specific" interactions are presented in section V, including a discussion of the "lower critical solution temperature" (LCST) phenomenon. Predictions for the SANS chi-parameter of structurally symmetric model blends are presented and discussed in section VI. The paper concludes in section VII with a brief summary. The details of the algebraic analysis of the general thread blend are presented in Appendix A, and the compressibility of real polymer fluids is the subject of Appendix B. Application and generalization of the analytic PRISM theory with the new molecular closures to determine the effects of single chain structural asymmetries in homopolymer blends, and random and block copolymers, are presented in the following paper.³⁰

II. PRISM Theory of Binary Blends

A. General PRISM Theory. The PRISM matrix equations for a mixture of homopolymers is given in Fourier-transform space by¹²

$$\hat{h}_{MM'}(k) = \hat{\omega}_M(k) [\hat{C}_{MM'}(k) \hat{\omega}_{M'}(k) + \sum_{M''} \hat{C}_{MM''}(k) \rho_{M''} \hat{h}_{M''M'}(k)] \quad (2.1)$$

where chain-end effects have been preaveraged in the usual manner.⁹ Here, ρ_M is the site number density of species M , $h_{MM'}(r) = g_{MM'}(r) - 1$, where $g_{MM'}(r)$ is the chain-averaged intermolecular pair correlation (or radial dis-

tribution) function between interaction sites of species M and M' , $C_{MM'}(r)$ is the corresponding intermolecular site-site direct correlation function, and $\hat{\omega}_M(k)$ is the intramolecular structure factor of species M .

The partial density-density collective structure factors are given by

$$\hat{S}_{MM'}(k) = \rho_M \hat{\omega}_M(k) \delta_{M,M'} + \rho_M \rho_{M'} \hat{h}_{MM'}(k) \quad (2.2)$$

For a binary homopolymer blend use of the PRISM eq 2.1 yields the more explicit forms¹²

$$\hat{S}_{AA}(k) = \rho_A \hat{\omega}_A(k) [1 - \rho_B \hat{\omega}_B(k) \hat{C}_{BB}(k)] / \Delta(k) \quad (2.3a)$$

$$\hat{S}_{BB}(k) = \rho_B \hat{\omega}_B(k) [1 - \rho_A \hat{\omega}_A(k) \hat{C}_{AA}(k)] / \Delta(k) \quad (2.3b)$$

$$\hat{S}_{AB}(k) = \rho_A \rho_B \hat{\omega}_A(k) \hat{\omega}_B(k) \hat{C}_{AB}(k) / \Delta(k) \quad (2.3c)$$

$$\Delta(k) = 1 - \rho_A \hat{\omega}_A(k) \hat{C}_{AA}(k) - \rho_B \hat{\omega}_B(k) \hat{C}_{BB}(k) + \rho_A \rho_B \hat{\omega}_A(k) \hat{\omega}_B(k) [\hat{C}_{AA}(k) \hat{C}_{BB}(k) - \hat{C}_{AB}^2(k)] \quad (2.4)$$

The direct correlation functions contain the fundamental microscopic information regarding interactions and correlations in blends. In general there are three independent functions for a binary homopolymer mixture, which enter the scattering functions in a nonlinear fashion. On the relatively long wavelengths relevant to small angle scattering measurements the approximation $\hat{C}_{MM'}(k) \approx \hat{C}_{MM'}(0) \equiv C_{MM'}$ is appropriate.

The spinodal condition is given by the simultaneous divergence at $k = 0$ of all the partial structure factors

$$0 = 1 - \rho_A N_A C_{AA} - \rho_B N_B C_{BB} + \rho_A \rho_B N_A N_B [C_{AA} C_{BB} - C_{AB}^2] \quad (2.5)$$

The total density fluctuations are characterized by the isothermal compressibility, κ_T , which is given by¹³

$$\begin{aligned} \kappa_T^{-1} &= k_B T \sum_{M,M'} \rho_M \rho_{M'} \hat{S}_{MM'}^{-1}(0) \\ &= k_B T \left\{ \frac{\rho_A}{N_A} + \frac{\rho_B}{N_B} - [\rho_A^2 \hat{C}_{AA}(0) + \rho_B^2 \hat{C}_{BB}(0) + 2\rho_A \rho_B \hat{C}_{AB}(0)] \right\} \end{aligned} \quad (2.6)$$

where $k_B T$ is the thermal energy and N_M is the number of interaction sites comprising a molecule of species M . The inverse isothermal compressibility vanishes at a purely density-fluctuation-induced liquid-gas spinodal.

Except for the hypothetical "symmetric mixture" model, the spinodal instability of a multicomponent fluid contains both concentration and density fluctuation aspects. This general issue has been the subject of several recent theoretical investigations of simple atomic mixtures.³¹ In particular, Chen and Forstmann³¹ present an analysis which allows the physical nature of the spinodal instability to be determined. In the present paper, I focus solely on determining the spinodal curves from eqs 2.5 and 2.6 and do not analyze the precise nature of the unstable eigenvector. Generalization of my analysis to include the latter aspect is straightforward and will be reported elsewhere.

B. Connections with the IRPA and SANS Chi-Parameter. The incompressible RPA is routinely used by experimentalists to analyze small angle scattering from polymer alloys and thereby deduce an empirical effective chi-parameter. It is also commonly employed in coarse-grained, phenomenological Landau-like field theories. A basic assumption is incompressibility, i.e. the presumed dominance of pure concentration fluctuations which

implies there is only one independent scattering function which obeys the relation³²

$$\hat{S}_{AA}(k) = \hat{S}_{BB}(k) = -\hat{S}_{AB}(k) \quad (2.7)$$

Such an assumption is incompatible with the PRISM integral equation approach which naturally includes pure density, pure concentration, and coupled density-concentration fluctuations on all length scales. However, an "incompressibility constraint" can be enforced on the PRISM theory in a post facto manner by employing a functional Taylor expansion of the free energy.¹² This procedure results in a single scattering function, $\hat{S}_c(k)$, of precisely the RPA form¹²

$$\hat{S}_c^{-1}(k) = r^{-1/2}[\phi_A \hat{\omega}_A(k)]^{-1} + r^{1/2}[\phi_B \hat{\omega}_B(k)]^{-1} - 2\chi_{\text{INC}} \quad (2.8)$$

where $r = V_A/V_B$ is the site volume ratio of species A and B, $\phi_M = \rho_M V_M/\eta$ is the volume fraction of sites of type M, $\eta = \rho_A V_A + \rho_B V_B$ is the total site packing fraction, and χ_{INC} is the incompressible effective chi-parameter

$$2\chi_{\text{INC}} = \rho[\phi_A r^{-1/2} + \phi_B r^{1/2}]^{-1}\{r^{-1}\hat{C}_{AA}(0) + r\hat{C}_{BB}(0) - 2\hat{C}_{AB}(0)\} \quad (2.9)$$

Here ρ is the total site number density, and the RPA-like long wavelength approximation $\hat{\chi}_{\text{INC}}(k) \cong \hat{\chi}_{\text{INC}}(k=0) = \chi_{\text{INC}}$ has been employed. The incompressible RPA spinodal condition is

$$2\chi_{\text{INC}} = r^{-1/2}(N_A \phi_A)^{-1} + r^{1/2}(N_B(1 - \phi_A))^{-1} \quad (2.10)$$

Note that in the hypothetical incompressible limit the form of both the scattering functions and spinodal condition is much simpler than that of the rigorous expressions. If the blend possesses segmental volume and degree of polymerization symmetries, i.e. $r = 1$ and $N_A = N_B = N$, eqs 2.9 and 2.10 become particularly simple

$$2\chi_{\text{INC}} = \rho[C_{AA} + C_{BB} - 2C_{AB}] \quad (2.11)$$

$$2\chi_{\text{INC}}\phi_A(1 - \phi_A)N = 1 \quad (2.12)$$

Although the RPA form can usually be fit to low wavevector experimental scattering data, and an apparent chi-parameter thereby extracted, the *literal* use of an incompressible RPA approximation for the calculation of thermodynamic properties and phase stability is generally expected to represent a poor approximation due to the importance of density-fluctuation-induced compressibility or equation-of-state effects.^{13,31,33,34} The latter are non-universal and are expected to increase in importance as the structural and/or intermolecular potential asymmetries characteristic of the molecules of the blend increase.

As forcefully emphasized by Dudowicz, Freed, and co-workers,³⁴ a procedure more akin to the experimental analysis is to simply treat the theoretical calculations based on the rigorous expressions of eqs 2.3 as "data" which are "fit" to the incompressible RPA scattering function in order to extract a single "effective chi-parameter". This is not a unique procedure since there are three independent $k = 0$ direct correlation functions even for the homopolymer binary blend. I shall first consider the simplest $k = 0$ extrapolation procedure which includes the influence of all partial scattering factors in the definition of an apparent SANS χ parameter.²⁻⁶ The resultant chi-parameter contains not only microscopic information concerning intermolecular interactions in blends (i.e. some combination of the independent C_{MM} 's) but also reflects all the errors made by the neglect of compressibility effects which depend on N , T , ϕ_A , et cetera.³⁴

The generalized RPA expression is given at $k = 0$ by^{2,4}

$$\frac{k_N}{\hat{S}_E(0)} = \frac{1}{\phi_A N_A V_A} + \frac{1}{\phi_B N_B V_B} - 2\frac{\chi_s}{V_0} \quad (2.13)$$

where χ_s denotes the apparent SANS chi-parameter. V_0 is a "reference volume" which has been defined in various ways (e.g., $V_0 = (V_A V_B)^{1/2}$ or $V_0 = [(\phi_A V_A)^{-1} + (\phi_B V_B)^{-1}]^{-1}$ or $V_0 = \phi_A V_A + \phi_B V_B$), and k_N is a scattering length density factor given by²

$$k_N = \left(\frac{b_A}{V_A} - \frac{b_B}{V_B}\right)^2 \quad (2.14)$$

where b_M is the total neutron scattering length of a site of species M. The quantity $\hat{S}_E(0)$ is the total experimental scattering intensity and is given by

$$\hat{S}_E(0) = \sum_{M,M'} b_M b_{M'} \hat{S}_{MM'}(0) \quad (2.15)$$

Note that this chi-parameter diverges as $\phi_M \rightarrow 0$ due to the unrealistic incompressibility assumption, and the SANS χ_s is, by construction, equivalent to the incompressible Flory value at the spinodal where $\Lambda(0) = 0$.

Substitution of eqs 2.3 and 2.15 into eq 2.13 yields a lengthy, but general, expression for the SANS chi-parameter which can be employed in numerical PRISM studies of specific blends. The experimental neutron scattering lengths generally enter in this definition, although at the spinodal this is not true and eq 2.10 is obtained if $V_0 = (V_A V_B)^{1/2}$. Note that χ_s does not contain any microscopic information concerning blend thermodynamics at the spinodal.

The common argument for the validity of the incompressible RPA expression is that the isothermal compressibility of dense fluids is very small. Although true, it is not zero, and for high polymers since χ_s itself must be very small in the homogeneous phase it is not a priori obvious that an incompressibility approximation is valid. Nevertheless, it is instructive to identify the conditions required for accuracy of an incompressibility assumption at the level of the scattering functions and spinodal condition. That is, one can understand how eqs 2.3 reduce to eqs 2.7 and 2.8 and eq 2.5 reduces to eq 2.10?

From eq 2.6 a small isothermal compressibility implies that

$$-\rho \hat{C}_{MM'}(0) \gg 1 \quad (2.16)$$

which is generally true for any dense fluid. In terms of eqs 2.3, if the related wavevector-dependent condition

$$-\rho_M \hat{\omega}_M(k) \hat{C}_{MM}(k) \gg 1 \quad (2.17)$$

applies, then considerable simplification of eqs 2.3 occurs

$$\begin{aligned} \hat{S}_{AA}^{-1}(k) &\cong \frac{\hat{\Lambda}(k)}{-\rho_A \rho_B \hat{\omega}_A(k) \hat{\omega}_B(k) \hat{C}_{BB}(k)} \\ &\cong (\rho_A \hat{\omega}_A(k))^{-1} + (\rho_B \hat{\omega}_B(k))^{-1} \frac{\hat{C}_{AA}(k)}{\hat{C}_{BB}(k)} - \\ &\quad \hat{C}_{BB}^{-1}(k) \{\hat{C}_{AA}(k) \hat{C}_{BB}(k) - \hat{C}_{AB}^2(k)\} \end{aligned} \quad (2.18a)$$

$$\hat{S}_{BB}^{-1}(k) \cong \frac{\hat{C}_{BB}(k)}{\hat{C}_{AA}(k)} \hat{S}_{AA}^{-1}(k) \quad (2.18b)$$

$$\hat{S}_{AB}(k) \cong -\frac{\hat{C}_{BB}(k)}{\hat{C}_{AB}(k)} \hat{S}_{AA}^{-1}(k) \quad (2.18c)$$

Equation 2.17 can be viewed as an *effective incompressibility condition*, and I shall refer to it as such in the remainder of this and the following paper.³⁰ For inverse wavevectors greater than some fraction of the radius-of-gyration eq 2.17 is easily obeyed at high densities, especially for high polymers since $\hat{\omega}_M(k \approx R_g^{-1}) \propto N_M$, and thus the SANS wavevector regime is well separated from the local, system-specific length scales. Hence, the “effective incompressible limit” and eqs 2.18 are expected to be quite accurate on long length scales for dense, high polymer blends. The general expression for the SANS chi-parameter as given by eqs 2.13–2.15 simplifies somewhat in the effective incompressible limit and is given by

$$2\chi_S \cong \frac{V_0}{\phi_A N_A V_A} + \frac{V_0}{\phi_B N_B V_B} + \left(\frac{b_A}{V_A} - \frac{b_B}{V_B} \right)^2 \frac{\eta V_0}{\rho_A \rho_B N_A N_B} \frac{\Lambda^*(0)}{\{b_A^2 C_{BB} + b_B^2 C_{AA} - 2b_A b_B C_{AB}\}}$$

$$\Lambda(0) \cong \Lambda^*(0) = -\rho_A N_A C_{AA} - \rho_B N_B C_{BB} + \rho_A \rho_B N_A N_B [C_{AA} C_{BB} - C_{AB}^2] \quad (2.19)$$

However, the inter-relationship between the three partial structure factors is *not* precisely given by the literal incompressibility relations of eq 2.7, and the form of $\tilde{S}_{AA}(k)$ is *not* the same as the RPA-like expression of eq 2.8. Most significantly, the analog of the effective chi-parameter is *not* of the simple linear arithmetic difference form of eq 2.9, but is fundamentally nonlinear. All these differences between the effective incompressible limit and the “literal incompressible RPA” will be shown to be very important for most systems of interest.

