Neutron Scattering from Compressible Polymer Blends: A Framework for Experimental Analysis and Interpretation of Interaction Parameters

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ABSTRACT: The random phase approximation (RPA) and the lattice fluid (LF) model are combined to formulate expressions for scattering, the spinodal, and the interaction parameter from compressible polymer mixtures. Effective fields of the RPA are shown to correspond to the interaction parameters of the LF model. A protocol is developed to determine polymer–polymer interaction parameters from scattering data. The formalism is applied successfully to both isotopic and nonisotopic binary polymer blends. It is concluded that some of the unexpected behavior of interaction parameters determined in neutron scattering experiments can be attributed to compressibility effects. The traditional and widely used formula that relates the interaction parameter to a second concentration derivative of an excess free energy is shown to be incorrect for compressible mixtures. Radii of gyration determined from the scattering dependence on wave vector tend to be overestimates unless compressibility is taken into account. It is also shown that the spinodal determined from a scattering experiment that probes a constant volume is identical to one obtained under conditions of constant pressure.

Introduction

In the last decade, the technique of small-angle neutron scattering (SANS) has evolved as a useful method of determining the interaction between components of a polymer blend.[1–10] The data are analyzed assuming the blend to be incompressible by a method first developed by de Gennes.[4,5] However, the interaction parameters often show unexpected dependencies on composition, molecular weight, temperature, and wave vector.[6–10] This raises the question, what effect does finite compressibility have on scattering properties of a polymer mixture and how does it influence the interaction parameters measured in a SANS experiment? This question has already been examined by a variety of theoretical approaches.[11–19] Tang and Freed,[13] using a path integral formulation, derive results that are formally identical to those of Benoit *et al.*,[15] who use the Ornstein–Zernicke theory. In another approach, RISM integral equation theory has been extended to polymer blends.[14,16,17] Recently, Dudowicz and Freed[18,19] combined lattice cluster theory with the random phase approximation (RPA) and examined neutron scattering from deuterated polystyrene (dPS)/poly(vinyl methyl ether) (PVME) blends. They found that the "least reasonable" monomer structure gives the best fit to data, and, at best, the agreement between theory and experiment was "modest". They attribute the observed deviations in the structure factor and correlation length to perturbed chain dimensions (with respect to a pure melt) of dPS and PVME caused by asymmetries in the intermolecular interactions. Recent experiments[20] suggest that changes in chain dimensions are small. In 1989, the situation with respect to the unusual behavior of χ interaction parameters was summarized by Schweizer and Curro:[14] "At present there is very little understanding of these observations and the SANS determined χ interaction parameter has become a *black box*."

We perceive a clear need to incorporate compressibility effects within a simple model formulation. As a basic framework, we use the recent RPA formulation of Akcasu *et al.*[21,22] for scattering from multicomponent, compressible, polymer blends. This allows us to formulate a general structure factor matrix for polymers with different architectures (homopolymers, random copolymers, block copolymers, etc.) in terms of "bare" response functions and RPA fields. Using the lattice fluid (LF) model, first derived by Sanchez and Lacombe,[23–26] we show that these fields correspond to the interaction parameters of the LF model. Our results are then specialized to binary isotopic and nonisotopic blends and applied to existing data. The model equations are able to describe both scattering functions and spinodal curves very well. We also derive a closed form expression for the interaction parameter measured in a SANS experiment on binary homopolymer blends (eq 28). This result is not equal to the usual second concentration derivative on a free energy. It helps to reconcile some of the unexpected behaviors, especially concentration, wave vector, and molecular weight dependencies of the interaction parameter. Finally, in Appendix II, we show that, although the scattering volume is fixed in a scattering experiment, the scattering spinodal is identical to one obtained at constant pressure.

Scattering and RPA Formalism

Consider a compressible, multicomponent, polymer blend with m kinds of different monomers. This compressible blend can be thought of as a $m + 1$ component mixture, with component 0 being "holes" or "voids". The holes make the mixture compressible, and its *PVT* properties satisfy the LF equation of state.[23–26] The m components scatter radiation, but the holes do not. The latter is designated as the "matrix component".[21,22] In such a mixture, the volume fractions of the $m + 1$ components sum to unity. One may write the differential scattering cross section as[27]

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$$\Xi(\mathbf{q}) = \sum_{i,j=1}^{m} b_i b_j \int \mathrm{d}^3\mathbf{r}\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \langle \delta\varrho_i \delta\varrho_j \rangle \tag{1a}$$

where b_i = scattering length of component i, $\varrho_i = n_i/V$ = monomer density of component i, n_i = number of monomers of component i, $\delta\varrho_i$ = fluctuation in monomer density of component i, $\langle \delta\varrho_i \delta\varrho_j \rangle$ = density−density correlation function at **r** for monomers i and j, **q** = scattering wave vector, **r** = position vector, and $\mathrm{d}^3\mathbf{r}$ = differential volume within the system volume V.

Since we are ultimately interested in using SANS to derive information about model-dependent interaction parameters, monomer densities are converted to a more natural set of concentration units for the LF model:

$$\Xi(\mathbf{q}) = \sum_{i,j=1}^{m} \bar{b}_i \bar{b}_j \int \mathrm{d}^3\mathbf{r}\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \langle \delta f_i \delta f_j \rangle \tag{1b}$$

where $\bar{b}_i = b_i/(m_i/\varrho_i^*)$, ϱ_i^* = close-packed *mass density* of component i, m_i = *monomer* molecular weight of component i, $f_i = m_i\varrho_i/\varrho_i^* = n_i(m_i/\varrho_i^*)/V$ = volume fraction of space occupied by type i monomers, $\sum_{i=1}^{m} f_i = 1 - f_0$, and f_0 = hole fraction. Note that the ratio m_i/ϱ_i^* is the close-packed monomer volume of component i.

If the mixture is spatially isotropic, the scattering depends only on the magnitude, $|\mathbf{q}|$, of the wave vector (hereafter denoted as q). The scattering equation can be written in a compact matrix form:

$$\Xi(q) = \bar{\mathbf{b}} \mathbf{S}(q)\, \bar{\mathbf{b}}^{\mathrm{T}} \tag{2}$$

where $\bar{\mathbf{b}} = 1 \times m$ row vector of $\bar{b}_i$, $\bar{\mathbf{b}}^{\mathrm{T}}$ is its transpose, and $\mathbf{S}(q)$ is called the static structure factor matrix. The elements of $\mathbf{S}(q)$ are related to Fourier transforms of the density−density correlation functions. To make the components of a square matrix clear, we will often write $\mathbf{M} = [M_{ij}]$. We can now use a general result developed recently by Akcasu *et al.*[21,22] Their results for a $m + 1$ component system can be specialized to our system of m components and holes (the matrix component) by requiring the holes to be randomly distributed in space (a mean-field approximation). This allows the inverse of the structure factor matrix to be expressed as

$$\frac{1}{\mathbf{S}(q)} = \frac{1}{\mathbf{S}^0(q)} + \mathbf{K}(q) + \left[\frac{1}{s_0(q)}\right] \tag{3}$$

where $\mathbf{S}^0(q) = [s_{ij}^0(q)]$ = structure factor matrix of the bare system, $s_{ij}^0(q)$ = bare response function for i to fluctuations in j, $\mathbf{K}(q) = [k_{ij}(q)]$ = matrix of effective fields, $k_{ij}(q)$ = excess effective field on i due to fluctuations in j, and $s_0(q)$ = response function for holes in the bare system.

It has been emphasized that $\mathbf{S}^0(q)$ and $\mathbf{K}(q)$ are coupled and depend on the choice of the bare system.[22] The bare system is commonly chosen to consist of noninteracting Gaussian chains. This choice allows $\mathbf{S}^0(q)$ to be calculated analytically for a variety of polymer architectures (homopolymers, random copolymers, block copolymers, etc.).[28] With this choice of the bare system, the $s_{ij}^0(q)$ represent correlation effects due to chain connectivity only. Components $k_{ij}(q)$ are the excess effective fields of the RPA that include all other correlation effects of j on i. In the next section the $k_{ij}(q)$ are evaluated in terms of the interaction parameters of the LF model.

