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Compressibility Effects in the Analysis and Interpretation of Neutron Scattering Data from Polymer Blends

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ABSTRACT: A thermodynamically consistent procedure, based on statistical mechanical fluctuation theory, has been developed for the analysis and interpretation of small-angle neutron scattering (SANS) data for compressible polymer blends. The development was motivated by inconsistencies between the interaction parameter obtained with an analysis based on the incompressible Flory−Huggins model, which is a function of composition, and the Flory−Huggins model itself, in which the interaction parameter is independent of composition. An expression is obtained that connects the forward scattering intensity with the curvature of the Gibbs energy for a binary blend of arbitrary compressibility. This expression, which forms the basis of the data analysis procedure, permits the contributions of various effects of compressibility to be estimated without the introduction of specific models. We show that contributions from both density fluctuations and excess volumes of mixing can safely be neglected in the analysis of SANS data for polymer blends. We illustrate the methodology with the lattice fluid model, which expresses the Gibbs energy curvature in terms of microscopic properties, thereby relating to the SANS intensity. A parameter characterizing system interactions can then be defined in terms of three energetic quantities, two of which can be evaluated from pure component *PVT* data. The remaining quantity, when treated as a system-specific constant, independent of temperature and blend composition, can quantitatively and self-consistently describe SANS data for weakly interacting blends, such as mixtures of saturated hydrocarbon polymers and isotopically substituted species.

1. Introduction

The phase behavior of polymer blends is commonly described in terms of the lattice model of Flory[1] and Huggins[2,3] (FH), which provides the following expression for the Gibbs energy of mixing per monomer:

$$g \equiv \frac{\Delta G_{\mathrm{m}}}{N} = k_{\mathrm{B}}T\left[\frac{\Phi_1}{r_1}\ln\Phi_1 + \frac{\Phi_2}{r_2}\ln\Phi_2 + \Phi_1\Phi_2\chi_{\mathrm{FH}}\right] \quad (1)$$

In this expression, T is the absolute temperature, k_{B} is Boltzmann's constant, r_i is the number of lattice sites occupied by a chain of type i, Φ_i is the volume fraction of component i, and $N = N_1r_1 + N_2r_2$, where N_i is the number of chains of type i, is the total number of chain segments. Apart from the use of a lattice in its derivation, the major assumptions underlying this model are those of incompressibility and random mixing of chain segments. The Flory−Huggins interaction parameter, χ_{FH}, is defined in terms of the normalized monomer−monomer interaction energies,

$$\chi_{\mathrm{FH}} = \epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22}) \quad (2)$$

where $\epsilon_{ij} = E_{ij}z/k_{\mathrm{B}}T$, z is the lattice coordination number, and E_{ij} is the interaction energy between nearest neighbor monomers of types i and j. Notice that since the energetic interaction E_{ij} is attractive, the quantity ϵ_{ij} is inherently negative in sign. In the FH theory, the interaction parameter is independent of blend composition and chain length and depends only on temperature and the chemical identity of the two monomers.

In practice, eq 1 is recast in terms of observable properties by expressing the r_i as a function of the degree of polymerization z_i, the volume per monomer in the pure state and at the temperature and pressure of interest v_i, and a reference volume, v_0, corresponding in principle to the volume of a lattice site.[4]

$$r_i = \frac{z_iv_i}{v_0} \quad (3)$$

Substitution into eq 1 yields an expression for the Gibbs energy of mixing per unit volume,

$$\frac{g}{v_0} = \frac{\Delta G_{\mathrm{m}}}{V} = k_{\mathrm{B}}T\left[\frac{\Phi_1}{z_1v_1}\ln\Phi_1 + \frac{\Phi_2}{z_2v_2}\ln\Phi_2 + \Phi_1\Phi_2\frac{\chi_{\mathrm{FH}}}{v_0}\right] \quad (4)$$

where $V = Nv_0$ is the system volume. Thus χ_{FH}/v_0 defines an interaction parameter density that can describe a system composed of polymer chains with different monomeric volumes. This formulation is more convenient for interpreting scattering data, but the primary assumptions underlying the FH model, incompressibility and random mixing, leading to a composition-independent interaction parameter density, continue to apply. The parameter χ_{FH}/v_0 is the only quantity in the free energy expression that cannot be obtained from independent measurements on the respective pure components. A determination of the interaction parameter as a function of temperature thus provides a complete description of the thermodynamics of polymer blends that can be described by the Flory−Huggins free energy expression.