An alternative approach to extracting an apparent chi-parameter from SANS data is to fit the scattering curves to an IRPA form over the entire measured wavevector range. Within the PRISM formalism one can approximately implement this procedure as follows. Using eqs 2.18 one obtains for the scattering profile in the “effective incompressible” approximation

$$\tilde{S}_c(k) \equiv \rho^{-1} \sum_{M,M'} b_M b_{M'} \tilde{S}_{MM'}(k) = F_A \tilde{S}_C(k) \quad (2.20a)$$

where the “amplitude” factor, F_A , and dimensionless concentration fluctuation scattering function, $\tilde{S}_C(k)$, are given by

$$F_A \equiv b_A^2 \sqrt{\frac{C_{BB}}{C_{AA}}} + b_B^2 \sqrt{\frac{C_{AA}}{C_{BB}}} - 2b_A b_B \frac{C_{AB}}{\sqrt{C_{AA} C_{BB}}} \quad (2.20b)$$

$$\tilde{S}_C^{-1}(k) \equiv \frac{\rho}{\rho_A \hat{\omega}_A(k)} \sqrt{\frac{C_{BB}}{C_{AA}}} + \frac{\rho}{\rho_B \hat{\omega}_B(k)} \sqrt{\frac{C_{AA}}{C_{BB}}} - \frac{C_{AA} C_{BB} - C_{AB}^2}{\rho \sqrt{C_{AA} C_{BB}}} \quad (2.20c)$$

The wavevector dependence is contained in $\tilde{S}_C(k)$ which is of the same general mathematical form as the empirical IRPA expression. To make direct contact with the experimental data analysis $\tilde{S}_C(k)$ can be equated to the IRPA form of eq 2.8. The result of this procedure is an explicit expression for the apparent SANS chi-parameter.

For the simpler case of equal A and B site volumes (generalizations are straightforward) one obtains

$$\hat{\chi}_S(k) = \frac{\rho}{2\sqrt{C_{AA} C_{BB}}} (C_{AA} C_{BB} - C_{AB}^2) + \frac{1 - \sqrt{C_{BB}/C_{AA}}}{2\phi_A \hat{\omega}_A(k)} + \frac{1 - \sqrt{C_{AA}/C_{BB}}}{2(1 - \phi_A) \hat{\omega}_B(k)} \quad (2.21)$$

Note that $\hat{\chi}_S(k)$ can acquire a k dependence even in the small angle regime via a “cross-term” between the intramolecular and intermolecular correlation contributions. Thus, the wavevector dependence may be viewed as an “artefact” of the incompressibility approximation. It may be particularly important for SANS experiments on strongly structurally asymmetric mixtures for which the quantity $|1 - C_{BB}/C_{AA}|$ is expected to be non-negligible. Such an “anomalous” k -dependent chi-parameter has been experimentally observed recently by Brereton et al.⁴ in a binary blend of polymers with significantly different aspect ratios (polystyrene and poly(tetramethyl carbonate)). For most amorphous blends composed of relatively flexible chains, experimental SANS data can apparently be adequately fit using the IRPA and a single, wavevector-independent chi-parameter. The latter can be identified with the $k = 0$ limit of eq 2.21:

$$2\chi_S = \frac{\rho}{\sqrt{C_{AA} C_{BB}}} (C_{AA} C_{BB} - C_{AB}^2) + \frac{1 - \sqrt{C_{BB}/C_{AA}}}{\phi_A N_A} + \frac{1 - \sqrt{C_{AA}/C_{BB}}}{(1 - \phi_A) N_B} \quad (2.22)$$

The results of the PRISM theory for the $k = 0$ values of the direct correlation functions can be substituted in this relation to make contact with SANS experiments which extract χ_S via the k -dependent fitting procedure. Note, however, that in general the predictions of an apparent SANS chi-parameter using eq 2.22 will not be the same as the extrapolated zero angle intensity approach of eq 2.19.

In closing this general analysis, it is instructive to inquire whether there are special case(s) and/or well-defined additional approximations for which eqs 2.18 will reduce to the *literal incompressible RPA* form. As discussed in section IIIC and elsewhere,²⁶ the one special case corresponds to the theoretically much-studied, but experimentally unrealizable, *symmetric polymer blend*. More generally, the *additional approximation* required to recover the incompressible RPA forms is well-known within the widely employed framework of phenomenological treatments. In the integral equation language it corresponds to an approximation of the form

$$C_{MM'} \cong C_0 - \beta v_{MM'} \quad \text{with} \quad -C_0 \rightarrow \infty \quad (2.23)$$

The physical motivation for this approximation is that the integrated strength ($k = 0$ part) of the direct correlation functions (often viewed as “excluded volume parameters”) consists of a purely repulsive (athermal) potential plus a weak attraction. If the former is viewed as the *bare* singular hard core potential (i.e., a literal $\rho \rightarrow \infty$ incompressibility approximation for the direct correlation function), then one obtains eq 2.23. It is easily shown that use of eq 2.23 in eqs 2.18 leads to the literal incompressible RPA form for the structure factors and the spinodal condition, with an effective *enthalpic* χ parameter given by the simple arithmetic difference Flory form of eq 2.11 expressed *solely* in terms of the “weak attractive” contributions $\beta v_{MM'}$. The

new molecular closures²⁵⁻²⁷ do possess a mathematical structure similar to eq 2.23, but with the *two crucial exceptions* that the large repulsive force contributions are not infinite and in general depend on the two interacting sites (i.e. M and M' labels) since the local interchain correlations are sensitive to molecular structure. Even in the hypothetical $\rho \rightarrow \infty$ incompressible limit, the repulsive interaction contribution to the direct correlations at $k = 0$ is generally species-dependent which destroys the reduction of eqs 2.3 and 2.5 to the literal incompressible RPA forms and also has serious consequences for phase diagrams.

C. Atomic and Molecular Closure Approximations.

A standard interaction site model of homopolymers is considered where the pairwise decomposable site-site intermolecular potential is taken to consist of a hard core repulsion plus a more spatially slowly varying tail.

$$u_{MM'}(r) = u_{MM'}^{(0)}(r) = \infty \quad r < d_{MM'} \\ = v_{MM'}(r) \quad r \geq d_{MM'} \quad (2.24)$$

The hypothetical "athermal" limit is defined by $v_{MM'}(r) = 0$. For this athermal situation the atomic site-site Percus-Yevick closure approximation (which is equivalent to the MSA closure for hard cores) is employed:

$$g_{MM'}(r) = 0 \quad r < d_{MM'} \quad (2.25a)$$

$$C_{MM'}(r) \cong 0 \quad r > d_{MM'} \quad (2.25b)$$

where eq 2.25a is the exact core condition. Extensive applications of the PRISM theory with this closure for purely athermal melts⁹⁻¹¹ and blends^{12,13} have been carried out. Detailed comparisons with both computer simulations and wide angle scattering measurements on dense polymer melts have documented that the theory is accurate on all length scales.

For finite temperature phase-separating blends a family of new molecular closures have been recently formulated by Yethiraj and Schweizer. The physical motivation and mathematical nature of these new closures has been discussed in depth elsewhere.^{26,27} The simplest molecular closure corresponds to the reference molecular mean spherical approximation (R-MMSA) and is given in real space for a homopolymer blend by eq 2.25a plus

$$\omega_M^* C_{MM'}^* \omega_{M'}(r) \cong \omega_M^* C_{MM'}^{(0)*} \omega_{M'}(r) - \omega_M^* \beta v_{MM'}^* \omega_{M'}(r) \quad r > d_{MM'} \quad (2.26)$$

where the "stars" denote spatial convolutions. Note that the latter cannot be "canceled" since eq 2.26 applies only over a restricted region of intersite separations. The "reference" direct correlation functions associated with the athermal blend are denoted by $C_{MM'}^{(0)}$ and are computed separately using the Percus-Yevick closure of eq 2.25. The second term on the right hand side of the above equation is the attractive potential contribution. Its MSA-like form is asymptotically exact, but certain local correlation effects are neglected.

A quantitatively more sophisticated molecular closure is based on using a Percus-Yevick estimation of the attractive potential contribution and is known as the reference molecular Percus-Yevick (R-MPY) approximation.^{26,27} It is defined by eq 2.25a plus

$$\omega_M^* C_{MM'}^* \omega_{M'}(r) \cong \omega_M^* C_{MM'}^{(0)*} \omega_{M'}(r) + \omega_M^* \Delta C_{MM'}^* \omega_{M'}(r) \quad r > d_{MM'} \quad (2.27)$$

where

$$\Delta C_{MM'}(r) \cong [1 - \exp(\beta v_{MM'}(r))] g_{MM'}(r) \quad r > d_{MM'}$$

This closure is nonperturbative in the strength (relative to $k_B T$) of the attractive potentials and weights their contributions by the species-dependent site-site radial distribution function in a fashion reminiscent of the calculation of an internal energy or heat of mixing.

In the analytical treatment presented below a limiting case of eq 2.27 corresponding to the high temperature/weak potential situation is also of interest. Standard thermodynamic perturbation theory, *but* at the level of the direct correlation functions *not* pair correlations, yields

$$\Delta C_{MM'}(r) \cong -\beta v_{MM'}(r) g_{MM'}^{(0)}(r) \quad r > d_{MM'} \quad \text{and} \quad |\beta v_{MM'}(r)| \ll 1 \quad (2.28)$$

where the superscript zero again denotes the reference athermal blend fluid. We shall refer to this closure as "R-MPY/HTA", where HTA denotes "high temperature approximation". For nonpolar high polymers this HTA may be particularly accurate since the relevant temperatures are large.

III. Analytic PRISM Theory of Threadlike Chains

A. Coarse-Grained Polymer Thread Model. The "threadlike chain" model has been discussed in depth elsewhere.²¹ Mathematically, it corresponds to the limit that all microscopic length scales approach zero but their ratios remain finite. In particular, the site hard core diameters $d_{MM'} \rightarrow 0$, but site densities $\rho_M \rightarrow \infty$ such that the reduced site densities, $\rho_M d_{MM'}^3$, are nonzero and finite. The hard core repulsion is effectively replaced by a δ -function interaction, and hence the thread model does *not* represent the continuous $d_{MM'} \rightarrow 0$ limiting case of a finite range hard core repulsion. The latter model would have trivial ideal gas properties. Gaussian statistics are assumed to describe the single chain structure factors $\hat{\omega}_M(k)$, which are thus characterized solely by the statistical segment length of species M, σ_M , and the number of segments N_M .

Implicit to the thread approach is a coarse-graining of molecular structure over the segmental length scale. Hence, local chemical information is lost (except in an average manner), and detailed structural features such as oscillatory $g_{MM'}(r)$ functions^{9,10} indicative of local solvation shells due to the nonzero space-filling volume of real monomers are not captured. However, it is interesting to note that $g(r)$ for chemically realistic models of polymer melts¹¹ display little or no sharp features due to the multiple chemical length scales characteristic of real molecules. Moreover, the thread idealization does yield analytic results which for many systems and properties are in excellent qualitative, or semiquantitative, agreement with numerical PRISM predictions for more realistic nonthread polymer models.^{13,17,21,22,25-27} This achievement is the motivation for constructing and studying the thread model.

At the single chain level the model binary polymer mixture is characterized by three local, and one global, structural asymmetry ratios

$$\gamma \equiv \sigma_B / \sigma_A \quad \Theta \equiv d_{BB} / d_{AA} \quad \Gamma \equiv \sigma_A / d_{AA} \\ R_N \equiv N_B / N_A \quad (3.1)$$

The thermodynamic state variables can be chosen to be temperature, T , total packing fraction, η , and volume fraction of polymer A, ϕ . Due to the coarse-graining aspect of the thread model, only relatively small wavevectors are

of significance ($k\sigma_M \leq 1$). Hence, a convenient and accurate mathematical approximation³⁶ for the Gaussian intrachain structure factor is employed:

$$\hat{\omega}_M(k) \cong [N_M^{-1} + k^2 \sigma_M^2/12]^{-1} \quad (3.2)$$

which exactly captures the $k = 0$ and "intermediate scaling regime" behavior. Equation 3.2 does not satisfy the trivial high wavevector limit of $\hat{\omega}_M(k \rightarrow \infty) = 1$. However, this is irrelevant since the continuum thread model is applicable only within the mathematical framework of a high wavevector cutoff, and for δ -function interactions the self-scattering term should be omitted. For analytical convenience, a Yukawa form for the attractive potential tail is employed

$$v_{MM'}(r) = \epsilon_{MM'}(a_{MM'}/r) \exp(-r/a_{MM'}) \quad r > d_{MM'} \rightarrow 0 \quad (3.3)$$

where $\epsilon_{MM'}$ are energy parameters and the $a_{MM'}$ are spatial range parameters. Since the thread idealization precludes a realistic assessment of the consequences of $\theta \neq 1$ and monomer shape, I set $\theta = 1$. Alternatively, one can imagine coarse-graining polymer structure such that the volumes of the effective segments of the different species are equal. For simplicity, the length scale characterizing the interchain attractions is also taken to be species independent, i.e. $a_{MM'} = a$.