Perhaps the most surprising term in the above equation is $s_0(q)$. This term arises from fluctuations in holes (i.e., density). This creates a thermodynamic field that acts equally on all components. As shown below, a simple approximation for $s_0(q)$ can be used to analyze SANS data.

Interpretation of Fields in RPA

Consider a blend made of m different homopolymers. When dealing with homopolymers, fluctuations in scattering species are also fluctuations of the polymer molecules themselves. Thus, we can use a thermodynamic relationship[12,29,30] to describe the scattering at $q = 0$. For homopolymers, the inverse structure factor matrix takes on a simple form at $q = 0$:

$$\mathbf{S}^{-1}(0) = \left[\left(\frac{\partial^2 \beta A}{\partial f_i \partial f_j}\right)_{V,T,f}\right] \tag{4}$$

where the subscript f indicates that derivatives with respect to f_i are performed holding all other f_j constant, A is the Helmholtz free energy density, and $\beta = 1/kT$ has its usual meaning.

Note that we have only m concentration variables instead of the $m + 1$ that one might expect. This results from our pseudo incompressibility constraint, $f_0 + \sum_{i=1}^{m} f_i = 1$. It implies that we have only m independent components. To make further progress, we need a model for the Helmholtz free energy density A and expressions for the bare response functions, $s_{ij}^0(q)$.

Bare response functions for ideal homopolymer chains are given by[2−5]

$$s_{ij}^{\;0}(q) = \delta_{ij} \mathbf{v}_i^* f_i g_i \equiv \delta_{ij} s_i \tag{5}$$

where δ_{ij} = usual Kronecker delta function, $\mathbf{v}_i^* = M_i/\varrho_i^*$ = close-packed molecular volume of component i, M_i = molecular weight of component i, $g_i(q) = (2/x_i^2)(\mathrm{e}^{-x_i} - 1 + x_i)$ = Debye function for component $i = 1 - x_i/3 + ...$, $x_i = q^2R_i^2$, and R_i = radius of gyration of component i. Note that Debye functions are normalized to unity at $q = 0$. The off-diagonal elements of $[s_{ij}^0(q)]$ are zero because for homopolymers monomer i is never connected through a series of chemical bonds to monomer j if $i \neq j$. Monomers i and j are completely uncorrelated in this sense. In copolymers containing i and j monomers, this would not be true.

For the hole response function, $s_0(q)$, we propose a simple Lorentzian form:

$$s_0(q) = \frac{v_0 f_0}{1 + \xi^2 q^2} \tag{6}$$

where v_0 = the volume of a hole and ξ = correlation length for density fluctuations. Note that $s_0(0) = v_0 f_0$ is analogous to $s_{ii}^0(0) \equiv s_i(0) = \mathbf{v}_i^* f_i$. Equation 6 is based on scattering from pure fluids where scattering from density fluctuations is, to a good approximation, Lorentzian.[31]

Thus, eq 3 becomes

$$\mathbf{S}^{-1}(q) = \left[\frac{\delta_{ij}}{s_i} + \frac{1}{s_0}\right] + \mathbf{K}(q) \tag{7}$$

To evaluate the matrix $\mathbf{K}(q)$, we use the LF model. There are two formulations of the LF model; one is a strict lattice version, while the second is a nonlattice version.[25,26] Both models are identical when describing pure fluids but differ in their description of mixtures. In the nonlattice model, the Helmholtz free energy density A is given by

$$\beta A = -\beta \sum_{i,j=1}^{m} f_i f_j P_{ij}^* + \sum_{i=1}^{m} \frac{f_i}{\mathbf{v}_i^*} \ln f_i + \frac{f_0}{v_0} \ln f_0 \qquad (8)$$

where $P_{ii}^* \equiv P_i^*$ = characteristic pressure of component i, P_{ij}^* = cross-interaction energy density between monomers i and j, $f_i = \phi_i \tilde{\varrho}$, $f_0 = 1 - \tilde{\varrho}$, $\phi_i = n_i(m_i/\varrho_i^*)/\sum_{i=1}^{m} n_i (m_i/\varrho_i^*) = N_i \mathbf{v}_i^* / \sum_{i=1}^{m} N_i \mathbf{v}_i^*$ = close-packed volume fraction of component i, N_i = number of homopolymer molecules of type i, and $\tilde{\varrho}$ = reduced density of mixture (fraction of space occupied by all molecules). The reduced density $\tilde{\varrho}$, or equivalently f_0, is determined from the LF equation of state. The hole volume v_0 for a mixture is determined by a mixing rule that is discussed later (also see Appendix I).

Using the above LF Helmholtz free energy density along with the thermodynamic relation (eq 4), we have

$$\mathbf{S}^{-1}(0) = \left[\frac{\delta_{ij}}{\mathbf{v}_i^* f_i} + \frac{1}{v_0 f_0}\right] + \mathbf{K}(0) \qquad (9)$$

with

$$\mathbf{K}(0) = [-2\beta P_{ij}^* + C_{ij}] \qquad (10)$$

and

$$C_{ij} = f_0 \ln f_0 \left(\frac{\partial^2 v_0^{-1}}{\partial f_i \partial f_j}\right) - (1 + \ln f_0)\left(\frac{\partial v_0^{-1}}{\partial f_i} + \frac{\partial v_0^{-1}}{\partial f_j}\right) \qquad (11)$$

The above equation shows that, in general, $\mathbf{K}(0)$ has both an energetic and an entropic-like (free volume) contribution. The parameter v_0^{-1} has entropic character[26] as can be seen clearly in eq 8 where v_0^{-1} scales the free volume term $f_0 \ln f_0$. The term C_{ij} is zero for isotopic blends and is relatively small compared to βP_{ij}^* for some nonisotopic blends. For simplicity and clarity, we hereafter assume that $C_{ij} = 0$. In Appendix I, the more general case is developed ($C_{ij} \neq 0$).

For a mean-field model, such as the LF model, $\mathbf{K}(q) = \mathbf{K}(0)$, because short-range order, induced by attractive and repulsive intermolecular interactions, is completely ignored. This also implies that eqs 10 and 11 are valid for arbitrary polymer architecture (homopolymers, copolymers, stars, etc.). Thus, we have

$$\mathbf{S}^{-1}(q) = \left[\frac{\delta_{ij}}{s_i} + \frac{1}{s_0} - 2\beta P_{ij}^*\right] \qquad (12a)$$

For future reference, the strict lattice version of the LF model yields

$$\mathbf{S}^{-1}(q) = \left[\frac{\delta_{ij}}{s_i} + \frac{1}{s_0} - \frac{2\beta \epsilon_{ij}^*}{v^*}\right] \qquad (12b)$$

where v^* is the volume of a lattice site. It is a function of composition and plays the same role in the strict lattice model as the hole volume v_0 in the nonlattice model. The energy parameter ϵ_{ij}^* is the interaction energy of "mer" i with "mer" j; a "mer" occupies one lattice site.

Equation 12 is a general result for an m component system. Transition between the two forms of eq 12 is easily accomplished by keeping in mind the following correspondences: $v^* = v_0 = kT^*/P^*$, $\epsilon_{ii}^*/v_i^* = P_i^*$, and $\mathbf{v}_i^* = r_i v_i^* = M_i/\varrho_i^*$ where v_i^* is the volume of a lattice site in pure component i, r_i is the number of lattice sites molecule i occupies, and T_i^* is the characteristic temperature of i. In the strict lattice version of the LF model, the canonical parameters ϵ_{ii}^*, v_i^*, and r_i do not have simple physical interpretations, whereas P_i^* and $\mathbf{v}_i^*$ are related to the cohesive energy density and close-packed molecular volume, respectively.[26] An advantage of the nonlattice LF model is that its canonical parameters are P_i^*, $\mathbf{v}_i^*$, and v_0 and only the hole volume v_0 does not have a simple physical interpretation.