Small-angle neutron scattering (SANS) has been widely used to evaluate thermodynamic interactions in

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polymer blends.[5−7] The measured quantity is the coherent scattering intensity per unit sample volume and subtended scattering angle, $d\Sigma/d\Omega(q)$[6] or $I(q)$.[7] For homogeneous, isotropic liquids, single-phase polymer blends in this case, $I(q)$ is a function of the magnitude of the scattering vector alone, $q = (4\pi/\lambda_n)\sin(\theta/2)$, where λ_n is the incident neutron wavelength and θ is the scattering angle. The assignment of an interaction parameter requires an analysis procedure which consists in principle of three steps: (1) extrapolation of the scattering data to $q = 0$ to obtain $I(0)$; (2) conversion of $I(0)$ to thermodynamic quantities through fluctuation theory; (3) expression of the thermodynamic quantities in terms of system parameters, which requires the application of a model.

In the usual data analysis procedure, step 1 is accomplished by invoking the random phase approximation, in which the blend is assumed to be incompressible.[8] The incompressibility constraint is applied in step 2 as well, with the result[7]

$$I(0) = v_0 S(0)\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \tag{5}$$

The quantity $(b_1/v_1 - b_2/v_2)^2$ is the contrast factor, denoted here by k_N, where b_i represents the coherent scattering length of a monomer of type i. The structure factor, $S(0)$, links the scattering intensity to general thermodynamic properties:

$$v_0 S(0) = k_B T\left(\frac{\partial^2(\Delta G_m/V)}{\partial\Phi^2}\right)_T^{-1} \tag{6}$$

In step 3, the curvature of the Gibbs energy, $(\partial^2(\Delta G_m/V)/\partial\Phi^2)_T^{-1}$, is evaluated with the FH model (eq 4). The combined result of steps 2 and 3 is an operational relationship between $I(0)$ and an interaction parameter that is commonly used to analyze SANS data for binary polymer blends:

$$\frac{\chi}{v_0} \equiv \frac{1}{2}\left[\frac{1}{z_1\Phi_1 v_1} + \frac{1}{z_2\Phi_2 v_2} - \frac{k_N}{I(0)}\right] \tag{7}$$

When this expression is used to *analyze* data, the resulting interaction parameter is *interpreted* as the Flory−Huggins interaction parameter,

$$\chi = \chi_{FH} \tag{8}$$

The significance of the emphasized terminology, analysis and interpretation, will be explained in detail below.

The interaction parameter defined in eq 7 characterizes the difference between the measured scattering intensity and an ideal FH (incompressible) scattering intensity (no interactions or $\chi = 0$). The ideal scattering is connected directly with the combinatorial entropy terms appearing in the FH model. The scattering intensity diverges at the spinodal, so the ideal FH scattering term also defines a value for the interaction parameter at the spinodal, χ^s. This procedure for data analysis, when applied to the coherent SANS intensity for various blend systems, has resulted in values for χ that almost invariably depend on blend composition.[4,9−12]

The blends studied thus far can be characterized as "strongly interacting" and "weakly interacting". The distinction refers to the relative contributions of ideal FH scattering and scattering attributed to interactions. We consider strongly interacting blends to be those for which $|\chi|/\chi^s \gg 1$, and weakly interacting blends to be those for which $|\chi|/\chi^s \approx 1$. A strongly interacting polymer blend will only be miscible if χ is negative, so these blends are characterized by large negative interaction parameters. Conversely, all miscible polymer blends with positive χ are by definition weakly interacting. The observed composition dependencies for strongly and weakly interacting blends are qualitatively different.

An example of a strongly interacting blend where the interaction parameter has been determined as a function of composition is the deuterated polystyrene (PSD) and hydrogenated poly(vinyl methyl ether) (PVME) system investigated by Han and co-workers.[4] These blends exhibit a lower critical solution temperature (LCST), and χ is large and negative in the single-phase region, except near the spinodal. In this system, the interaction parameter varies linearly with composition:

$$\chi(\Phi_1,T) = A_s(T) + B_s(T)\Phi_1 \tag{9}$$

Han et al. found no dependence on molecular weight for this system within the three molecular weight combinations studied.