B. Closures in the Thread Limit. For the reference thread blend the most severe "hard core condition" is imposed, i.e., $g_{MM'}(r=0) = 0$, for $M, M' = A, B$, which serves to determine the "direct correlation function inside the core". [An alternative, more complicated approach has been suggested by a reviewer of this paper: set $g_{MM'}(r=0) = \text{species-dependent constant}$ which is chosen from some thermodynamic constraints or self-consistency conditions.] For the athermal reference blend with the Percus-Yevick closure of eq 2.25, the direct correlation functions are fully determined by a *single parameter*.^{13,21,22}

$$C_{MM'}^{(0)}(r) = C_{MM'}^{(0)} \delta(\tilde{r}) \quad \text{for} \quad r < d_{MM'} \rightarrow 0$$

$$\hat{C}_{MM'}^{(0)}(k) = \hat{C}_{MM'}^{(0)}(0) \equiv C_{MM'}^{(0)} \quad (3.4)$$

Equation 3.4 can be viewed as the MSA (or RPA) closure for a fluid interacting via a site-site δ -function potential of $-\beta^{-1} C_{MM'}^{(0)} \delta(\tilde{r})$. The amplitude factor $C_{MM'}^{(0)}$ is "self-consistently" determined by enforcing the pointlike hard core constraint on the intermolecular radial distribution function. An exact analytical solution of the athermal thread blend problem has been obtained in the long chain limit¹³ and is explicitly employed in the study of structurally asymmetric blends presented in the following paper.³⁰

For the molecular closures one can show that in the $d_{MM'} \rightarrow 0$ thread polymer limit the hard core condition becomes a *point of measure zero* in the sense that the molecular closure relations of eqs 2.26–2.28 completely define the species-dependent $\hat{C}_{MM'}(k)$ functions.²⁶ Fourier-transforming eq 2.26 then yields the thread polymer version of the R-MMSA closure:

$$\hat{C}_{MM'}(k) = \hat{C}_{MM'}^{(0)}(k) - \beta \delta_{MM'}(k) \quad (3.5)$$

This relation has the analytical structure of a "high temperature/mean field" approximation about the hard core blend system and is similar in *mathematical form* to the RPA-like ansatz of eq 2.23. The leading contribution contains the "athermal" (packing) information, which in general depends on polymer density, blend composition, and single chain structural asymmetries. The second term

is a purely "enthalpic" mean field contribution. At the thread level the only relevant aspect of the attractive potentials for thermodynamics ($k = 0$) are their integrated strengths in units of the thermal energy.

For the R-MPY closure the convolutions in eq 2.27 can also be "canceled" in the thread limit, thereby yielding a simpler expression, which in the $k = 0$ limit becomes²⁸

$$C_{MM'} \cong C_{MM'}^{(0)} + \int d\tilde{r} \{1 - \exp[\beta v_{MM'}(r)]\} g_{MM'}(r) \quad (3.6)$$

$$= C_{MM'}^{(0)} - \beta v_{MM'} + \int d\tilde{r} [\beta v_{MM'}(r) + 1 - \exp\{\beta v_{MM'}(r)\}] + \int d\tilde{r} [1 - \exp\{\beta v_{MM'}(r)\}] h_{MM'}(r)$$

where the explicit $k = 0$ Fourier-transform notation has been dropped. In the second line of eq 3.6 the first two terms represent the R-MMSA part, the third term is a mean field-like correction to the high temperature/weak potential limit, and the fourth term contains the influence of structural fluctuations due to a nonzero "total" site-site pair correlation function, $h_{MM'}(r)$. The latter fluctuation correction can be *either* positive or negative depending on system-specific details. In contrast with the R-MMSA thread closure, the general k -dependent analog of eq 3.6 *functionally* relates the direct and interchain pair correlation functions and hence must be solved in conjunction with the blend PRISM integral equations in a self-consistent fashion. Numerical analysis is generally required, and hence this closure, although the most quantitatively accurate,²⁷ will not be considered in this paper.

In the high temperature/weak potential limit, $\beta v_{MM'}(r) \ll 1$, eq 3.6 reduces to the simpler R-MPY/HTA closure:

$$C_{MM'} \cong C_{MM'}^{(0)} - \int d\tilde{r} \beta v_{MM'}(r) g_{MM'}^{(0)}(r) \quad (3.7)$$

which is of the same general form as the R-MMSA closure, but the enthalpic contribution now contains athermal packing corrections which depend on density, composition, and single chain structural asymmetries.

As a general comment, the clean separation of repulsive packing and attractive potential contributions to the direct correlation functions in eqs 3.5–3.7 is a consequence of the thread idealization; only in this $d_{MM'} \rightarrow 0$ limit is the hard core constraint "irrelevant" in the sense that the convolution integrals in eqs 2.26 and 2.27 can be "canceled". Numerical calculations for nonthread models reveal significant deviations of the $C_{MM'}(r)$ functions from the above forms, even for the simplest symmetric blend. However, the long wavelength ($k = 0$) or "integrated" consequences of a nonzero hard core diameter (which determine the thermodynamics) seem to be remarkably small.²⁷

An analytical calculation of the spinodal curve for the general structurally asymmetric thread polymer blend model is presented in Appendix A for PRISM theory with the R-MMSA and R-MPY/HTA closures. The mathematical structure of these two closures can be generically written as

$$C_{MM'} = C_{MM'}^{(0)} - \beta \tilde{H}_{MM'} \quad (3.8)$$

where $\tilde{H}_{MM'}$ is implicitly defined via comparison with eqs 3.5 and 3.7 and is *independent of temperature*. The latter fact implies the spinodal condition of eq 2.5 is at most a quadratic equation in temperature.³⁷

C. Results for Symmetric Blends. A "symmetric" binary blend is defined as consisting of two types of homopolymer chains, A and B, which are *structurally*

identical in every respect. Hence, the corresponding single chain structure factors obey the identity $\omega_A(r) = \omega_B(r) \equiv \omega(r)$. The pair potentials between sites are

$$\begin{aligned} u_{AA}(r) &= u_{BB}(r) = u_0(r) + v_{AA}(r) \\ u_{AB}(r) &= u_0(r) + v_{AB}(r) \end{aligned} \quad (3.9)$$

where $u_0(r)$ is a hard core potential with diameter d and the $v_{MM'}(r)$ potentials are defined for $r > d$ as in eq 2.24. It is important to emphasize that isotopic mixtures are not symmetric since hydrogen-hydrogen and deuterium-deuterium dispersion interactions are obviously not the same.

The structurally symmetric aspect implies that the molecular closures can be generically written as

$$C_{MM'} = C_0 - \beta \tilde{H}_{MM'} \quad (3.10)$$

where C_0 is the athermal thread homopolymer melt direct correlation parameter.³⁸ For the Gaussian thread model this parameter is given by

$$C_0 = (-12\rho)^{-1} \left\{ \frac{\pi}{3} \rho \sigma^3 + \sqrt{\frac{12}{N}} \right\}^2 \quad (3.11a)$$

or in terms of the $k = 0$ reference structure factor

$$S_0 \equiv (-\rho C_0)^{-1} \cong 12(2\eta)^{-2} \Gamma^{-6} \quad (3.11b)$$

where $N \gg 1$, $\eta = \pi \rho d^3/6$ is the packing fraction, d is the segmental hard core diameter, and $\Gamma = \sigma/d$ is the aspect ratio. Since the form of eq 3.10 is rigorously obtained from the molecular closures only in the thread limit, one might argue that the coarse-grained Gaussian model should be employed to estimate the value of reference athermal fluid C_0 . The literal thread result of eq 3.11 implies for meltlike packing fractions and an aspect ratio of 1.4 (which is typical of amorphous polymers) that $S_0 \cong 1.5$. An alternative viewpoint, which I adopt in subsequent calculations and which is supported by numerical studies,³⁹ is that the form of eq 3.10 is a good approximation for nonthread chains but the precise value of C_0 is that appropriate for the "real" polymer fluid, i.e. for a chemically realistic model. In this case C_0 is significantly larger in absolute magnitude than given by eq 3.11. For example, PRISM calculations for hard core polyethylene melts yield $S_0 \cong 0.2$, which is also roughly the value for alkane and polyethylene melts as deduced from experimental values of density and isothermal compressibility (see Appendix B).¹¹

The spinodal is determined by eq 2.5, which using eq 3.10 yields

$$1 + N\rho\beta_S \tilde{H}_{AA} - N\rho C_0 + 2\tilde{\chi}_{\text{INC}} N^2 \phi(1-\phi)\rho \{C_0 - \beta_S [\tilde{H}_{AA} + \tilde{H}_{AB}]/2\} = 0 \quad (3.12)$$

where β_S is the inverse thermal energy at the spinodal, and

$$\tilde{\chi}_{\text{INC}} \equiv \rho\beta [\tilde{H}_{AB} - \tilde{H}_{AA}] \quad (3.13)$$

Equation 3.12 is a simple quadratic equation, and the solution can be immediately written down.³⁷ The general symmetric blend analysis is given elsewhere²⁸ where it is shown that the spinodal condition is precisely of the Flory-Huggins form

$$k_B T_S = 2N\phi(1-\phi)\rho [\tilde{H}_{AB} - \tilde{H}_{AA}] \quad (3.14)$$

under the very weak condition that $-\rho N C_0 \gg 1$. Note

that the repulsive force direct correlation parameter "cancels out" of the spinodal condition in this effective incompressible limit. In addition, use of eq 3.10 in eqs 2.3 immediately implies that the partial collective scattering structure factors are to an excellent approximation of the literal incompressible RPA form if $-\rho \tilde{C}_0(k) \gg |\beta \tilde{H}_{MM'}(k)|$ and $-\rho \tilde{\omega}(k) \tilde{C}_{MM'}(k) \gg 1$.

Thus, compressibility effects are not important for a symmetric blend with regards to the form of the spinodal condition, the scattering functions at small k , and the usefulness of a single chi-parameter in accord with recent computer simulation studies of Binder and co-workers.^{23,28} These conclusions are adopted by assumption by the IRPA approach. However, the validity of such a conclusion derives from the nearly precise decoupling of concentration and density fluctuations in symmetric mixtures.^{12,31} Significant errors may be incurred when any type of asymmetry is present. Moreover, the neglect of density correlations is not generally valid on the length scales which determine the magnitude of the phase transition temperature.

For the R-MMSA closure, the predictions of analytic thread PRISM follows from substitution of eq 3.10 in eq 2.11:

$$\chi_{\text{INC}} = \beta \rho \int d\tilde{r} \{u_{AB}(r) - v_{AA}(r)\} = \chi_0 \quad (3.15)$$

Hence, for the symmetric threadlike blend, PRISM theory with the R-MMSA closure represents the integral equation realization of Flory-Huggins theory with regards to the effective chi-parameter and critical temperature! The R-MMSA closure displays the standard mean field linear dependences on inverse temperature and polymer density. Such simplicities are a consequence of the "weak coupling" or "asymptotic" nature of a MSA-like closure, i.e. the $r \rightarrow \infty$ limit of $g_{MM'}(r) = 1$ is assumed to hold for all r with regards to determining the effects of the attractive potential on the direct correlation functions. However, the PRISM/R-MMSA theory does predict nontrivial density correlations and nonzero intermolecular concentration fluctuations, but these low amplitude correlations are now thermodynamically irrelevant.

The R-MPY closure is more sophisticated than the R-MMSA approximation since it includes local correlation corrections. The effective incompressible chi-parameter for long chains is given by²⁶

$$\chi_{\text{INC}} = \chi_0 + (\beta \rho / 2) \int d\tilde{r} \{2v_{AB}(r)h_{AB}(r) - v_{AA}(r)[h_{AA}(r) + h_{BB}(r)]\} \quad (3.16)$$

Since the $h_{MM'}(r)$ correlation functions depend on blend composition, the effective chi-parameter will also be ϕ -dependent due to structural changes on the length scale of $v_{MM'}(r)$. Numerical calculations are required to precisely determine the three independent $h_{MM'}(r)$ correlation functions. However, if one adopts the HTA approximation (see eq 2.18) then eq 3.16 simplifies to

$$\chi_{\text{INC}} = \chi_0 + \int d\tilde{r} \{\beta v_{AB}(r) - \beta v_{AA}(r)\} \rho h_m(r) \quad (3.17)$$

where $h_m(r)$ is the reference thread homopolymer melt function.²¹

$$\rho \sigma^3 h_m(r) = \frac{3\sigma}{\pi r} [\exp[-r/\xi_\rho] - \exp[-r/\xi_c]] \quad (3.18)$$

where

$$\xi_c \equiv R_g/\sqrt{2} \quad \xi_\rho^{-1} = \xi_c^{-1} + \frac{\pi}{3} \rho \sigma^3 \quad (3.19)$$

For the analytic thread model, and also the fluctuating

bond lattice model²³ and real polyethylene melts,¹¹ $g_m(r) < 1$ locally. This reduction of $g_m(r)$ from unity (local "correlation hole") increases as N increases and/or polymer density decreases. Straightforward analysis yields²⁶

$$\chi_0 = 4\pi\beta[\epsilon_{AB} - \epsilon_{AA}]\rho a^3 \quad (3.20)$$

$$\frac{\chi_{\text{INC}}}{\chi_0} = 1 - \frac{3}{\pi} \frac{\sigma}{a} (\rho\sigma^3)^{-1} \left[\frac{1}{1 + (a/\xi_c)} - \frac{1}{1 + (a/\xi_p)} \right] \quad (3.21)$$

The above results apply for either a phase-separating symmetric blend ($\chi_0 > 0$) or a "purely miscible" blend ($\chi_0 < 0$), as recently studied by Kumar⁴⁰ using off-lattice simulations. For the phase-separating case of primary interest, the renormalization ratio is predicted to *decrease weakly* with N , and in the $N \rightarrow \infty$ limit reduces to²⁶

$$\begin{aligned} \frac{\chi_{\text{INC}}}{\chi_0} &= 1 - \frac{3\sigma}{\pi a} (\rho\sigma^3)^{-1} \frac{a}{\xi_p + a} \\ &= \frac{a}{a + \xi_p} \quad N \rightarrow \infty \end{aligned} \quad (3.22)$$

where the second equality follows from using the literal thread result of eq 3.19. Since the density fluctuation length scale decreases with polymer density, the renormalization ratio is predicted to become smaller as the polymer concentration is reduced. Physically, this is simply a consequence of the "local correlation hole" which deepens as the density is lowered and interacting segments on different chains are pushed farther apart on average. Within the Gaussian thread model, one has²¹

$$\xi_p = \sqrt{\frac{\hat{S}(0)}{12}} \sigma \quad (3.23)$$

For a 6-12 Lennard-Jones potential $a \cong \sigma/2$, and at meltlike densities $\hat{S}(0) \cong 0.2$.¹¹ This implies a melt renormalization ratio of roughly 0.8 in accord with detailed numerical calculations for more realistic polymer models.²⁷ On the other hand, for moderately dense solutions $\hat{S}(0)$ is significantly larger and renormalization ratios of the order of 1/3 or smaller are predicted²⁷ in accord with the simulations.^{23,28} Equation 3.22 also predicts that at fixed density and statistical segment length the renormalization ratio decreases as the spatial range of the tail potential decreases. Such behavior has been observed in the most recent simulations of Deutsch and Binder.²³ Finally, note that the renormalization effect *vanishes*, i.e. $\chi_{\text{INC}} = \chi_0$, in the *hypothetical* $\rho \rightarrow \infty$ incompressible limit.