Compressible Binary Blends of Homopolymers

From eq 12a, we have

$$\frac{1}{\mathbf{S}(q)} = \begin{bmatrix} \frac{1}{s_1} + \frac{1}{s_0} - 2\beta P_1^* & \frac{1}{s_0} - 2\beta P_{12}^* \\ \frac{1}{s_0} - 2\beta P_{12}^* & \frac{1}{s_2} + \frac{1}{s_0} - 2\beta P_2^* \end{bmatrix} \qquad (13)$$

Inverting $\mathbf{S}^{-1}(q)$ and using eq 2, we obtain for the differential scattering cross section:

$$\Xi(q) = \{(\bar{b}_1 - \bar{b}_2)^2 (1 - s_0/v_b)\}/ \left\{\frac{1}{s_1} + \frac{1}{s_2} - 2\left\{\beta \Delta P^* + 2s_0\left[(\beta P_{12}^*)^2 - \left(\beta P_1^* - \frac{1}{2s_1}\right)\left(\beta P_2^* - \frac{1}{2s_2}\right)\right]\right\}\right\} \qquad (14a)$$

where

$$\Delta P^* = P_1^* + P_2^* - 2P_{12}^* \qquad (15)$$

and

$$\frac{1}{v_b(q)} = \frac{2\beta[\bar{b}_2^{\,2} P_1^* + \bar{b}_1^{\,2} P_2^* - 2\bar{b}_1 \bar{b}_2 P_{12}^*] - \left(\frac{\bar{b}_2^{\,2}}{s_1} + \frac{\bar{b}_1^{\,2}}{s_2}\right)}{(\bar{b}_1 - \bar{b}_2)^2}, \qquad \bar{b}_1 \neq \bar{b}_2 \qquad (16)$$

Note that $v_b(q)$ has units of volume (like s_0 and s_i) but may be negative. The b subscript reminds us that v_b depends on the scattering lengths, b_i. Since $\Xi(q)$ must be positive definite, this requires $s_0/v_b < 1$; positive definiteness of $\Xi(q)$ is assumed if Det $\mathbf{S}^{-1}(q) > 0$ and $f_0(\beta P_i^* v_0) \langle \, ^1\!/_2$ for all i. Since $f_0 \approx 0.1$ and $\beta P_i^* v_0 \approx 1$ for polymers, the latter requirement is always satisfied in the normal experimental temperature range. The former requirement is required for phase stability (see eq 4 and Appendix II), and, therefore, the scattering equation is limited to the one-phase region of the phase diagram. For high molecular weights, $\Delta P^* < 0$ is necessary for phase stability.

Note that $\Xi(q)$ is symmetric with respect to the indices 1 and 2 and that we recover the traditional incompressible RPA form in the limit $s_0 \to 0$:

$$\lim_{s_0 \to 0} \Xi(q) = \frac{(\bar{b}_1 - \bar{b}_2)^2}{\frac{1}{\mathbf{v}_1^* \phi_1 g_1} + \frac{1}{\mathbf{v}_2^* \phi_2 g_2} - 2\beta \Delta P^*} \qquad (14b)$$

In the high contrast limit, we have

$$\lim_{b_1 \to \infty} \frac{\Xi(q)}{\bar{b}_1^{\,2}} = \{[1 - s_0(2\beta P_2^* - 1/s_2)]\}/ \left\{\frac{1}{s_1} + \frac{1}{s_2} - 2\left\{\beta \Delta P^* + 2s_0\left[(\beta P_{12}^*)^2 - \left(\beta P_1^* - \frac{1}{2s_1}\right)\left(\beta P_2^* - \frac{1}{2s_2}\right)\right]\right\}\right\} \qquad (14c)$$

A similar equation has been derived by Dudowicz and Freed within the lattice cluster theory.[19]

In the low contrast limit, we have

$$\lim_{\bar{b}_1,\bar{b}_2\to\bar{b}} \frac{\Xi(q)}{\bar{b}^2} = \frac{s_0}{1 - \dfrac{4s_0\left[(\beta P_{12}{}^*)^2 - \left(\beta P_1{}^* - \dfrac{1}{2s_1}\right)\left(\beta P_2{}^* - \dfrac{1}{2s_2}\right)\right]}{\dfrac{1}{s_1} + \dfrac{1}{s_2} - 2\beta\Delta P^*}} \tag{14d}$$

In the limit of zero contrast, the scattering is dominated by density fluctuations.

Scattering from Isotopic Blends. Equation 14a is now applied to data for binary isotopic blends available in the literature. We use two studies: blends of deuterated and hydrogenated polybutadiene (dPBD/PBD)[32] and blends of deuterated and hydrogenated polystyrene (dPS/PS).[33] Component 1 is designated as the deuterated component hereafter. For isotopic blends, we have two important simplifications: $P_{12}{}^* = (P_1{}^*P_2{}^*)^{1/2}$ and v_0 is independent of composition which implies $C_{12} = 0$. Because of the chemical similarity of nuclear isotopes, the geometric mean approximation for $P_{12}{}^*$ should be excellent.

The characteristic pressure for the deuterated component $P_1{}^*$ is the only requisite parameter that is not known in eq 14a. The scattering lengths b_i are tabulated or can be easily determined.[1,27] The LF parameters ($T_2{}^*$, $P_2{}^*$, and $\varrho_2{}^*$) for many hydrogenated polymers are tabulated,[26,42] and for isotopes, the close-packed monomer volumes are equal. Kuhn segment lengths, required to calculate gyration radii and the corresponding response functions s_i, are available in their respective references. We assume that $s_0 \cong s_0(0) = v_0 f_0$. Since the length scale associated with density fluctuations is very small (~1−10 Å) and SANS experiments are performed at much larger length scales (q^{-1} ~ 100−1000 Å), s_0 is expected to be independent of q in the region of interest. The fraction of holes f_0, or, equivalently, the reduced density $\tilde{\varrho} = 1 - f_0$, is calculated from the LF equation of state. At low pressure and high molecular weight, the equation of state is[23−26]

$$\tilde{\varrho}^2 + (T/T^*)[\ln(1 - \tilde{\varrho}) + \tilde{\varrho}] = 0 \tag{17}$$

where T^* is the characteristic temperature of the mixture; for the nonlattice LF model, it is given for isotopic blends by

$$T^* = \frac{T_2{}^*}{P_2{}^*}[\phi_1 P_1{}^{*1/2} + \phi_2 P_2{}^{*1/2}]^2 \tag{18}$$

To extract the self-interaction parameter $P_1{}^*$ for the deuterated polymer from scattering data, eq 17 is solved simultaneously with eq 14a with $q = 0$ [$\Xi(0)$ obtained by extrapolating scattering data to $q = 0$]. For both blends, two values of $P_1{}^*$ satisfied the equations. Of these, we choose $P_1{}^* < P_2{}^*$. This choice is based on the expectation that the cohesive energy density for the deuterated polymer is smaller than that of the hydrogenated polymer.[34] Now scattering can be predicted for finite q. The results are shown in Figure 1. Solid circles are experimentally measured $\Xi(q)$ for a 50/50 (v/v) blend of dPS/PS at 433 K; solid diamonds are for a 31/69 blend of dPBD/PBD at 294.9 K. For the dPS/PS system, we find that $P_1{}^*$ = 354.805 MPa ($P_2{}^*$ = 357 MPa). For dPBD/PBD, $P_1{}^*$ = 417.021 MPa ($P_2{}^*$ = 424 MPa). It is clear that predicted curves (solid lines) represent the experimental data well. The calculated values of $P_1{}^*$ for the deuterated polymers are about 1−2% lower than the hydrogenated polymer. Even a 0.1% change in $P_1{}^*$ from those given above results in an unacceptable reproduction of scattering curves. That is why $P_1{}^*$ is quoted to six significant figures. Uncertainties involved in P^* values determined by *PVT* measurements are typically on the order of 1−3%. Therefore, *PVT* measurements alone might not discriminate between P^* values of isotopic polymers, whereas SANS measurements can easily make this distinction.

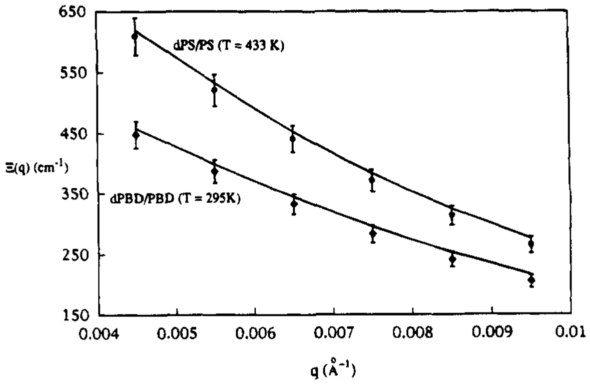

Figure 1. Differential scattering cross section for a dPBD/PBD (31/69, v/v) isotopic blend[32] at 295 K and a dPS/PS blend[33] at 433 K. Curves are calculated from eq 14a; solid symbols are experimental points. Values of interaction parameters used in the calculation are given in the text.