The analytic results presented above are in excellent qualitative, and nearly quantitative, agreement with numerical PRISM studies of symmetric blends with more realistic chain models.²⁷ However, both the R-MPY/HTA and R-MMSA closures predict a ϕ -independent chi-parameter for symmetric polymer blends. Numerical studies using the full R-MPY closure show this is not generally true since the $\tilde{H}_{\text{MM}'}$ of eq 3.8 depends on composition via the local pair correlations $g_{\text{MM}'}(r)$. A concave upward, parabolic-like concentration dependence is found, the magnitude of which depends on temperature, polymer density, degree of polymerization, and attractive potential choice.^{27,35}

In the remainder of this work and the companion paper we consider analytic PRISM theory predictions at the R-MMSA and R-MPY/HTA levels. Certain relatively small quantitative features associated with the attractive potential induced changes in packing may be missed by these closures, but they should be adequate for accessing

the influence of structural and attractive potential *asymmetries* on blend thermodynamics and scattering.

IV. Phase Separation of Structurally Symmetric Blends

Real blends do not satisfy the "symmetric" criterion with regards to the attractive intermolecular potentials $v_{\text{MM}'}(r)$. The consequences of asymmetries at the "pure concentration fluctuation" level are contained in the IRPA effective chi-parameter defined in eq 2.11. Deviations between the spinodal boundary predicted by the incompressible RPA condition of eq 2.10 and eq 2.5 reflect the explicit influence of density fluctuations, or compressibility, on phase stability. Such non-Flory-Huggins effects are distinct from the possible "intrinsic" correlation processes contained in the three individual interaction parameters, $\hat{C}_{\text{MM}'}(0)$.

A. Attractive Interactions in Nonpolar Fluids. The attractive intermolecular potentials between nonpolar molecules are of the van der Waals, or London dispersion, form. To a reasonable approximation they obey the "Berthelot scaling relations" for the Lennard-Jones parameters.⁴¹ Of course, significant deviations are possible, especially for idealized descriptions of molecular structure where the true microscopic parameters become "renormalized" by the coarse-graining procedure. For a locally structurally symmetric mixture the Berthelot model corresponds to a relationship between the energy parameters of the form

$$\epsilon_{\text{BB}} = \lambda^2 \epsilon_{\text{AA}} \quad \epsilon_{\text{AB}} = \lambda \epsilon_{\text{AA}} \quad (4.1)$$

where λ is a positive constant. Such scaling relations are also often employed for the integrated strength of the entire attractive potential, $\hat{v}_{\text{MM}'}(0)$, or for the internal or cohesive energies in a multicomponent fluid, $\int d\mathbf{r} v_{\text{MM}'}(r) g_{\text{MM}'}(r)$. The latter is the basis of the empirical "solubility or Hildebrand parameter" of regular solution theory.⁴² These two interpretations correspond to Berthelot scaling in the analytic thread closures of the form

$$\tilde{H}_{\text{BB}} = \lambda^2 \tilde{H}_{\text{AA}} \quad \tilde{H}_{\text{AB}} = \lambda \tilde{H}_{\text{AA}} \quad (4.2)$$

If incompressibility is assumed, then the effective chi-parameter and spinodal temperature of structurally symmetric blends is obtained by substituting eqs 3.10 and 4.2 into eqs 2.11 and 2.12 to obtain for $\tilde{H}_{\text{MM}'} < 0$:

$$\begin{aligned} \chi_{\text{INC}} &= \rho\beta\{\tilde{H}_{\text{AA}} + |\tilde{H}_{\text{BB}}| - 2|\tilde{H}_{\text{AB}}|\}/2 \\ &= \rho\beta(\lambda - 1)^2 \tilde{H}_{\text{AA}}/2 \end{aligned} \quad (4.3)$$

$$k_{\text{B}}T_{\text{S}} = \rho(\lambda - 1)^2 \tilde{H}_{\text{AA}}|\phi(1 - \phi)N/4 \quad (4.4)$$

where the second line in eq 4.3 follows for Berthelot scaling. The enthalpic χ_{INC} of eq 4.3 is equivalent to the literal mean field Flory-Huggins value, χ_0 , only within the R-MMSA closure for the structurally symmetric blend. If the R-MPY/HTA closure is employed, then athermal density correlations are accounted for, and if the full R-MPY closure is employed, then temperature-dependent local compositional fluctuation effects are also included via the weighting of the interaction potentials by the species-dependent site-site radial distribution functions.²⁷

Real isotopic blends are expected to conform to the structurally symmetric criterion and van der Waals potential law very closely.⁴³ If AA denotes the interaction between a pair of deuterated monomers, then the param-

eter λ is proportional to the ratio of a C-H bond to C-D bond polarizability which is ≈ 1.02 .⁴³ We shall refer to a model blend which is structurally symmetric and obeys eq 4.4 as a "symmetric Berthelot" mixture. Of primary physical interest is the case where $\tilde{H}_{AA} < 0$, but the opposite case corresponding to a $\chi_{\text{INC}} < 0$ is a crude model of a blend in which "strong or specific attractions" are present. The latter case will be treated in section V. The isotopic blend is one physical realization of the symmetric Berthelot mixture model, but the general properties of such a blend (i.e. all values of λ) are of theoretical interest and can be studied by computer simulation methods.

B. Analytic Predictions for $N_A = N_B$ Symmetric Berthelot Blends. Within the general molecular closure approximation approach the symmetric Berthelot blend is special in the sense that all the quadratic terms in β cancel out in the compressible spinodal condition of eq 2.5 resulting in a trivial linear equation³⁷ for the spinodal temperature (see Appendix A). Nevertheless, the incompressible Flory-Huggins behavior is *not* exactly recovered due *solely* to compressibility effects. Simple algebra yields

$$2\chi_{\text{INC}}N\phi(1-\phi) = \frac{1+Q}{1+Z} \quad (4.5)$$

$$Q \equiv (-N\rho C_0)^{-1} \quad Z \equiv \frac{1 + (\lambda^2 - 1)\phi}{(\lambda - 1)^2\phi(1-\phi)(-N\rho C_0)} \quad (4.6)$$

These compressibility effects are distinct from the "volume change upon mixing" effect recently discussed by Kumar.⁴⁰ In the limit that the factors $Q, Z \rightarrow 0$, the Flory-Huggins form is recovered. This limit is rigorously achieved if $N \rightarrow \infty$ or in the hypothetical incompressible (infinite density) limit where $-C_0 \rightarrow \infty$. For dense polymer fluids Q is effectively zero, so we will drop it, in which case the spinodal temperature becomes

$$k_B T_s = \rho(\lambda - 1)^2 |\tilde{H}_{AA}| \phi(1-\phi) N [1 + Z] \quad (4.7a)$$

or alternatively,

$$\frac{k_B T_s}{\rho |\tilde{H}_{AA}|} = (\lambda - 1)^2 N \phi(1-\phi) + S_0 [1 + (\lambda^2 - 1)\phi] \quad (4.7b)$$

which explicitly displays the pure concentration fluctuation and density fluctuation (compressibility) contributions. The corresponding critical composition and temperature are given by

$$\phi_c = \frac{1}{2} \left\{ 1 + \frac{S_0}{N} \frac{\lambda + 1}{\lambda - 1} \right\} \quad (4.8)$$

$$\frac{k_B T_c}{\rho |\tilde{H}_{AA}|} = \frac{1}{4} (\lambda - 1)^2 N + \left(\frac{\lambda^2 + 1}{2} \right) S_0 - \frac{(\lambda + 1)^2 S_0}{4N} (2 - S_0) \quad (4.9)$$

The predicted enhancement of the critical temperature relative to the incompressible limit, $T_{c,\text{INC}}$ is given by

$$\frac{T_c}{T_{c,\text{INC}}} = 1 + \frac{2S_0}{N} \left[\frac{\lambda^2 + 1}{(\lambda - 1)^2} \right] \quad (4.10)$$

where the very small third term in eq 4.9 has been dropped. The above formulas are easily generalized to the experimentally relevant case of an isotopic blend where the deuteration is only partial. When A is denoted as the partially deuterated species, eqs 4.8-4.10 apply if $|\tilde{H}_{AA}|$

corresponds to its purely deuterated value, $(\lambda - 1)^2 \rightarrow (\lambda - 1)^2 x_D^2$, and $\lambda \rightarrow \lambda[\lambda + (1 - \lambda)x_D]^{-1}$, where x_D is the fraction of deuteration.

There are only quantitative differences between the R-MMSA and R-MPY/HTA closure predictions which enter via the \tilde{H}_{AA} factor. The latter is given by $\tilde{v}_{AA}(0)$ for the R-MMSA and $\int d\mathbf{r} v_{AA}(r) g_m(r)$ for the R-MPY/HTA. For thread blends the ratio of the latter two factors is identical to the chi-parameter renormalization ratio of eqs 3.21 and 3.22. This implies the spinodal temperature predicted by the R-MPY/HTA theory is *lower* than its R-MMSA analog due to the influence of local density fluctuations. This correction may be particularly important for the case of polymer blends diluted with nonselective solvents.

The most important feature of eq 4.7 is the strong dependence of the factor Z on the absolute magnitude of the attractive potential asymmetry parameter λ , the composition, and the homopolymer melt quantity S_0 which is directly proportional to the reference melt isothermal compressibility. At high densities S_0 is of order 0.1 for chemically realistic models.¹¹ Thus, compressibility effects for dense, structurally symmetric Berthelot high polymer blends are expected to be small *unless* $(\lambda - 1)^2 \ll 1$. The extreme example is isotopic blends, where the factor of $\{S_0/[N(\lambda - 1)^2]\} \approx 250/N$ if $\lambda \approx 1.02$ and $S_0 = 0.1$. This factor is enormously reduced by moderate increases of λ (e.g., to $10/N$ if λ increases to 1.1). The compressibility correction also increases as the composition becomes more asymmetric. Thus for simple isotopic-like blends significant system-specific compressibility effects may be present for N of the order of 1000 and less. These compressibility effects *destabilize* the miscible phase and result in a spinodal temperature *higher* than predicted by Flory-Huggins theory. A related point is that the ratio of the absolute magnitude of attractive potential contribution to the isothermal compressibility to its hard core (athermal) counterpart is given by

$$\frac{\rho \beta_c |\tilde{H}_{AA}|}{-\rho C_0} = \frac{4}{2(1 + \lambda^2) + (\lambda - 1)^2 (N/S_0)} \quad (4.11)$$

Although this factor formally vanishes in either the $N \rightarrow \infty$ or hypothetical $\rho \rightarrow \infty$ limits, it might not be small for some isotopic or related blends of experimental interest.

Since the compressibility effects vanish in the long chain limit, they also will introduce a non-Flory-Huggins *apparent* power law scaling of T_c with N for low and moderate values of N . The *apparent* exponent relating T_c and N will be *smaller than unity* in the regime where the compressibility effects are significant. Such scaling has been observed in a variety of low and moderate molecular weight blends and copolymers^{4,44,45} and perhaps is related to such density fluctuation processes.

A related issue is the effective chi-parameter as deduced from the spinodal curve. If the standard empirical data analysis approach is employed, then the right hand side of eq 4.5 is *defined* to be of the Flory-Huggins form but with an effective composition-dependent chi-parameter:

$$\chi_{\text{EFF}} = \chi_{\text{INC}} \frac{1 + Z(\phi)}{1 + Q} \quad (4.12)$$

Note that χ_{EFF} is *not* the same as the apparent SANS χ_S . The effective composition dependence of χ_{EFF} at the spinodal is of a concave upward, parabolic form *due solely* to density fluctuations associated with the potential asymmetries which are ignored in the standard incompressible Flory-Huggins approach. As a simple, but realistic, estimate of the size of this compressibility effect

for typical laboratory isotopic polymer blends, one can employ the following values: $S_0 = 0.1$, $N = 1000$, $\lambda = 1.02$ in eq 4.12 to obtain:

$$\frac{\chi_{\text{EFF}}}{\chi_{\text{INC}}} \cong 1 + \frac{1}{4\phi(1-\phi)} \quad (4.13)$$

which predicts that *along the spinodal* the effective chi-parameter is roughly a factor of 1.8 larger for $\phi = 0.9$ (or 0.1) than at $\phi = 0.5$.

C. Low Temperature Liquid-Gas Transition in Blends. Any dense one-component fluid can undergo a liquid-gas-like phase transition at low temperatures corresponding to the "triple point" region of the ρ - T phase diagram.⁴⁶ This phenomenon should not be confused with the high temperature vaporization transition. For one-component fluids this problem was considered within the analytic PRISM theory in Appendix B of ref 27. Low temperature liquid-gas-like spinodals have also been observed in theoretical studies of simple atomic mixtures.³¹ For polymer melts and blends such a phase transition is possible in principle, but in the laboratory appears to be always pre-empted by either liquid-liquid phase separation, crystallization, or a glass transition. Nevertheless, since the liquid-gas transition is driven by density fluctuations, its location relative to the liquid-liquid phase separation temperature provides a measure of the influence of compressibility, or equation-of-state, effects on thermally-induced demixing in polymer blends. In this section we study this liquid-gas transition for the analytic thread model of structurally symmetric blends using the PRISM/R-MMSA or R-MPY/HTA theories.

For simplicity we consider blends composed of chains of equal degrees of polymerization, N , and attractive potential contributions to the thread direct correlation functions at $k = 0$ which obey Berthelot scaling. Generalizations are straightforward. Employing the results of section IVA for the $k = 0$ direct correlation functions in eq 2.6 yields the explicit result

$$\hat{S}(0) \equiv \rho k_B T \kappa_T = \{N^{-1} + [(-\rho C_0) - \rho \beta |\tilde{H}_{AA}|(\phi + \lambda(1-\phi))^2]\}^{-1} \quad (4.14)$$

The liquid-gas spinodal temperature, T_{LG} , is defined by the divergence of κ_T which yields³⁷

$$k_B T_{\text{LG}} = \rho |\tilde{H}_{AA}| \frac{[\phi + \lambda(1-\phi)]^2}{(-\rho C_0) + N^{-1}} = \rho |\tilde{H}_{AA}| \hat{S}_0(0) [\phi + \lambda(1-\phi)] \quad (4.15)$$

In the literal incompressible limit, $-\rho C_0 \rightarrow \infty$, the liquid-gas spinodal temperature goes to zero. As expected for a density fluctuation process, T_{LG} is independent of N for long chains and high densities.

The liquid-liquid spinodal temperature, T_S , for the same model is given by eq 4.7. In the large N regime the ratio of these two temperatures is

$$\frac{T_S}{T_{\text{LG}}} = N\phi(1-\phi)(\lambda-1)^2 S_0^{-1} \left[\frac{1}{\phi + \lambda(1-\phi)} \right]^2 \quad (4.16)$$

Since $T_S \propto N$ for dense, high polymer blends, one clearly has the inequality $T_S \gg T_{\text{LG}}$ unless the quantity $(N/S_0)(\lambda-1)^2$ is of order unity. If the latter condition holds, then the influence of density fluctuations on liquid-liquid phase separation, and the compressibility-related errors incurred by Flory-Huggins theory, will be maximized.

It is instructive to rewrite the compressibility contribution to the spinodal temperature of eq 4.7 in terms of

the liquid-gas temperature as

$$k_B T_S = N\phi(1-\phi)\rho |\tilde{H}_{AA}|(\lambda-1)^2 + k_B T_{\text{LG}} \left[\frac{1}{\phi + \lambda(1-\phi)} \right] \quad (4.17)$$

which displays the N -independent elevation of the liquid-liquid spinodal temperature associated with the explicit contribution of density fluctuations.

D. Analytic Predictions for $N_A \neq N_B$ Symmetric Berthelot Blends. If the degree of polymerization symmetry is broken, i.e. $N_A \neq N_B$, then the deviations from Flory-Huggins theory are enhanced. The analog of eq 4.5 is easily shown to be

$$2\chi_{\text{INC}} \frac{N_A N_B}{\phi N_A + (1-\phi)N_B} \phi(1-\phi) = \frac{1+Q}{1+Z} \quad (4.18)$$

$$Q \equiv -\{\rho C_0 [\phi N_A + (1-\phi)N_B]\}^{-1}$$

$$Z \equiv \frac{\phi N_A + \lambda^2(1-\phi)N_B}{N_A N_B (-\rho C_0) \phi(1-\phi)(\lambda-1)^2} \quad (4.19)$$

and the analogs of eqs 4.7 and 4.8 are

$$\frac{k_B T_S}{\rho |\tilde{H}_{AA}|} = (\lambda-1)^2 \phi(1-\phi) \frac{N_A N_B}{N_A \phi + N_B(1-\phi)} + S_0 \left[1 + (\lambda^2 - 1) \frac{(1-\phi)N_B}{N_A \phi + N_B(1-\phi)} \right] \quad (4.20)$$

$$\frac{\chi_{\text{EFF}}}{\chi_{\text{INC}}} \cong 1 + \frac{S_0}{(\lambda-1)^2} \left[\frac{1}{(1-\phi)N_B} + \frac{\lambda^2}{\phi N_A} \right] \quad (4.21)$$

where the generally valid approximation $Q \ll 1$ has been employed. The first term on the right hand sides of eqs 4.20 and 4.21 represents the Flory-Huggins-like contribution, and the second term, the compressibility modification. The latter has a negligible influence only if $Z \ll 1$.

The critical composition is given by

$$\phi_c = \frac{1 - \sqrt{R + (4S_0/N_B)[(\lambda+1)/(\lambda-1)]}}{1-R} \quad R \equiv N_A/N_B \quad (4.22)$$

which reduces to the classic Flory-Huggins relation, $1/(1+R^{1/2})$, in the $S_0 \rightarrow 0$ incompressible limit. The corresponding critical temperature is

$$\frac{k_B T_c}{\rho |\tilde{H}_{AA}|} = (\lambda-1)^2 \sqrt{N_A N_B} \frac{\sqrt{R}}{(1+\sqrt{R})^2} + S_0 \left(\frac{R + \lambda^2}{R + 1} \right) \quad (4.23)$$

Note that the composition dependence of the apparent chi-parameter in eq 4.21 *along the spinodal* is predicted by the thread PRISM theory to be "skewed" about $\phi = 0.5$. The effective chi-parameter will be larger when the short chain is the minority component. Such skewing has been observed *at constant temperature* for the SANS chi-parameter of isotopic poly(ethylene), poly(vinylethylene) mixtures,⁵ and isotopic polyethylene blends.⁷

V. Attractive and Specific Interaction Effects

The Berthelot scaling relations for the integrated ($k = 0$) attractive potentials may often be a reasonable approximation for nonpolar blends with positive enthalpic

Flory-Huggins chi-parameters. However, if there exist stronger "chemically specific" interactions between the A and B polymers, then the Berthelot scaling relations will badly fail, and the mean field χ_0 can become negative. Such cases are of great interest for polymer alloys since specific attractive interactions represent the major miscibility strategy based on mean field energetic considerations.⁴⁷ In this section I consider this case for the structurally symmetric thread model blend. For algebraic simplicity only the symmetric degree of polymerization case is considered.

A. Analytic Results at the R-MMSA and R-MPY/HTA Levels. Interchain attractions are taken to consist of a nonpolar part which obeys the Berthelot scaling relations plus an extra A-B attraction, $\Delta V(r) < 0$. In terms of the integrated strengths of the attractive potential contribution to the $k = 0$ thread direct correlations one has

$$\tilde{H}_{BB} = \lambda^2 \tilde{H}_{AA}$$

$$\tilde{H}_{AB} = \lambda \tilde{H}_{AA} - \Delta \tilde{H} \quad \text{where} \quad \Delta \tilde{H} > 0 \quad (5.1)$$

The corresponding incompressible chi-parameter and spinodal temperature are

$$\chi_{\text{INC}} = \rho \beta |\tilde{H}_{AA}| \frac{(\lambda - 1)^2}{2} - \rho \beta |\Delta \tilde{H}| \quad (5.2)$$

$$k_B T_S = 2N\phi(1 - \phi) \rho |\tilde{H}_{AA}| \left\{ \frac{(\lambda - 1)^2}{2} - \frac{|\Delta \tilde{H}|}{|\tilde{H}_{AA}|} \right\} \quad (5.3)$$

The specific interaction is predicted by the incompressible Flory-Huggins-like theory to always stabilize the homogeneous phase, and "infinite miscibility", i.e. a negative chi-parameter, is predicted if $|\Delta \tilde{H}| > (\lambda - 1)^2 |\tilde{H}_{AA}|/2$.

The influence of the specific interaction on the liquid-gas-like transition is easily determined following the analysis of section IVC. The result is

$$k_B T_{\text{LG}} = \rho |\tilde{H}_{AA}| \frac{[\phi + \lambda(1 - \phi)]^2 + 2(|\Delta \tilde{H}|/|\tilde{H}_{AA}|)\phi(1 - \phi)}{(-\rho C_0) + N^{-1}} \quad (5.4)$$

Comparing eqs 5.4 and 4.13, one sees that the specific interaction *increases* the liquid-gas spinodal temperature. Hence, one can conclude quite generally that an attractive AB specific interaction will tend to "push" the liquid-liquid and liquid-gas phase transition temperatures *toward each other*, and hence will *increase* the importance of density fluctuations. The general spinodal predicted by PRISM using the R-MMSA and R-MPY/HTA closure levels is discussed in Appendix A. Specializing to the specific interaction model yields the quadratic equation

$$0 = -\{\phi(1 - \phi)N^2 J(J + 2\lambda)\}X^2 - \{\phi(1 - \phi)N^2 \rho C_0[2J - (\lambda - 1)^2] + N\phi + N(1 - \phi)\lambda^2\}X + 1 - (\rho C_0)N \quad (5.5)$$

where X is a dimensionless inverse spinodal temperature and J is the absolute magnitude of the ratio of the specific attraction to the nonpolar contribution

$$X = \rho \beta_s |\tilde{H}_{AA}| \quad J \equiv |\Delta \tilde{H}|/|\tilde{H}_{AA}| \quad (5.6)$$

Since within a coarse-grained Gaussian segment model the "interaction site" is a composite particle which consists of several distinct chemical groups, the J parameter is highly system-specific and can be larger or smaller than

unity depending on the concentration and chemical nature of strongly interacting elements. Breaking the Berthelot scaling symmetry leads to the *possibility* of two distinct solutions to the spinodal condition. The general solution of eq 5.5 is given by the elementary formula

$$\frac{\rho |\tilde{H}_{AA}|}{k_B T_S} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \quad (5.7)$$

where the quantities A , B , and C are given by

$$A \equiv -J(J + 2\lambda)N^2\phi(1 - \phi) \quad (5.8)$$

$$B \equiv (-\rho C_0)\phi(1 - \phi)N^2[2J - (\lambda - 1)^2] - N[\phi + (1 - \phi)\lambda^2] \quad (5.9)$$

$$= [2J - (\lambda - 1)^2](-\rho C_0)\phi(1 - \phi)N^2 - N[\phi + (1 - \phi)\lambda^2] \\ C \equiv (-\rho C_0)N + 1 \quad (5.10)$$

The nature of the solutions depends on the sign and magnitude of the above three factors. For $J \neq 0$, the inequalities $A < 0$ and $C > 0$ always hold. The factor B can be either positive or negative, and for dense high polymer blends $B > 0$ corresponds to $\chi_{\text{INC}} < 0$ and $B < 0$ implies a $\chi_{\text{INC}} > 0$. The sign constraints on A and C imply that the quantity under the square root is always positive and hence there is only a single physical solution to the spinodal condition. We proceed by analyzing the two distinct cases ($B > 0$ and $B < 0$), and for simplicity consider the large N /high density regime.

In the *effectively very strong* specific attractive interaction case, defined as $2J > (\lambda - 1)^2$, and hence $\chi_{\text{INC}} < 0$, the factor $B > 0$ and is proportional to N^2 for large N . Since the factor $AC \propto -N^3$, eq 5.7 with the negative root reduces to

$$\frac{\rho |\tilde{H}_{AA}|}{k_B T_S} \approx -\frac{B}{A} \quad \text{for} \quad B > 0, B^2 \gg AC, N \gg 1 \\ \frac{k_B T_S}{\rho |\tilde{H}_{AA}|} \approx S_0 \frac{J + 2\lambda}{2} \quad (5.11)$$

This result implies an N -independent density-fluctuation-induced transition at low temperatures. From comparison with eq 5.4 one sees that under the assumed condition of $2J \gg (\lambda - 1)^2$ one has

$$\frac{T_S}{T_{\text{LG}}} \approx \frac{(J/2) + \lambda}{2J\phi(1 - \phi) + [\phi + \lambda(1 - \phi)]^2} \approx \frac{1}{4\phi(1 - \phi)} \geq 1 \quad (5.12)$$

where the equality occurs at the critical point only. More generally, the presence of the strong specific interaction stabilizes the system against concentration fluctuations but tends to raise the liquid-gas low temperature instability relative to the analogous $J = 0$ blend.

The $B < 0$ case for moderate and large N corresponds to an effectively weak specific interaction, i.e. $2J < (\lambda - 1)^2$. The positive root of eq 5.7 applies, and there are two extreme subcases depending on the size of the factor $Y \equiv -B^2/AC$ relative to unity.

$$Y \approx N \frac{(-\rho C_0)\phi(1 - \phi)[(\lambda - 1)^2 - 2J]^2}{4J(J + 2\lambda)} \quad (5.13)$$

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 phase transition of the usual UCST form occurs at a temperature

$$k_B T_S \cong \rho |\tilde{H}_{AA}| N \phi (1 - \phi) \{(\lambda - 1)^2 - 2J\} \quad \text{if} \quad Y \gg 1 \quad (5.14)$$

which is equivalent to the incompressible Flory-Huggins result of eq 5.3. Comparison with the nonpolar analog given by eq 4.7 shows that the presence of the specific interaction simply reduces the effective energy scale associated with the mean field-like UCST.