Scattering from Nonisotopic Blends. Although we have not attempted to describe scattering data from nonisotopic blends, we outline here how it would be done. The only unknown parameter in eq 14a is the cross-interaction parameter $P_{12}{}^*$, or equivalently, ΔP^*. All requisite pure-component parameters ($T_i{}^*$, $P_i{}^*$, and $\varrho_i{}^*$) are presumably tabulated or can be determined from experimental *PVT* data. Usually, one of the polymers is deuterated to provide the requisite contrast. The T^* and P^* parameters for the deuterated polymer are equated to those of the hydrogenated polymer to a good approximation.[36] However, we have the additional complication that the hole volumes for each component (equal to $kT_i{}^*/P_i{}^*$) are, in general, unequal. This implies that $C_{ij} \neq 0$ (see eq 11). A simple and convenient mixing rule for v_0 is[25,26]

$$\frac{1}{v_0} = \phi_1\frac{P_1{}^*}{kT_1{}^*} + \phi_2\frac{P_2{}^*}{kT_2{}^*} \tag{19}$$

Using this rule, the characteristic temperature of the mixture, required in solving the equation of state (eq 17), is given by

$$T^* = \frac{\phi_1{}^2P_1{}^* + 2\phi_1\phi_2P_{12}{}^* + \phi_2{}^2P_2{}^*}{\phi_1(P_1{}^*/T_1{}^*) + \phi_2(P_2{}^*/T_2{}^*)} \tag{20}$$

As before, the $\Xi(0)$ value of eq 14a is solved simultaneously with the equation of state (eq 17) by choosing the appropriate value for $P_{12}{}^*$. If the $T_i{}^*/P_i{}^*$ ratios are not too different, it is safe to set $C_{12} = 0$. If not, C_{12} is given in Appendix I for the above mixing rule. *It is important to note that this compressible analysis is a single parameter fitting procedure just like the traditional incompressible analysis based on eq 14b.*

The results can be easily generalized to an m component homopolymer blend. There are $(m^2 - m)/2$ cross-interaction parameters $P_{ij}{}^*$ to be determined. For the LF model, the $P_{ij}{}^*$ are independent of polymer architecture. Scattering depends on molecular architecture through the bare response functions $s_{ij}^0(q)$. In principle, P_{ij}^* parameters calculated from homopolymer blend data could be used to make predictions in systems containing molecules of complex architecture (e.g., multiblock copolymer melts, homopolymer−copolymer mixtures, etc.).

Spinodals. Spinodal surfaces describe the limits of phase stability consistent with the constraints on the system. Compositions within the spinodal surface are unstable, whereas those outside are stable or metastable. Since the RPA uses a constant-volume constraint and a scattering experiment only probes a fixed volume, it has been questioned whether this RPA or scattering spinodal is the same as a spinodal determined at constant pressure.[12] The spinodal curve derived from a SANS experiment describes the stability limit of the grand canonical ensemble (V,T,μ_i), where μ_i is the chemical potential of component i. Although the scattering volume is fixed, all components can freely pass in and out of the volume (open system). In Appendix II we show that this stability limit is the same as that of the more familiar isothermal−isobaric ensemble (P,T,N_i).

Experimentally, one observes that $\Xi(0) \to \infty$ as the spinodal is approached. Thus, the condition for the experimental scattering spinodal is defined by

$$\mathrm{Det}\ \mathbf{S}^{-1}(0) = 0 \tag{21}$$

For a binary homopolymer blend, this condition combined with eq 4 and the nonlattice LF model yields

$$\frac{1}{v_1^*f_1} + \frac{1}{v_2^*f_2} - 2\left\{\beta\Delta P^* + 2v_0f_0\left[(\beta P_{12}^*)^2 - \left(\beta P_1^* - \frac{1}{2v_1^*f_1}\right)\left(\beta P_2^* - \frac{1}{2v_2^*f_2}\right)\right]\right\} = 0 \tag{22a}$$

The strict lattice version of the above equation is

$$\frac{1}{r_1f_1} + \frac{1}{r_2f_2} - 2\left\{\chi + 2f_0\left[(\beta\epsilon_{12}^*)^2 - \left(\beta\epsilon_{11}^* - \frac{1}{2r_1f_1}\right)\left(\beta\epsilon_{22}^* - \frac{1}{2r_2f_2}\right)\right]\right\} = 0 \tag{22b}$$

where χ is the familiar dimensionless χ interaction parameter:

$$\chi = \beta(\epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^*) \tag{23}$$

The only unknown parameter in the spinodal equations is the cross-interaction parameter, P_{12}^* or ϵ_{12}^*, or, equivalently, ΔP^* or χ.

The spinodal for deuterated polystyrene (dPS) and poly(vinyl methyl ether) (PVME)[35] has been previously calculated[36] using the strict lattice version of the LF model with one modification. The dPS/PVME blend is thought to have specific interactions, and ref 36 treats ϵ_{12}^* as a *free energy* that is temperature dependent. Excellent agreement with the experimental scattering spinodals was obtained. The spinodal given in ref 36 is functionally different in appearance than eq 22b, but both equations yield numerically identical spinodals for the parameters listed in ref 36. This is consistent with the proof given in Appendix II that a spinodal determined in a scattering experiment, defined by eq 21, is identical to the more familiar one defined by setting the second composition derivative of the Gibbs free energy equal to zero.

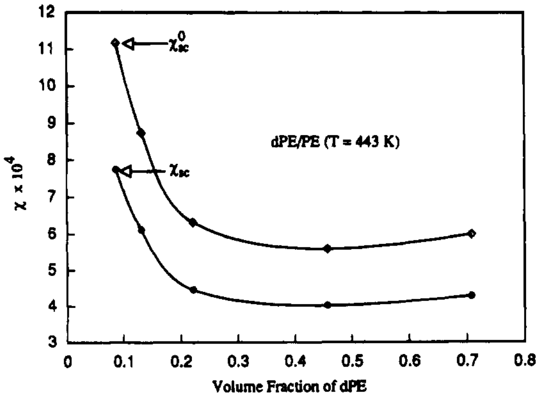

Figure 2. Illustration of the difference between "experimental" values of χ_{sc} interaction parameters for an isotopic PE system.[37] The actual numerical values of χ_{sc} obtained from SANS data depend sensitively on parameters used in conjunction with the classical RPA formula (eq 24). An alternative protocol has been suggested, eq 25 which yields χ_{sc}^0.

Interpretation of the SANS Interaction Parameter. The polymer−polymer interaction parameter χ_{sc} determined in a *sc*attering experiment has the following *operational definition*:

$$\Xi(q) = \frac{(\bar{b}_1^{\,\mathrm{ex}} - \bar{b}_2^{\,\mathrm{ex}})^2}{\dfrac{1}{v_1\phi_1^{\mathrm{ex}}g_1} + \dfrac{1}{v_2\phi_2^{\mathrm{ex}}g_2} - 2\dfrac{\chi_{\mathrm{sc}}}{v_\mathrm{r}}} \tag{24}$$

where v_i = *molecular* volume of component i at temperature T, ϕ_i^{ex} = experimental volume fraction of component i measured at T, v_r = arbitrary reference or monomer volume, $\bar{b}_i^{\mathrm{ex}}$ = scattering length b_i divided by the *monomer* volume at T, and, as before, the g_i are Debye functions. Equation 24 is the *incompressible* RPA formula first derived by de Gennes.[4] Equation 24 can be fitted to experimental scattering data to determine χ_{sc}/v_r as a function of blend composition, temperature, wave vector, and the molecular weights of the polymers. However, it is important to note that the numerical value of χ_{sc}/v_r that is extracted from a data analysis depends on the temperature- and investigator-dependent definitions of v_i, ϕ_i^{ex}, $\bar{b}_i^{\mathrm{ex}}$. Some investigators use the experimental temperature to evaluate these parameters or some other convenient temperature, such as room temperature. In a polydisperse system, the value of χ_{sc}/v_r is also sensitive to whether number- or weight-average molecular weights are used to calculate the v_i.

An alternative to eq 24 is to use an incompressible version of eq 14a ($f_0 = 0$):

$$\Xi(q) = \frac{(\bar{b}_1 - \bar{b}_2)^2}{\dfrac{1}{\mathbf{v}_1^*\phi_1g_1} + \dfrac{1}{\mathbf{v}_2^*\phi_2g_2} - 2\dfrac{\chi_{\mathrm{sc}}^{\ 0}}{v_\mathrm{r}}} = \frac{(\bar{b}_1 - \bar{b}_2)^2}{\tilde{\varrho}\left(\dfrac{1}{s_1} + \dfrac{1}{s_2}\right) - 2\dfrac{\chi_{\mathrm{sc}}^{\ 0}}{v_\mathrm{r}}} \tag{25}$$

to reduce data. Here the advantage is that $\bar{b}_i$, $\mathbf{v}_i^*$, and ϕ_i are all *temperature independent*. All scattering temperature dependence is now directly attributable to χ_{sc}^0/v_r. If eq 25 is used to reduce scattering data, the "experimental" value of χ_{sc}^0/v_r will differ from the experimental value of χ_{sc}/v_r obtained from eq 24. To compare calculated values of χ_{sc}^0/v_r with those calculated in the literature, we equate eqs 24 and 25 to obtain:

$$\frac{\chi_{\mathrm{sc}}}{v_{\mathrm{r}}} = \frac{(\bar{b}_1{}^{\mathrm{ex}} - \bar{b}_2{}^{\mathrm{ex}})^2}{(\bar{b}_1 - \bar{b}_2)^2}\left\{\frac{\chi_{\mathrm{sc}}{}^0}{v_{\mathrm{r}}} - \frac{1}{2}\left[\frac{1}{\mathbf{v}_1{}^*\phi_1 g_1} + \frac{1}{\mathbf{v}_2{}^*\phi_2 g_2}\right]\right\} + \frac{1}{2}\left[\frac{1}{v_1\phi_1{}^{\mathrm{ex}}g_1} + \frac{1}{v_2\phi_2{}^{\mathrm{ex}}g_2}\right] \quad (26)$$

which can also be inverted to obtain $\chi_{\mathrm{sc}}{}^0/v_{\mathrm{r}}$ from $\chi_{\mathrm{sc}}/v_{\mathrm{r}}$. In Figure 2 the difference between χ_{sc} and $\chi_{\mathrm{sc}}{}^0$ is illustrated for the isotopic dPE/PE blend system studied by Londono *et al.*[37]

At $q = 0$ and within the framework of classical polymer thermodynamics, $\chi_{\mathrm{sc}}/v_{\mathrm{r}}$ has a strict thermodynamic interpretation:[4,36,39–41]

$$\frac{\chi_{\mathrm{sc}}}{v_{\mathrm{r}}} = -\frac{1}{2}\frac{\mathrm{d}^2(\beta A_{\mathrm{ex}})}{\mathrm{d}\phi^2} \quad (27)$$

where A_{ex} is the excess Helmholtz free energy *density* and ϕ is the experimental volume fraction of either component. The excess free energy is relative to the free energy contribution of the classical Flory–Huggins entropy of mixing. For the classical incompressible theory, $\beta A_{\mathrm{ex}} = \phi_1\phi_2\chi/v_{\mathrm{r}}$, and $\chi_{\mathrm{sc}} = \chi$ with χ given by eq 23. Equation 27 is correct for any *incompressible* model. If χ is composition dependent, then χ_{sc} also depends on both first and second concentration derivatives on χ.[41] This seems to be well-known.

What has not been appreciated before is that eq 27 does not apply to a *compressible* mixture. To demonstrate this, $\chi_{\mathrm{sc}}{}^0/v_{\mathrm{r}}$ in eq 25 is calculated by equating eq 25 to the $\Xi(q)$ given by eq 14a:

$$\frac{\chi_{\mathrm{sc}}{}^0(q)}{v_{\mathrm{r}}} = \frac{\beta\Delta P^* + s_0\left[2\beta^2(P_{12}{}^{*2} - P_1{}^*P_2{}^*) + \dfrac{s_1\beta P_1{}^* + s_2\beta P_2{}^* - {}^1\!/_2}{s_1 s_2}\right]}{1 - s_0/v_{\mathrm{b}}} - \frac{1}{2}\left(\frac{1}{s_1} + \frac{1}{s_2}\right)\left(\frac{s_0/v_{\mathrm{b}}}{(1 - s_0/v_b)} + f_0\right) \quad (28a)$$

where v_b is given by eq 16. The thermodynamic interpretation of χ_{sc} given in eq 27 is independent of the nonthermodynamic scattering lengths b_i, whereas eq 28a depends on b_i even at $q = 0$. Only in the incompressible limit (see below) do we recover eq 27.

There are now several limiting forms of interest for $\chi_{\mathrm{sc}}{}^0$:

Incompressible Limit. In this limit $f_0 \to 0$, $s_0 \to 0$, and we recover a familiar result:

$$\lim_{f_0 \to 0} \frac{\chi_{\mathrm{sc}}{}^0}{v_{\mathrm{r}}} = \beta\Delta P^* \quad (28b)$$

In the strict lattice version of the LF model, we recover χ/v^*.

Infinite Contrast Limit. If $b_1 \to \infty$, then $1/v_b \to 2\beta P_2{}^* - 1/s_2$ and

$$\lim_{b_1 \to \infty} \frac{\chi_{\mathrm{sc}}{}^0(q)}{v_{\mathrm{r}}} = \frac{\beta\Delta P^* + s_0\beta\{2\beta(P_{12}{}^{*2} - P_1{}^*P_2{}^*) + (P_1{}^* - P_2{}^*)/s_2\} + \dfrac{s_0}{2s_2{}^2}}{1 - s_0(2\beta P_2{}^* - 1/s_2)} - \frac{f_0}{2}\left(\frac{1}{s_1} + \frac{1}{s_2}\right) \quad (28c)$$

Infinite Molecular Weight Limit.

$$\lim_{s_1,s_2 \to \infty} \frac{\chi_{\mathrm{sc}}{}^0}{v_{\mathrm{r}}} = \frac{(\bar{b}_1 - \bar{b}_2)^2\beta\{\Delta P^* + 2s_0\beta(P_{12}{}^{*2} - P_1{}^*P_2{}^*)\}}{(\bar{b}_1 - \bar{b}_2)^2 - 2s_0\beta\{\bar{b}_2{}^2P_1{}^* + \bar{b}_1{}^2P_2{}^* - 2\bar{b}_1\bar{b}_2P_{12}{}^*\}} \quad (28d)$$

Infinite Contrast and Molecular Weight Limit. Obtained by letting s_1, $s_2 \to \infty$ in eq 28c or letting $\bar{b}_1 \to \infty$ in eq 28d:

$$\lim_{b_1,s_1,s_2 \to \infty} \frac{\chi_{\mathrm{sc}}{}^0(q)}{v_{\mathrm{r}}} = \frac{\beta\Delta P^* + s_0\beta[2\beta(P_{12}{}^{*2} - P_1{}^*P_2{}^*)]}{1 - 2s_0\beta P_2{}^*} \quad (28e)$$

Dilute Limit. In this limit, if one of the components becomes very dilute, $f_1 \to 0$, and then $\chi_{\mathrm{sc}}{}^0$ diverges to *positive infinity* as $1/f_1$:

$$\frac{\chi_{\mathrm{sc}}{}^0(q)}{v_{\mathrm{r}}} \to \frac{1}{2\mathbf{v}_1{}^*\phi_1 g_1(q)} + (\bar{b}_1/\bar{b}_2 - 1)^2\beta P_2{}^* + \ldots \to \infty \qquad \text{as } \phi_1 \to 0 \quad (28f)$$

Recently, Londono *et al.*[37] have studied isotopic blends of polystyrene (dPS/PS) and polyethylene (dPE/PE). Their data yield $P_1{}^* = 418.085$ MPa ($P_2{}^* = 425$ MPa) for the PE blend and $P_1{}^* = 354.638$ MPa ($P_2{}^* = 357$ MPa) for the PS blend. These values were determined by procedures similar to those described earlier in the section on differential scattering cross section. The difference is that the equation of state (eq 17) is solved simultaneously with eq 26 for $\chi_{\mathrm{sc}}(0)$ rather than eq 14a for $\Xi(0)$. A single datum near the middle of the composition range is used in this procedure. In both cases, LF parameters for the hydrogenated component were taken from ref 26. Note that $P_1{}^* = 354.638$ MPa for dPS determined here from χ_{sc} is nearly identical to the 354.805 MPa value determined earlier from $\Xi(0)$ data from a different study.[33] This is very encouraging self-consistency.