The opposite subcase, $Y \ll 1$, is much less likely but might be realized for effectively very strong specific interactions (large J) and a very special choice of nonpolar attractive potentials (λ parameter) such that

$$[(\lambda - 1)^2 - 2J]^2 N \ll J(J + 2\lambda)$$

Equation 5.7 then yields

$$\frac{k_B T_S}{\rho |\tilde{H}_{AA}|} \cong \sqrt{\frac{-A}{C}} = \sqrt{N \phi (1 - \phi) \frac{J(J + 2\lambda)}{(-\rho C_0)}} \quad (5.15)$$

Since the predicted UCST 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*.

In summary, analytic PRISM theory for structurally symmetric "specific interaction" blends with either the R-MMSA or R-MPY/HTA closures predicts distinct low temperature phase separation behaviors, although the most common case is of the classic UCST instability form. More complex behavior is also possible and is briefly discussed in Appendix A.

High temperature (LCST) phase separation for the present model is apparently not predicted by PRISM for threadlike chains at the R-MMSA or R-MPY/HTA closure levels. This would seem to be consistent with the physical idea that the specific interactions stabilize the blend at low temperatures due to the pre-eminence of energetic considerations, but at higher temperatures the structural ordering required to maintain the specific interaction costs too much local interaction entropy. The subsequent disordering of the local packing may result in a net repulsive enthalpic interaction thereby inducing phase separation. The key to properly describing such a process would seem to be to allow the local interchain pair correlations to depend on temperature. In terms of the present thread model this scenario would correspond to a temperature-dependent J factor which increases upon cooling. This physical feature is explicitly included in the general R-MPY closure of eq 2.27. Numerical calculations, and possibly a more chemically realistic polymer model, are required to fully access this idea. However, a very simple "toy model" can be constructed which is now described.

B. LCST Phase Transitions. Consider the $\phi = 1/2$ "symmetric" model discussed in section III. The A/B symmetry suppresses the *explicit* compressibility effects in the sense that a single chi-parameter given by eq 3.17 is appropriate. However, local density and concentration fluctuations still implicitly enter χ_{INC} when using the R-MPY closure via the temperature-dependent pair correlation functions, $h_{\text{MM}}(r)$. This can be more easily

seen by rewriting eq 3.17 as

$$\chi_{\text{INC}} = \chi_0 + \rho \beta \int d\tilde{r} [v_{\text{AB}}(r) - v_{\text{AA}}(r)] h_0(r) - (\rho \beta / 2) \int d\tilde{r} [v_{\text{AB}}(r) + v_{\text{AA}}(r)] \Delta h(r) \quad (5.16)$$

where

$$h_0(r) \equiv [h_{\text{AA}}(r) + h_{\text{AB}}(r)]/2 \quad \Delta h(r) \equiv h_{\text{AA}}(r) - h_{\text{AB}}(r) \quad (5.17)$$

Prior PRISM studies of symmetric UCST blends^{26,27} suggest the dominant fluctuation contribution to the effective chi-parameter is due to the density correlation correction, which is very nearly that of the corresponding homopolymer fluid. Hence, we ignore the $\Delta h(r)$ contribution and estimate $h_0(r) \cong h_{\text{m}}(r)$ as in eq 3.18 *with the important exception* that the density-density correlation length is that appropriate for a melt at a temperature T , as given by eq 3.23.

The interchain potential model is taken to be eq 3.9 but with the AB interaction consisting of two contributions: a nonpolar component $v_{\text{AB}}(r)$ and a specific attraction $\Delta V(r)$. The Yukawa form of eq 3.3 is employed with a species-independent range parameter, a , for the nonpolar v interactions, and a *different* range parameter, a_{SI} , for the specific attraction. Common specific interactions, such as hydrogen bonding or charge transfer, correspond to more spatially rapidly varying potentials, and hence are spatially shorter range. The length scale ratio

$$b \equiv a/a_{\text{SI}}$$

is introduced and reasonable values might be in the range of 2–5. Specific interactions are also often orientation-dependent, but this aspect cannot be properly described using the coarse-grained thread model within the PRISM formalism.

Repeating the analytical analysis of section III, one easily obtains the analog of eq 3.21:

$$\chi_{\text{INC}} = \chi_0 \frac{a}{a + \xi_p} - \rho \beta |\Delta \hat{V}(0)| \frac{a_{\text{SI}}}{a_{\text{SI}} + \xi_p} \quad (5.18)$$

where the positive Flory-Huggins chi-parameter associated with the "nonpolar" groups is given by

$$\chi_0 = \rho \beta [\hat{v}_{\text{AB}}(0) - \hat{v}_{\text{AA}}(0)] \quad (5.19)$$

For Lennard-Jones interactions $a \cong \sigma/2$ and using eq 3.23 in 5.18 one obtains

$$\chi_{\text{INC}} = \frac{\chi_0}{1 + \sqrt{\hat{S}(0)/3}} - \rho \beta |\Delta \hat{V}(0)| [1 + b \sqrt{\hat{S}(0)/3}]^{-1} \quad (5.20)$$

There are two important limiting cases. For real liquids at low temperatures one expects the compressibility is small and hence the "incompressible" simplification applies whence

$$\chi_{\text{INC}} \rightarrow \chi_0 - \rho \beta |\Delta \hat{V}(0)| \equiv \chi_0 [1 - J] \quad T \rightarrow 0 \quad (5.21)$$

where J is defined in eq 5.6. The classic specific interaction blend case corresponds to a negative chi-parameter, and hence complete miscibility, at low temperatures which implies $J > 1$. In the *hypothetical* infinite temperature limit $\hat{S}(0) = N$, the Flory-Huggins χ_0 approaches zero,

and hence χ_{INC} goes to zero as

$$\chi_{\text{INC}} \rightarrow \chi_0 [1 - b^{-1}J] N^{-1/2} \quad T \rightarrow \infty \quad (5.22)$$

If $J > b$, then the approach to zero is from below which implies miscibility is retained at high temperatures. However, if $1 < J < b$, then the effective chi-parameter is negative at low temperatures, attains a positive maximum at a higher finite temperature, and then approaches zero from above. For long chains the attainment of a positive value of the effective chi-parameter will imply the phase separation condition of $\chi_{\text{INC}} N > 2$ will hold over a finite temperature interval. Thus, for this choice of J and b , one will have low and high temperature miscibility, and a finite immiscibility window at intermediate temperatures. The corresponding phase diagram is expected to be of the closed loop form, which implies a LCST phase transition upon heating from low temperatures.³⁷

Further analysis can be done by recognizing that at the temperatures of common experimental interest ($T = 250$ – 500 K), the density correlation length in the melt state is very short so that the quantity $[\hat{S}(0)/3]^{1/2}$ is relatively small [i.e., $\hat{S}(0) \approx 0.1$ – 0.4 , as discussed in Appendix B]. If $b[\hat{S}(0)/3]^{1/2} < 1$, then eq 5.20 can be written through first order as

$$\chi_{\text{INC}} = \chi_0 \{ (1 - J) + (bJ - 1) \sqrt{\hat{S}(0)/3} \} \quad (5.23)$$

Now, $\chi_0 \propto T^{-1}$, $1 < J < b$, and over moderate temperature intervals $\hat{S}(0) \propto T^x$ where $x \approx 2$. These features imply eq 5.23 is of the commonly observed⁴ empirical form $A + B/T$ with a negative enthalpic B term given by $(1 - J)\chi_0$ and a positive entropic A term given by $(bJ - 1)\chi_0$.⁴

For real LCST blends there are many other potentially complicating factors such as mixing volume changes, structural interaction potential asymmetries, "concentration fluctuation" corrections associated with the $\Delta h(r)$ contribution in eq 5.16, and Angstrom level chemical architecture. More generally, as emphasized by others,^{33,47,48} the LCST phenomenon may not require "strong specific attractions" but rather only chemically distinct groups in the monomers which for certain packing arrangements can result in a negative enthalpy of mixing associated with AB contacts. Nevertheless, the present "toy model" does contain such effects in an oversimplified way, and the demonstration that a LCST is possible within the PRISM/R-MPY theory is encouraging for future applications.

VI. SANS Chi-Parameters

The general connections between chi-parameters extracted from SANS data using the incompressible RPA analysis and the compressible PRISM theory were presented in section IIB. In this section the general formulas are specialized to the structurally symmetric Berthelot thread polymer blend and qualitative trends are established. Generalization to symmetric or specific interaction blends are immediate but will not be discussed here. Applications to SANS experiments on particular isotopic blends will be presented elsewhere.³⁵

For structurally symmetric blends $V_A = V_B = V_0 = V$. Using this result, and eq 2.19 based on the $k \rightarrow 0$ extrapolated scattering intensity and the effective com-

pressibility limit, yields

$$2\chi_S = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B} + (b_A - b_B)^2 \left[\rho C_{AA} \rho C_{BB} - \rho^2 C_{AB}^2 - \frac{\rho C_{AA}}{N_B \phi_B} - \frac{\rho C_{BB}}{N_A \phi_A} \right] \rho^{-1} \{ b_A^2 C_{BB} + b_B^2 C_{AA} - 2b_A b_B C_{AB} \}^{-1} \quad (6.1)$$

where ρ is the total blend number density and the usual dense "latticelike" relation, $\rho V = \eta = 1$, has been employed for consistency with the RPA definition of volume fraction (corrections to this may be important as emphasized recently by Kumar⁴⁰). To proceed further, I adopt the "generic" molecular closure form of eq 3.10 appropriate for the structurally symmetric thread polymer blend which yields

$$2\chi_S = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B} + W \quad (6.2)$$

$$W = -(1 - \delta)^{-1} \left\{ \beta \rho [\tilde{H}_{AA} + \tilde{H}_{BB} - 2\tilde{H}_{AB}] + [(N_A \phi_A)^{-1} + (N_B \phi_B)^{-1}] + (\beta/C_0) \left[\beta \rho \{ \tilde{H}_{AA} \tilde{H}_{BB} - \tilde{H}_{AB}^2 \} + \frac{\tilde{H}_{AA}}{N_B \phi_B} + \frac{\tilde{H}_{BB}}{N_A \phi_A} \right] \right\}$$

$$\delta \equiv \frac{\beta}{C_0 (b_A - b_B)^2} [b_A^2 \tilde{H}_{BB} + b_B^2 \tilde{H}_{AA} - 2b_A b_B \tilde{H}_{AB}]$$

In the hypothetical literal incompressible limit, $C_0 \rightarrow -\infty$ or, equivalently, the "very high temperature" limit defined as $|\beta \tilde{H}_{MM}/C_0| \rightarrow 0$, eq 6.2 greatly simplifies. Through lowest order one obtains precisely the incompressible Flory-Huggins form of eq 4.3, but in terms of the \tilde{H}_{MM} quantities. However, as discussed in Appendix B, under normal dense liquid state conditions the $|\beta \tilde{H}_{MM}/C_0| \ll 1$ inequality is not expected to hold.

For the Berthelot potential model, eq 6.2 simplifies:

$$W = -(1 - b_S \Delta)^{-1} \left\{ -\beta \rho (\lambda - 1)^2 |\tilde{H}_{AA}| + \frac{1}{N_A \phi_A} + \frac{1}{N_B \phi_B} - \beta |\tilde{H}_{AA}| \rho S_0 \left[\frac{\lambda^2}{N_A \phi_A} + \frac{1}{N_B \phi_B} \right] \right\} \quad (6.3)$$

$$\Delta \equiv \rho \beta |\tilde{H}_{AA}| S_0 \quad b_S \equiv \left(\frac{\lambda b_A - b_B}{b_A - b_B} \right)^2 \quad (6.4)$$

Using eqs 4.3 and 6.4 one obtains

$$\chi_S = \frac{\chi_{\text{INC}}}{1 - b_S \Delta} - \frac{b_S \Delta}{1 - b_S \Delta} \left\{ \frac{1}{2N_A \phi_A} (1 - \lambda^2 b_S^{-1}) + \frac{1}{2N_B \phi_B} (1 - b_S^{-1}) \right\} \quad (6.5)$$

which contains both chain length independent and dependent contributions. Equation 6.5 reduces to the incompressible form, $\chi_S = \chi_{\text{INC}}$, if $S_0 \rightarrow 0$ (literal incompressibility), $N \rightarrow \infty$, and/or $\beta \rightarrow 0$. Within the R-MMSA and R-MPY/HTA closure approximations χ_{INC} is independent of composition for the *structurally symmetric* blend. Hence, the only composition dependence enters via the compressibility correction. On the other hand, for the full R-MPY closure and a semiflexible chain model χ_{INC} does acquire a parabolic-upward, system-specific composition dependence which builds in as the blend is cooled,²⁷ and/or N is decreased.³⁵

I now proceed to further analyze eq 6.5 at the R-MMSA and R-MPY/HTA level. The experimental implications are most easily seen if it is rewritten in terms of the temperature relative to its critical value. Using eq 4.23 yields

$$\chi_S = \chi_{\text{INC,CRIT}} \frac{T_c}{T} \frac{1}{1 - b_S \Delta_c (T_c/T)} \times \left\{ 1 - \frac{b_S S_0}{(\lambda - 1)^2} \left[\frac{1 - \lambda^2 b_S^{-1}}{N_A \phi_A} + \frac{1 - b_S^{-1}}{N_B \phi_B} \right] \right\} \quad (6.6)$$

where

$$\chi_{\text{INC,CRIT}} = \frac{(\sqrt{R} + 1)^2}{2N_A} \left[1 + \frac{S_0(1 + \sqrt{R})^2}{(\lambda - 1)^2 N_A} \left(\frac{R + \lambda^2}{R + 1} \right) \right]^{-1} \quad (6.7)$$

$$\Delta_c = \frac{2S_0}{(\lambda - 1)^2} \chi_{\text{INC,CRIT}} \quad (6.8)$$

and $R = (N_A/N_B)^{1/2}$. If $|\lambda - 1| \ll 1$, as for isotopic blends, then eq 6.6 simplifies to

$$\chi_S \cong \chi_{\text{INC,CRIT}} \frac{T_c}{T} \frac{1}{1 - \Delta_c (T_c/T)} \times \left\{ 1 - \frac{S_0}{(\lambda - 1)} (b_A - b_B)^{-1} \left[\frac{b_B}{N_A \phi_A} + \frac{b_A}{N_B \phi_B} \right] \right\} \quad (6.9)$$

The corrections associated with a nonzero Δ_c parameter are the extrapolated $k = 0$ SANS chi-parameter analog of the explicit compressibility enhancements of the spinodal temperature discussed in section IV.