Figure 3 compares the composition dependence of χ_{sc} for these two systems as predicted by eqs 28a and 26 with the experimental χ_{sc} values. As can be seen, the agreement is satisfactory. The upturn in χ_{sc} at composition extremes for the dPE/PE blend is consistent with the dilute limit analysis presented above.

Londono *et al.*[37] have also studied the molecular weight and temperature dependence effects. Table 1 compares the experimental values of χ_{sc} for the dPE/PE blend system with those calculated from eqs 28a and 26. Except for one entry in Table 1, the results are within the experimental error (about 10–15% depending on composition). A comparison of the theoretical and experimental temperature dependences of χ_{sc} is

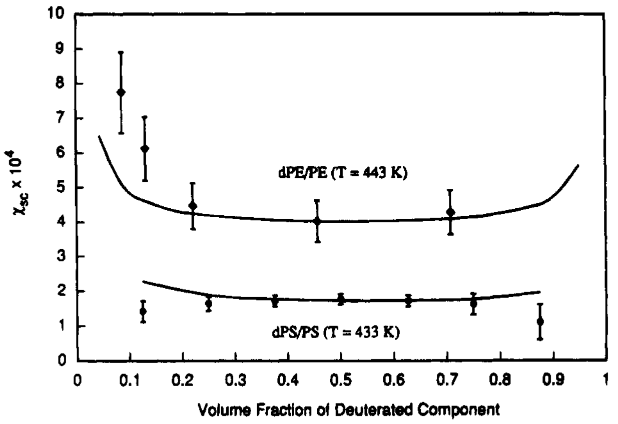

Figure 3. Comparison of experimental[37] and calculated (solid lines) values of χ_{sc} as a function of composition for isotopic blends. An experimental data point in the middle of the composition range was used to fix the value of the characteristic pressure P^* of the deuterated polymer (see text).

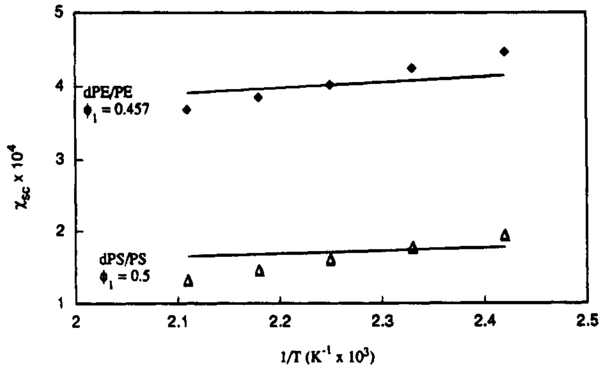

Figure 4. Comparison of experimental[37] and calculated values of χ_{sc} as a function of reciprocal temperature for isotopic blends.

Table 1. Effect of Molecular Weight on χ_{sc} for dPE/hPE Blend

degree of polymerization			$\chi_{sc} \times 10^{-4}$	
dPE	PE	ϕ_{dPE}	expt[37]	calc
2460	2540	0.221	5.9	4.7
3275	3300	0.457	4.5	4.1
5240	5200	0.221	4.2	4.2
		0.457	3.8	4.0
6240	6630	0.176	4.6	4.2

shown in Figure 4. In general, the predicted temperature dependence is linear in $1/T$ as is the experimental, but the slope tends to be uniformly underestimated.

Experimentally[9,38] it has been observed that χ_{sc} can be q dependent. In Figure 5, our theoretical χ_{sc} is plotted against q^2 for the dPBD/PBD blend at three compositions. Note that the q dependence (as measured by the slope) is larger at the composition extremes as expected from the dilute limit analysis presented above. A recent study with statistical copolymers exhibits the same trends predicted here for dPBD/PBD blends.[38] Unfortunately, the requisite LF parameters are not available for the copolymers so that a direct comparison is not possible.

Interpretation of the Wave Vector Dependence of Scattering. Expanding the classical RPA formula for $\Xi^{-1}(q)$ (eq 24) in powers of q, we obtain:

$$\Xi^{-1}(q) = \Xi^{-1}(0) + \frac{1}{(\bar{b}_1^{\,ex} - \bar{b}_2^{\,ex})^2}\left(\frac{R_1^{\,2}}{v_1\phi_1^{\,ex}} + \frac{R_2^{\,2}}{v_2\phi_2^{\,ex}}\right)q^2 + \dots \quad (29)$$

where, as before, the R_i are the radii of gyration of the respective chains. Thus, the coefficient of the q^2 term yields information on polymer chain size.[1] Does finite compressibility affect this conclusion?

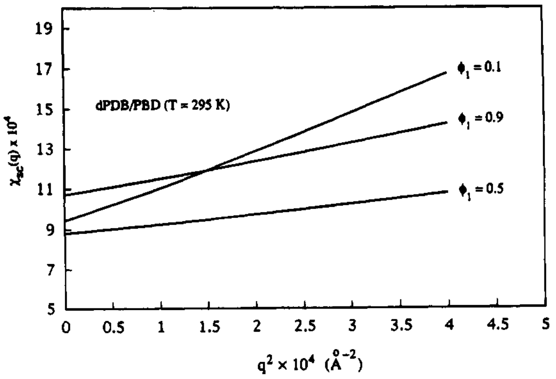

Figure 5. Predicted dependence of the q^2 dependence of χ_{sc} for the isotopic blend system dPBD/PBD. Interaction parameters and molecular weights used are the same as those used for Figure 1. Note that more pronounced q dependence at composition extremes as predicted by eq 28g.

In general, we have

$$\Xi^{-1}(q) = \Xi^{-1}(0) + B(f_0)q^2 + \dots \quad (30)$$

where the coefficient B of that q^2 term depends on the hole fraction f_0 and is given by

$$B(f_0) = \frac{1}{2}\frac{\partial^2 \Xi^{-1}(q)}{\partial q^2}\bigg|_{q=0} \quad (31)$$

Since the general case is complicated, we analyze the simplest situation of an isotopic blend where the isotopes have identical degrees of polymerization that are large so that $R_1 = R_2$, $v_1 = v_2 \to \infty$, and $P_1^* \cong P_2^* = P_{12}^* \equiv P^*$. We also assume high contrast, $b_1 \gg b_2$, and ignore the contribution of density fluctuations ($\xi = 0$). For these conditions, we evaluate the ratio $B(f_0)/B(0) \equiv B/B_0$. Compressibility effects are ignorable only when this ratio is unity. The ratio is given by

$$\frac{B}{B_0} = \frac{1 - 3f_0(\beta P^* v_0) + 2f_0^{\,2}(\beta P^* v_0)^2(1 + \phi_1)}{(1 - f_0)[1 - 2f_0(\beta P^* v_0)]^2} \quad (32a)$$

Using the LF relation among parameters, $P^*v_0/kT^* = 1$, we can express the result in terms of the characteristic temperature, T^*, or the reduced temperature, $\tilde{T} \equiv T/T^*$:

$$\frac{B}{B_0} = \frac{1 - 3f_0/\tilde{T} + 2f_0^{\,2}(1 + \phi_1)/\tilde{T}^2}{(1 - f_0)(1 - 2f_0/\tilde{T})^2} \quad (32b)$$

The LF equation of state (eq 17) relates the f_0 to $\tilde{T}$:

$$1/\tilde{T} = -\frac{\ln f_0 + 1 - f_0}{(1 - f_0)^2} \quad (33)$$

Substituting eq 33 into eq 32b yields an expression for B/B_0 that is only a function of composition and f_0. In Figure 6, B/B_0 is plotted against f_0. Since typical values of f_0 are about 0.1, corresponding to $\tilde{T} \approx 0.6$, we see that finite compressibility has a significant effect on the experimental determination of gyration radii. If corrections are not made, gyration radii will be overestimated or, more correctly, Kuhn lengths will be overestimated. The experimentally determined gyration radius, assuming incompressibility, should be divided by $(B/B_0)^{1/2}$ to correct for compressibility effects. Although the above results are specific for isotopic blends, similar

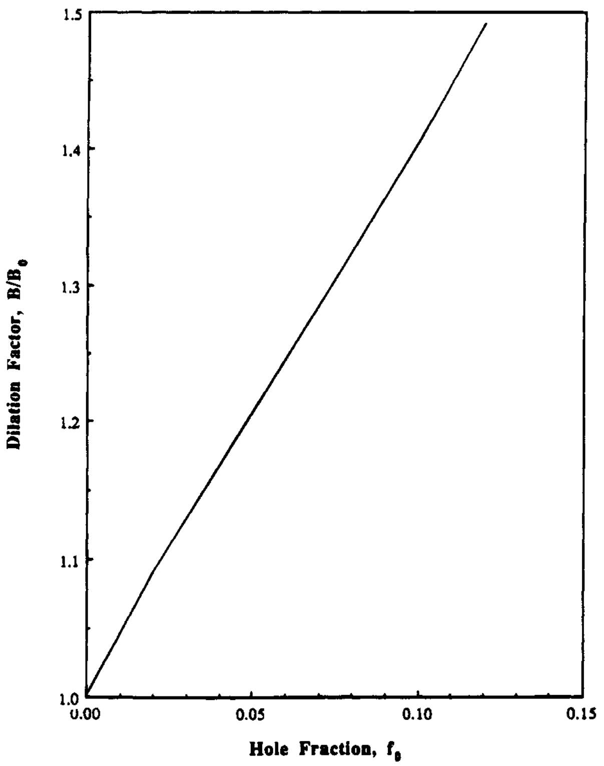

Figure 6. Dilation factor B/B_0 for the gyration radius (eq 32b) plotted as a function of the hole fraction f_0 for a typical isotopic blend ($\phi_1 = 0$). The experimentally determined gyration radius, assuming incompressibility, should be divided by $(B/B_0)^{1/2}$ to correct for compressibility effects.

behavior is observed for nonisotopic blends; specifically, $B/B_0 > 1$, $\partial B/\partial f_0 > 0$, and $1.2 < B/B_0 < 1.5$. Dudowicz and Freed have also reached similar conclusions.[19]

Since pressure decreases f_0, B decreases with pressure, which left uncorrected, would lead to the faulty conclusion that the gyration radius is decreasing with pressure. Pressure effects are currently being investigated.[43] The decrease of f_0 with pressure can be determined from the equation of state:

$$f_0 = \exp\{-[(1 - f_0)^2 + \tilde{P}]/\tilde{T} + f_0 - 1\} \qquad (34)$$

where $\tilde{P} \equiv P/P^*$ is the reduced pressure. Written in this way, the equation of state can easily be solved by iteration. A plot of B/B_0 as a function of reduced pressure is shown in Figure 7. Most polymers have P^* values in the range 300–500 MPa.[26,42] Thus, a pressure of 100 MPa corresponds to a reduced pressure of about 0.25.

Summary

When eq 24, the classical RPA formula, is used to reduce scattering data from binary polymer blends, an experimental interaction parameter, χ_{sc}, is obtained. For an incompressible blend, this parameter has a strict thermodynamic interpretation; i.e., it is equal to a second concentration derivative of an excess free energy (eq 27). *What we have shown is that, for a compressible blend, this interpretation no longer holds.* This statement should not be construed to mean that the scattering does not approach the correct thermodynamic limit at $q = 0$. The requirement that the scattering cross section $\Xi(q)$ is a positive number requires that the matrix $\mathbf{S}(q)$ be positive definite (see eq 2); a necessary condition for positiveness is that the determinant of $\mathbf{S}(q)$ be positive, $|\mathbf{S}(q)| > 0$. However, since $|\mathbf{S}(q)\ \mathbf{S}^{-1}(q)| = |\mathbf{S}(q)||\mathbf{S}^{-1}(q)| = 1$, this is equivalent to requiring $|\mathbf{S}^{-1}(q)| > 0$. Of course, this condition must also hold at $q = 0$; i.e., $|\mathbf{S}^{-1}(0)| > 0$. The matrix elements of $\mathbf{S}^{-1}(0)$ are related to second concentration derivatives on the Helmholtz free energy density (see eq 4). In Appendix II we show that, for a binary mixture, $|\mathbf{S}^{-1}(0)| > 0$ is equivalent to the more familiar requirement that the second concentration derivative of the Gibbs free energy at constant pressure be positive. So there is no thermodynamic inconsistency in our statement that for compressible mixture χ_{sc} is not related to a second concentration derivative of an excess free energy. At $q = 0$, eq 28 indicates that χ_{sc} depends not only on the thermodynamic matrix elements of $\mathbf{S}^{-1}(0)$ but also on the nonthermodynamic scattering lengths b_i. *This dependence of χ_{sc} on b_i disappears only in the incompressible limit.*

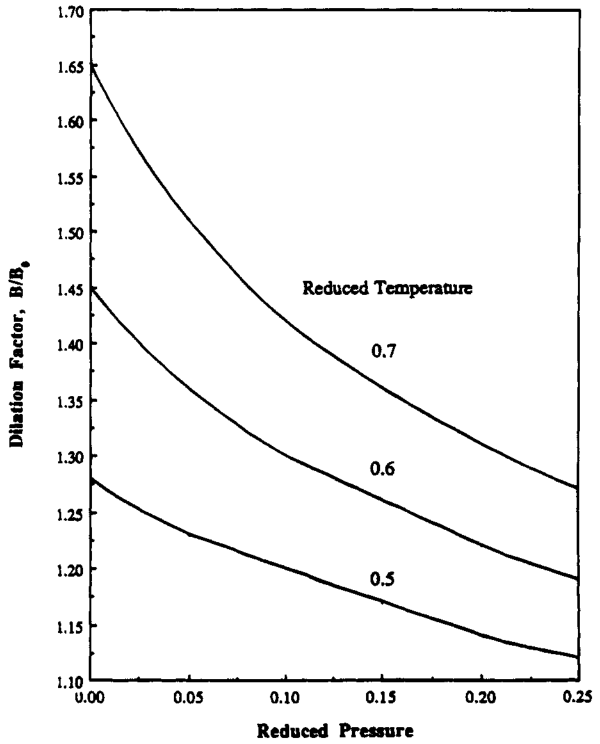

Figure 7. Dilation factor B/B_0 for the gyration radius (eq 32b) plotted as a function of reduced temperature and pressure for a typical isotopic blend ($\phi_1 = 0.1$); f_0 determined from the equation of state (eq 34).

Numerical values of χ_{sc} obtained from experimental scattering data depend on temperature- and investigator-dependent definitions of v_i, ϕ_i^{ex}, and $\bar{b}_i^{ex}$ used in the classical RPA formula (eq 24). We have recommended an alternative procedure where temperature-independent definitions of these quantities (see eq 25) are used to defined a new experimental interaction parameter χ_{sc}^0. The transformation equation between χ_{sc} and χ_{sc}^0 is given by eq 26. As an illustration, a comparison of χ_{sc} and χ_{sc}^0 is given for isotopic polyethylene blends in Figure 2.

For the compressible LF model eq 28a and its various limiting forms (eqs 28b–g) are theoretical expressions for χ_{sc}^0. In general, χ_{sc}^0 depends on the nonthermodynamic scattering lengths b_i. Important implications of this result are as follows:

(1) χ_{sc} values will appear to be composition, molecular weight, and q dependent, especially at composition extremes (see Figures 3 and 5 and Table 1).