There are several interesting features of eqs 6.6 and 6.9.

(1) χ_S is a purely enthalpic function but contains nonlinear contributions in inverse temperature due to a nonzero compressibility. For a hard core repulsion model these corrections increasingly destabilize the blend as the temperature is lowered.⁴⁹

(2) Over a small region of temperature eqs 6.6 and 6.9 will follow the oft-observed empirical law

$$\chi_S \equiv A + \frac{B}{T} \quad (6.10)$$

where A and B are generally interpreted as entropic and enthalpic contributions, respectively. In the experimentally unattainable asymptotic $T \rightarrow \infty$ limit, or more practically $T \gg T_c$, eq 6.10 rigorously holds with $A = 0$. However, for experimentally realistic conditions the nonlinear in inverse temperature compressibility contributions may give rise to a system-specific A parameter which depends on the region of temperature studied. This A parameter will be negative and will increase in absolute magnitude as the degree of polymerization decreases, the polymer density is lowered (e.g., concentrated solutions), the temperature is lowered, and/or the potential asymmetry parameter λ becomes closer to unity. As a caution, I note that these conclusions are sensitive to the use of a temperature-independent hard core reference system.⁴⁹

SANS experiments are generally performed relatively close to the critical temperature (typically $|T - T_c|/T_c < 0.2$) in order to ensure a significant scattering signal from concentration fluctuations. This suggests that useful analytic results can be obtained by expanding eq 6.9 about the critical temperature through first order in T^{-1} . An effective chi-parameter of the form of eq 6.10 is obtained where⁴⁹

$$A = -\frac{\Delta_c}{(1 - \Delta_c)^2} \chi_{\text{INC,CRIT}} \left\{ 1 - \frac{S_0}{(\lambda - 1)(b_A - b_B)} \times \left[\frac{b_B}{N_A \phi_A} + \frac{b_A}{N_B \phi_B} \right] \right\} \quad (6.11a)$$

$$B = \frac{T_c}{(1 - \Delta_c)^2} \chi_{\text{INC,CRIT}} \left\{ 1 - \frac{S_0}{(\lambda - 1)(b_A - b_B)} \times \left[\frac{b_B}{N_A \phi_A} + \frac{b_A}{N_B \phi_B} \right] \right\} \quad (6.11b)$$

Due to their common physical origin, the A and B coefficients are highly correlated

$$A = -\Delta_c B / T_c \quad (6.12)$$

and hence the designation of " A " as entropic is misleading. Such a correlation between the empirical A and B coefficients, and the fact that $A < 0$, has been observed in several isotopic blend experiments,^{5-7,24,43} although I do not claim the present interpretation is unique. For relatively large degrees of polymerization the second contribution in the braces of eq 6.11 is small which implies

$$B \cong \frac{(\lambda - 1)^2}{2k_B} \rho |\bar{H}_{AA}| (1 - \Delta_c)^{-2} \quad (6.13)$$

$$A \cong -\frac{(\lambda - 1)^2}{2S_0} \left[\frac{\Delta_c}{1 - \Delta_c} \right]^2 \quad (6.14)$$

where the nonzero compressibility correction factor is given explicitly by

$$\Delta_c = \left\{ \frac{\lambda^2 + R}{1 + R} + \frac{(\lambda - 1)^2}{S_0} \frac{N_A N_B}{(\sqrt{N_A} + \sqrt{N_B})^2} \right\}^{-1} \quad (6.15)$$

Note that the B factor is given by its simple incompressible form multiplied by a compressibility correction greater than unity.

(3) The qualitative form of the apparent composition dependence of χ_S is due solely to explicit compressibility effects arises from the terms in braces of eqs 6.11. For most isotopic blends where $\lambda > 1$, $b_A - b_B > 0$, and $b_M > 0$, the apparent composition dependence predicted by eq 6.11 is roughly parabolic, concave downward, and asymmetric about $\phi = 1/2$. Such behavior has apparently been observed in high molecular weight isotopic blends of polystyrene.^{6,7} Moreover, the compressibility-induced composition dependence will become more pronounced as the degree of polymerization, polymer density, potential asymmetry $|\lambda - 1|$, and/or inverse compressibility are lowered. An explicit dependence on the neutron scattering lengths is also predicted. Most of the qualitative conclusions regarding explicit compressibility effects on χ_S are in accord with the extensive lattice-cluster-based theoretical work of Dudowicz, Freed, and co-workers.^{34,48}

Repeating the above analysis for the symmetric potential case of eq 3.9 leads precisely to the Flory-Huggins-like result, i.e. $\chi_S = \chi_{\text{INC}}$. Thus, the explicit composition dependence of the SANS chi-parameter for structurally symmetric blends is fundamentally due to the asymmetry between AA and BB interactions and hence can also be thought of as a compressible fluid equation-of-state effect.

An important caveat to the analytic predictions derived in this section is that the leading "incompressible" contribution, χ_{INC} as defined in eq 4.3, may exhibit an "intrinsic" composition dependence due to local intermolecular packing changes in the blend.^{27,35} Such local fluctuation effects may also destroy the precise Berthelot scaling relations. As numerically shown elsewhere for

symmetric blends, such intrinsic composition dependences are roughly parabolic, *concave upward*, increase as the spinodal is approached, and dependent on molecular weight, total polymer density, and nonuniversal chemical structural aspects.^{27,35} Hence, from eq 6.5 the qualitative form (e.g., concave upward versus concave downward) of the observed composition dependence of χ_S of even simple isotopic blends depends on several *nonuniversal* factors.

Finally, we caution that although deuteration does not appear to significantly change the segment volume or length,^{2-6,43,45} even small changes could contribute to the effective chi-parameter and particularly the value of A . Such effects are examples of a "structural asymmetry" and are considered in the following paper.³⁰

VII. Discussion

The spinodal phase diagram predictions of the new molecular closures to the PRISM equations have been analytically determined in the thread polymer limit for structurally symmetric binary blends. In contrast with the popular fully symmetric blend, within the idealized Berthelot scaling model of the interchain attractive potentials, strong compressibility, or density fluctuation, modifications of the phase separation temperatures, critical composition, and effective SANS chi-parameter are possible for chains of short and intermediate lengths. Deviations from the Berthelot scaling model may arise from a variety of physical sources including specific AB attractions, weak non-Berthelot corrections for nonpolar materials, and the temperature- and composition-dependent corrections to the species-dependent direct correlation functions which arise within the most sophisticated R-MPY closure.^{26,27} In the latter case the spinodal condition will no longer be of a simple quadratic equation form even in the thread limit, and new phase behavior may emerge such as thermally-induced LCST demixing.

Although the present analysis has employed the spinodal instability (concentration fluctuation divergence) as a measure of the phase separation condition, the binodal can be determined by integration of the partial compressibilities supplemented by the standard Maxwell construction procedure. Moreover, an alternative way of computing the thermodynamics of *nonthreadlike* models using integral equation theory is from the so-called "free energy, or charging parameter, route".^{20,46} This approach generally entails far more numerical work than a spinodal analysis which may render it particularly inconvenient from a practical viewpoint, especially for chemically complex polymer blends. However, since integral equation theory represents an approximate description of pair correlations, the thermodynamics calculated from different *formally* equivalent routes are not generally the same. The differences in thermodynamic predictions from the different routes (e.g. free energy versus compressibility) are referred to as the "thermodynamic inconsistency" problem.⁴⁶ I shall not consider this issue any further here but hope to study this question in future work.

In the following paper the PRISM analysis is generalized to include structural asymmetries, in particular stiffness differences.³⁰ Compressibility corrections are even larger, and often of a qualitative character when single chain and intermolecular potential asymmetries are simultaneously present. The accuracy, limitations, and extensions of the analytic thread PRISM approach are discussed in depth there.

Finally, several different apparent χ parameters have been presented and discussed throughout this and the following paper. The motivation for this is solely to allow contact to be made with common data representation

methods and incompressible phenomenological field theory approaches. Endorsement of these empirical representations is not implied. Clearly, it is more desirable to analyze scattering and thermodynamic data in such a way that the three independent "direct correlation" parameters (for a binary homopolymer mixture) are extracted. This philosophy has been emphasized recently by Freed and co-workers^{34,48} and becomes even more important for polymer mixtures characterized by large asymmetries and hence compressibility effects. If experimental data accuracy and/or technique does not allow such a detailed approach, then for the purpose of developing a microscopic understanding it would seem particularly appropriate to focus attention directly on the phase boundaries (binodal and spinodal) rather on a single empirical chi-parameter extracted using incompressible RPA formulas.

Acknowledgment. Helpful and stimulating discussions with A. Yethiraj, D. Chandler, S. Kumar, G. Szamel, D. Lohse, W. W. Graessley, and R. Krishnamurti are gratefully acknowledged. This work was supported by the Division of Materials Science, Office of Basic Energy Sciences, of the United States Department of Energy in cooperation with Oak Ridge National Laboratory.

Appendix A

The spinodal analysis of the general binary thread polymer blend at the R-MMSA and/or R-MPY closure levels is presented. The spinodal condition is given by eq 2.5 and the latter closures by eq 3.8 where $\tilde{H}_{MM'}$ is temperature-independent. Thus, eq 2.5 is a simple quadratic equation³⁷ in the inverse thermal energy variable, β_S , the solution(s) of which are

$$\beta_S = -\frac{B}{2A} [1 \pm \sqrt{1 - (4AC/B^2)}] \quad (A1)$$

$$C \equiv 1 - \rho_A N_A C_{AA}^{(0)} - \rho_B N_B C_{BB}^{(0)} + \rho_A \rho_B N_A N_B \delta C^{(0)} \quad (A2)$$

$$B \equiv \rho_A N_A \tilde{H}_{AA} + \rho_B N_B \tilde{H}_{BB} - \rho_A \rho_B N_A N_B \delta G \quad (A3)$$

$$A \equiv \rho_A \rho_B N_A N_B \delta \tilde{H} \quad (A4)$$

where the nonlinear " δ " quantities are defined by

$$\begin{aligned} \delta C^{(0)} &= C_{AA}^{(0)} C_{BB}^{(0)} - C_{AB}^{(0)2} & \delta \tilde{H} &\equiv \tilde{H}_{AA} \tilde{H}_{BB} - \tilde{H}_{AB}^2 \\ \delta G &\equiv \{C_{AA}^{(0)} \tilde{H}_{BB} + C_{BB}^{(0)} \tilde{H}_{AA} - 2C_{AB}^{(0)} \tilde{H}_{AB}\} \end{aligned} \quad (A5)$$

In principle, these quantities can be either positive, negative, or zero depending on the particular blend and thermodynamic state. Physical solutions occur if the factor $1 - 4AC/B^2 > 0$.

Consider first the "literal thread" model which contains single chain structural asymmetry associated with $\gamma = \sigma_B/\sigma_A$. As derived previously,^{13,22} and discussed further in the following paper,³⁰ in the long chain limit the athermal direct correlation parameters obey the simple scaling relations

$$C_{BB}^{(0)} = \gamma^4 C_{AA}^{(0)} \quad C_{AB}^{(0)} = \gamma^2 C_{AA}^{(0)} \quad (A6)$$

$$C_{AA}^{(0)} = -\frac{\pi^2}{108} \sigma_A^6 [\rho_A + \gamma^2 \rho_B] \quad (A7)$$

and eqs A5 become

$$\begin{aligned} \delta C^{(0)} &= 0 & \delta \tilde{H} &\equiv \tilde{H}_{AA} \tilde{H}_{BB} - \tilde{H}_{AB}^2 \\ \delta G &\equiv C_{AA}^{(0)} \{ \tilde{H}_{BB} + \gamma^4 \tilde{H}_{AA} - 2\gamma^2 \tilde{H}_{AB} \} \end{aligned} \quad (A8)$$

The vanishing of the nonlinear $\delta C^{(0)}$ factor implies that

the quantity C of eq A2 is rigorously positive which guarantees that the athermal reference thread blend is miscible. The latter aspect is expected to be correct at *constant volume* for flexible, amorphous polymers (but possibly not rod-coil mixtures^{39,50} for example). However, the quantities δG and δH can still be of either sign and hence so can the above factors A and B .

If the interchain attractive potential contributions obey the Berthelot scaling laws of eq 4.2, then $A = 0$ and $B < 0$ rigorously. In this case the spinodal equation is linear and has only one solution given by

$$|\tilde{H}_{AA}|_{\beta_S} = -\frac{C}{B} = \frac{1 - C_{AA}^{(0)}[\rho_A N_A + \gamma^4 \rho_B N_B]}{\rho_A N_A + \lambda^2 \rho_B N_B - C_{AA}^{(0)} \rho_A \rho_B N_A N_B (\gamma^2 - \lambda)^2} \quad (A9)$$

which corresponds to a UCST phase separation process.