(2) χ_{sc} is not invariant to an interchange of scattering lengths ($b_1 \rightarrow b_2$, $b_2 \rightarrow b_1$). In the classical incompress-

ible RPA formula, $\Xi(q)/(\bar{b}_1 - \bar{b}_2)^2$ does not depend on the scattering lengths b_i, whereas the compressible RPA formula (eq 14a) does. This means that, in label-switching experiments, different interaction parameters can be obtained.[44]

The q^2 dependence of $\Xi^{-1}(q)$ has been traditionally used to determine the radii of gyration of polymer chains[1] (see eq 29). If the finite compressibility of the mixture is ignored, gyration radii will be overestimated, or, more correctly, Kuhn lengths will be overestimated. Errors of 10–20% are typical.

The new compressible RPA formula for scattering from a binary polymer blend (eq 14a), like its incompressible cousin (eq 14b or eq 24), involves a single adjustable parameter. For isotopic blends, the only unknown parameter is the characteristic pressure (P_1^*) of the deuterated polymer, which typically we have found to be about 1–2% below the value for the hydrogenated polymer. The LF parameters (T_2^*, P_2^*, and ϱ_2^*) for the hydrogenated components are tabulated[26,41] and, for isotopes, $\mathbf{v}_1^* = \mathbf{v}_2^* = M_2/\varrho_2^*$. For the cross-interaction parameter, the geometric mean approximation is invoked: $P_{12}^* = (P_1^*P_2^*)^{1/2}$. The characteristic temperature of the isotopic blend is given by eq 18. For nonisotopic blends, the only adjustable parameter is the the cross-interaction parameter, P_{12}^*, or, equivalently, ΔP^*. All requisite pure-component parameters (T_i^*, P_i^*, and ϱ_i^*) are presumably tabulated or can be determined from experimental *PVT* data. The T^* and P^* parameters for the deuterated polymer are equated to those of the hydrogenated polymer to a good approximation. The characteristic temperature of the blend is given by eq 20.

Appendix I

This appendix derives equations for the case when the hole volume v_0 of the nonlattice LF model or "mer" volume v^* of the strict lattice LF model are functions of composition. For the nonlattice version, eq 11 gives

$$\beta\bar{P}_{ij} = \beta P_{ij} - \frac{1}{2}\left(-(\ln f_0 + 1)\left(\frac{\partial {v_0}^{-1}}{\partial f_i} + \frac{\partial {v_0}^{-1}}{\partial f_j}\right) + f_0 \ln f_0 \frac{\partial^2 {v_0}^{-1}}{\partial f_i \partial f_j}\right) \tag{I.1}$$

A reciprocal mixing rule is natural for the nonlattice version of the LF model;[26] v_0 is then given by

$$\frac{1}{v_0} = \sum_{i=1}^{m} \frac{\phi_i}{v_{0i}} \equiv \frac{\sum_{i=1}^{m} \frac{f_i}{v_{0i}}}{\sum_{i=1}^{m} f_i} \tag{I.2}$$

where v_{0i} is the hole volume associated with component i. Using this in eq I.1 yields

$$\beta\bar{P}_{ij} = \beta P_{ij} - \frac{1}{2}\left[\frac{\ln f_0 + (1 - f_0)}{(1 - f_0)^2}\left[\frac{2}{v_0} - \frac{1}{v_{0i}} - \frac{1}{N_{0j}}\right]\right] \tag{I.3}$$

All the other equations derived in the paper can now be simply "rederived" by replacing P_{ij} by $\bar{P}_{ij}$ derived above.

For the strict lattice version of the LF model, the Helmholtz free energy per mer given by

$$\beta a_{\text{mer}} = -\sum_{i,j=1}^{m} f_i f_j \epsilon_{ij} + \sum_{i=1}^{m} \frac{f_i}{r_i} \ln f_i + f_0 \ln f_0 \tag{I.4}$$

so that $A/V \equiv A \equiv a_{\text{mer}}/v^*$. Here v^* is the average mer volume in the mixture. If we now assume by analogy with eq I.2 that

$$\frac{1}{v^*} = \sum_{i=1}^{m} \frac{\phi_i}{{v_i}^*} \equiv \frac{\sum_{i=1}^{m} \frac{f_i}{{v_i}^*}}{\sum_{i=1}^{m} f_i} \tag{I.5}$$

where v_i^* is the mer volume characteristic of component i (same as the hole volume for the lattice version of LF model), then

$$\mathbf{S}^{-1}(q) = \left[\frac{\delta_{ij}}{v^* r_i f_i g_i(q)} - \frac{2\beta\bar{\epsilon}_{ij}}{v^*} + \frac{1 + \xi^2 q^2}{v^* f_0}\right] \tag{I.6}$$

where

$$\beta\bar{\epsilon}_{ij} = \beta\epsilon_{ij} - \frac{1}{2}\left(\left(\frac{\partial \beta a_m}{\partial f_i}\right)_{f_j} \frac{(v^*/{v_j}^* - 1)}{(1 - f_0)} + \left(\frac{\partial \beta a_m}{\partial f_j}\right)_{f_i} \frac{(v^*/{v_i}^* - 1)}{(1 - f_0)} + \frac{\beta a_m}{(1 - f_0)^2}\left[\frac{2}{v_0} - \frac{1}{v_{0i}} - \frac{1}{N_{0j}}\right]\right)$$

As in the nonlattice case, all the corresponding equations are obtained by simply using $\bar{\epsilon}_{ij}$ in place of ϵ_{ij} at appropriate places in this paper.

Appendix II

Scattering experiments probe isothermal, constant-volume, open systems. Thus, SANS (and other scattering) experiments probe a (V,T,μ_i) ensemble, whereas the stability limits of a mixture are usually specified in terms of a (P,T,N_i) ensemble. To our knowledge, the relationship between the stability conditions of the two ensembles is not available in the literature, and, therefore, we present a derivation here. We confine our treatment to a binary mixture. For a binary mixture in the (V,T,μ_i) ensemble, the system is stable with respect to concentration fluctuations if[29]

$$\text{Det}\left(\frac{\partial^2 \text{A}}{\partial N_i\, \partial N_j}\right)_{V,T,(N_1,N_2)} > 0 \tag{II.1}$$

where A = Helmholtz free energy. This is equivalent to requiring Det $\mathbf{S}^{-1}(0) > 0$ (*cf.* eq 4).

Second concentration derivatives on the Helmholtz free energy are related to those on the Gibbs free energy by[29]

$$\text{A}_{ij} \equiv \left(\frac{\partial^2 \text{A}}{\partial N_i\, \partial N_j}\right)_{V,T,N_k} = \left(\frac{\partial^2 G}{\partial N_i\, \partial N_j}\right)_{P,T,N_k} + \frac{\bar{v}_i \bar{v}_j}{V\kappa} \equiv G_{ij} + \frac{\bar{v}_i \bar{v}_j}{V\kappa} \tag{II.2}$$

where G = Gibbs free energy, κ = isothermal compressibility of the mixture, and $\bar{v}_i$ = partial molar volume of component i. From the Gibbs–Duhem relationship for a binary mixture, we have

$$G_{ij} = -\frac{N_i}{N_j} G_{ii} = -\frac{N_j}{N_i} G_{jj} \tag{II.3}$$

and

$$G_{11}G_{22} - G_{12}^2 = 0 \qquad \text{(II.4)}$$

Using eqs II.2–II.4, eq II.1 yields

$$\mathrm{Det}\left(\frac{\partial^2 A}{\partial N_i\,\partial N_j}\right)_{V,T,(N_1,N_2)} = A_{11}A_{22} - A_{12}^2 = \frac{VG_{11}}{N_2^2\kappa} \qquad \text{(II.5)}$$

and we have used $V = N_1\bar{v}_1 + N_2\bar{v}_2$.

Thus, the stability conditions for an open system at constant volume are equivalent to those of a closed system at constant pressure:

$$G_{11} \equiv \left(\frac{\partial^2 G}{\partial N_1^2}\right)_{P,T,N_2} > 0 \qquad \text{(II.6)}$$

and *vice versa*. Equation II.6 is exactly the well-known stability condition for a (P,T,N_1,N_2) ensemble. This also establishes that the spinodal determined in scattering experiments Det $\mathbf{S}^{-1}(0) = 0$ is equivalent to that determined at fixed pressure in a closed system, $G_{11} = 0$.

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