For the specific interaction model case considered in section V (generalized to arbitrary sign of J), one obtains

$$C = 1 - C_{AA}^{(0)}[\rho_A N_A + \gamma^4 \rho_B N_B] > 0 \quad (A10a)$$

$$B = -|\tilde{H}_{AA}|\{\rho_A N_A + \lambda^2 \rho_B N_B - C_{AA}^{(0)} \rho_A \rho_B N_A N_B [(\gamma^2 - \lambda)^2 - 2\gamma^2 J]\} \quad (A10b)$$

$$A = -\rho_A \rho_B N_A N_B |\tilde{H}_{AA}|^2 J(J + 2\lambda) \quad (A10c)$$

There are two subcases in the long chain limit. (i) If the non-Berthelot correction term J of eq 5.6 obeys the inequality $J > 0$ or $J < -2\lambda$, then the factor $A < 0$. This implies there is a single physical solution to eq A1 of the usual UCST form for all values (and signs) of the B factor. (ii) If $-2\lambda < J < 0$, then the factor $A > 0$ and $B < 0$. This implies there are two physical solutions of eq A1. Straightforward analysis shows that the two spinodal temperatures, $T_{S,+}$ and $T_{S,-}$ correspond to miscibility in the very high and low temperature limits, respectively. Hence, a "window of immiscibility" is predicted corresponding to a phase diagram of the "re-entrant" or "closed loop" form.

In the more general case, which transcends the literal thread model, the repulsive packing factor $\delta C^{(0)}$ may be nonzero. If it is negative, then the factor C of eq A2 may become negative, in which case the athermal blend will be phase-separated for purely packing reasons. To date, numerical PRISM calculations of structurally asymmetric athermal binary blends at constant volume have not found spinodals except in the extreme case of a blend of rods and coils at high density.^{39,50} All such calculations have utilized semiflexible polymer models under the assumptions of additivity of intermolecular hard core diameters. If the latter is relaxed in a specific way, then it is known for both atomic⁵¹ and polymeric mixtures⁵² that athermal phase separation can occur. Unfortunately, there does not exist any well-defined prescription for *a priori* determining whether or how the required hard core nonadditivity law applies to real molecules.

If $C > 0$, then there are multiple possibilities depending on the signs of A and B . (i) For the Berthelot potential scaling case, $A = 0$. Then if $B > 0$ eq A1 has one solution of the simple LCST form, while if $B < 0$ then the blend is phase-separated at all temperatures. (ii) For the specific interaction model, if $A > 0$ then eq A1 has one solution for all values (and signs) of B corresponding to a LCST case. If $A < 0$, then eq A1 predicts phase separation at all temperatures for $B < 0$, but for $B > 0$ there are two solutions corresponding to a "re-entrant" phase diagram where the blend is phase-separated in the high and low temperature limits. Hence, this case is characterized by a "window of miscibility" as a function of temperature

and hence can be viewed as possessing both a UCST and LCST behavior.

Finally, for the more accurate R-MPY closure the spinodal condition will not be a quadratic equation in temperature since the attractive potential contributions to the direct correlation functions, \tilde{H}_{MM} , depend nonlinearly on temperature via the interchain pair correlation functions.

Appendix B

The site-site intermolecular potential between nonpolar molecules generally consists of a spatially rapidly varying repulsion plus a relatively weak, slower varying attractive branch.^{46,53} The former can often be replaced by an *effective* hard core repulsion characterized by a diameter, d , which usually *decreases* with temperature.^{46,53} The influence of the different branches of the potential on the zero angle scattering function of a one-component fluid, $\hat{S}(0)$, and isothermal compressibility, κ_T , enter via the $k = 0$ direct correlation function. For long chains⁹

$$\hat{S}(0) = \rho k_B T \kappa_T \cong (-\rho \hat{C}(0))^{-1} \quad (B1)$$

where ρ is the number density. Repulsive forces make a negative contribution to $\hat{C}(0)$ and hence decrease the compressibility, while attractive forces contribute in the opposite manner. For the threadlike polymer model, the one-component fluid analog of eq 4.14 implies

$$\hat{S}^{-1}(0) = -\rho C_0 + \rho \beta \tilde{H} = S_0^{-1} [1 - \rho \beta \tilde{H} S_0] \quad (B2)$$

As the fluid is heated, the attractive contribution obviously decreases, but the corresponding repulsive part, $-\rho C_0$, decreases even faster via the reduction of the effective hard core diameter. Thus, both the "reference" S_0 and the net isothermal compressibility (and fluid volume) increase with temperature. This implies that the athermal fluid is not realizable in practice but serves only as a theoretical reference system.

The magnitude and temperature dependence of $\hat{S}(0)$ are readily computed from eq B1 and experimental data.⁵⁴ For polyethylene $\hat{S}(0) = 0.20$ ($T = 423$ K), 0.24 ($T = 453$ K), 0.326 ($T = 503$ K), 0.464 ($T = 563$ K); for a pentadecane melt $\hat{S}(0) = 0.108$ ($T = 293$ K), 0.147 ($T = 333$ K), 0.274 ($T = 408$ K). Note that $\hat{S}(0)$ increases quite rapidly with temperature. Also, as previously discussed for small molecule fluids⁵⁵ under dense liquid state conditions the inequality $|\rho \beta \tilde{H} S_0| = \beta \tilde{H} / C_0 \ll 1$ (assumed by incompressible RPA approaches) does not hold. Rather, $C_0 \approx f(\beta \tilde{H})$ where f is in the range 1.2–2 in the dense liquid region and when temperatures are in the range 250–400 K.⁵⁵

References and Notes

- See, for example: Bates, F. S. *Science* **1991**, *251*, 898. Sanchez, I. C. *Annu. Rev. Mater. Sci.* **1983**, *13*, 387.
- Wignall, G. D. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1987; Vol. 12, p 112.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
- See, for example: Jung, W. G.; Fischer, E. W. *Makromol. Chem. Makromol. Symp.* **1988**, *16*, 281. Brereton, M. G.; Fischer, E. W.; Herkt-Maetzky, C.; Mortensen, K. *J. Chem. Phys.* **1987**, *87*, 6114. Han, C. C.; Bauer, B. J.; Clark, J. C.; Moroga, Y.; Matsushita, Y.; Okada, M.; Tran-cong, Q.; Chang, T.; Sanchez, I. C. *Polymer* **1988**, *29*, 2002.
- Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 5351.
- Schwahn, D.; Hahn, K.; Streib, J.; Springer, J. *J. Chem. Phys.* **1990**, *93*, 8383.
- Londono, J. D.; Wignall, G. D.; Narten, A. H.; Honnell, K. G.; Yethiraj, A.; Schweizer, K. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 829.

- (8) For recent reviews see: Binder, K. Preprint, 1993. Kumar, S. In *Computer Simulation of Polymers*; Colbourn, E. A., Ed.; Longmann: Harlow, United Kingdom, 1992; Chapter 8.
- (9) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1987**, *58*, 246. Curro, J. G.; Schweizer, K. S. *Macromolecules* **1987**, *20*, 1928; *J. Chem. Phys.* **1987**, *87*, 1842. Schweizer, K. S.; Curro, J. G. *Macromolecules* **1988**, *21*, 3070 and 3082. Curro, J. G.; Schweizer, K. S.; Grest, G. S.; Kremer, K. *J. Chem. Phys.* **1989**, *91*, 1357. For a comprehensive review, see: Schweizer, K. S.; Curro, J. G. *Adv. Polym. Sci.*, in press.
- (10) Honnell, K. G.; Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 3496.
- (11) Honnell, K. G.; McCoy, J. D.; Curro, J. G.; Schweizer, K. S.; Narten, A. H.; Habenschuss, A. *J. Chem. Phys.* **1991**, *94*, 4659. Narten, A. H.; Habenschuss, A.; Honnell, K. G.; McCoy, J. D.; Curro, J. G.; Schweizer, K. S. *J. Chem. Soc., Faraday Trans.* **1992**, *13*, 1791.
- (12) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1988**, *60*, 809; *J. Chem. Phys.* **1989**, *91*, 5059.
- (13) Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 1402; (op. cit.) **1991**, *24*, 6736.
- (14) McCoy, J. D.; Honnell, K. G.; Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1991**, *95*, 9348.
- (15) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1988**, *89*, 3342 and 3350.
- (16) Yethiraj, A.; Curro, J. G.; Schweizer, K. S.; McCoy, J. D. *J. Chem. Phys.* **1993**, *98*, 1635. Curro, J. G.; Yethiraj, A.; Schweizer, K. S.; McCoy, J. D.; Honnell, K. G. *Macromolecules* **1993**, *26*, 2655.
- (17) Schweizer, K. S.; Honnell, K. G.; Curro, J. G. *J. Chem. Phys.* **1992**, *96*, 3211.
- (18) Melenkevitz, J.; Curro, J. G.; Schweizer, K. S. *J. Chem. Phys.*, in press. Grayce, C.; Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.*, submitted.
- (19) Chandler, D.; Andersen, H. C. *J. Chem. Phys.* **1972**, *57*, 1930.
- (20) Chandler, D. In *Studies in Statistical Mechanics VIII*; Montroll, E., Lebowitz, J., Eds.; North-Holland: Amsterdam, 1982; p 274.
- (21) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1990**, *149*, 105.
- (22) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1991**, *94*, 3986.
- (23) Deutsch, H.-P.; Binder, K. *Europhys. Lett.* **1992**, *17*, 697; *Macromolecules* **1992**, *25*, 6214; *J. Phys. II, Fr.* **1993**, *3*, 1049.
- (24) Gehlsen, M. P.; Rosedale, J. H.; Bates, F. S.; Wignall, G. D.; Hansen, L.; Almdal, K. *Phys. Rev. Lett.* **1992**, *68*, 2452.
- (25) Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.* **1992**, *97*, 5927.
- (26) Schweizer, K. S.; Yethiraj, A. *J. Chem. Phys.* **1993**, *98*, 9053.
- (27) Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.* **1993**, *98*, 9080.
- (28) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711.
- (29) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
- (30) Schweizer, K. S. *Macromolecules*, following paper in this issue.
- (31) Chen, X. S.; Forstmann, F. *J. Chem. Phys.* **1992**, *97*, 3696 and references cited therein.
- (32) Equation 2.7 assumes the sites on A and B chains have the same volume. Generalization of the incompressibility approximation to the nonequal volume case is straightforward. See, for example, ref 13.
- (33) Sanchez, I. C. *Macromolecules* **1991**, *24*, 908.
- (34) Dudowicz, J.; Freed, M. S.; Freed, K. F. *Macromolecules* **1991**, *24*, 5096.
- (35) Yethiraj, A.; Schweizer, K. S. In preparation.
- (36) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, U.K., 1986.
- (37) This statement is true only if one neglects the (generally weak) dependence on temperature of quantities such as the segmental density, statistical segment lengths, effective hard core diameter, et cetera. If these dependences are retained, then the equations for the spinodal temperatures quoted throughout the paper in principle represent transcendental equations for the spinodal temperature. Also, at very high temperatures the fluid will undergo a liquid-vapor transition which is not addressed by the analysis of this paper (see ref 26) and which would be sensitive to the implicit temperature dependences of the various molecular factors.
- (38) The exact analytical solution of the athermal thread blend derived in ref 13 assumes the degree of polymerization is infinity. Throughout the paper I shall adopt this result for the long, but finite length, chains of practical interest. This is an excellent approximation since the direct correlation functions of the miscible athermal blend are determined by local packing considerations and hence attain their large N limiting values for relatively small degrees of polymerization.
- (39) Yethiraj, A.; Schweizer, K. S. Unpublished calculations.
- (40) Kumar, S. *Phys. Rev. Lett.*, submitted for publication; preprint, 1993.
- (41) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquid Mixtures*; Butterworth Scientific: London, 1982.
- (42) Hildebrand, J.; Scott, R. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold: New York, 1949.
- (43) Bates, F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086.
- (44) Hashimoto, T.; Ijichi, Y.; Fetters, L. J. *J. Chem. Phys.* **1989**, *89*, 2463. Marie, P.; Selb, J.; Rameau, A.; Gallot, Y. *Makromol. Chem. Makromol. Symp.* **1988**, *16*, 301.
- (45) Bates, F. S.; Schulz, M. F.; Rosedale, J. H. *Macromolecules* **1992**, *25*, 5547.
- (46) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1986.
- (47) Paul, D. R.; Barlow, J. W. In *Polymer Compatibility and Incompatibility*; Solc, K., Ed.; MMI: Midland, MI, 1981; p 1. Sanchez, I. C. *Ibid.*, p 59.
- (48) Freed, K. F.; Dudowicz, J. *Theor. Chim. Acta* **1992**, *82*, 357.
- (49) This conclusion depends on the use of a purely hard core repulsion model (and hence $dS_0/dT = 0$) and constant system volume. If a soft repulsive potential is considered, then the effective hard core diameter and fluid density are usually decreasing functions of temperature⁵³ which implies S_0 is an increasing function of temperature (see Appendix B). Thus conclusions regarding the temperature dependence of the "explicit compressibility" corrections, and even the sign of the apparent "A" factor, depend on the detailed, system-specific temperature dependence of S_0 and S_0/T . If there are significant, composition-dependent volume changes upon mixing, then they may also influence the effective SANS chi-parameter.
- (50) Honeycutt, J. D. *ACS Polym. Prepr.* **1992**, *33* (1), 529; private communication, 1992.
- (51) Gazillo, D. *J. Chem. Phys.* **1991**, *96*, 4565.
- (52) Honeycutt, J. D. *Proceedings of CAMSE 92*, Yokohama, Japan, 1992 (in press).
- (53) Andersen, H. C.; Chandler, D.; Weeks, J. D. *Adv. Chem. Phys.* **1976**, *34*, 105.
- (54) Zoller, P. *J. Appl. Polym. Sci.* **1979**, *23*, 1051; *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 897. Honnell, K. G. private communication.
- (55) Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1982**, *76*, 2296.