The composition dependence of χ for weakly interacting blends has been extensively studied for a wider range of systems, including isotopic mixtures[9−11] and blends of model polyolefins.[12] The composition dependence of χ for all weakly interacting blends examined thus far is approximately parabolic:

$$\chi(\Phi_1,T) = A_w(T) + \frac{B_w(T)}{\Phi_1\Phi_2} \tag{10}$$

The coefficient $B_w(T)$ is usually found to be positive, corresponding to an upward trend in χ at the composition extremes. Isotopic mixtures of polystyrene,[10,11] which display downward curvature ($B_w(T) < 0$), provide the only exception. The magnitude of the curvature appears to be uncorrelated with the distance from the critical temperature of the blend.[12] Some studies also suggest the possibility of a weak dependence of χ on component molecular weights.[9,13] Perhaps the most surprising (and intriguing) feature of these observations is that even blends with extraordinarily weak interactions are characterized by interaction parameters with large composition dependencies. These are as prominent as those for strongly interacting systems, although different in form. The qualitative difference between isotopic mixtures of polystyrene and the other weakly interacting blends (downward vs upward curvature) has also seemed puzzling.

All of these composition-dependent interaction parameters have been obtained from the coherent SANS intensity by application of eq 7. This equation is a specific example of what will be referred to below as the *analysis* expression. The analysis expression incorporates steps 2 and 3 mentioned earlier, and relates the experimentally observable scattering intensity to the derived quantity, χ. The specific form of the analysis expression is dependent on the model used to derive it, with eq 7 being the result for the incompressible FH model. The composition dependence of the interaction parameters described earlier, as determined by applying the FH analysis expression to the measured scattering intensity, is inconsistent with their corresponding interpretation as expressed by eq 8. This equation is a specific example of what will be referred to below as the *interpretation* expression. The interpretation expression provides the link between the derived experimental quantity, χ, and the microscopic parameters it represents. For the FH model, the interpretation expression is particularly simple in that χ is represented by a single quantity, $\chi_{FH} = \epsilon_{12} - {}^1/_2(\epsilon_{11} + \epsilon_{22})$. In other words, the interaction parameter determined from SANS data is *interpreted* for the FH model as an exchange energy.

The fact that the set of analysis and interpretation expressions derived from the FH model do not provide consistent results has prompted a fair amount of theoretical attention.[14−21] Many of these efforts are based on the premise that the FH analysis expression provides acceptable results, and shortcomings in FH theory are manifested in the inability of the interpretation expression to explain the experimental data. Accordingly, the objective has frequently been to formulate an interpretation expression based on something other than the FH model. In a typical calculation, the scattering intensity, $I(0)$, is obtained from the appropriate fluctuation expressions, with a model or theory which in some sense improves upon the FH model. This intensity is substituted into eq 7, to produce a new expression for χ as a function of thermodynamic variables, e.g., temperature, pressure, and composition, as well as system parameters, e.g., molecular weights and the ϵ_{ij}. This new interaction parameter replaces the FH interpretation in eq 8 ($\chi = \chi_{FH}$) with

$$\chi = f(\{r_i\},\{\Phi_i\},...) \tag{11}$$

where the specific form of the function f depends on the choice of model or theory. The interpretation expression is thus modified to reflect the improvements made to the FH model. This new interpretation is compared to results obtained with the FH analysis expression (eq 7) to evaluate the ability of the model or theory to capture trends in experimental scattering data.

One example of the application of this procedure is the work of Muthukumar[14] and of Olvera et al.,[15] who suggested that the primary shortcoming of the FH model is its mean field nature. However, departures from mean field behavior depend on proximity to the critical point, and the experimental results[12] suggest that the composition dependence of χ is uncorrelated with the distance from T_c. Accordingly, it appears that non-mean field corrections alone cannot explain the experimental results.

A second example, which has been extensively investigated, is the incorporation of effects that arise from the small, but nonzero, compressibilities of polymer blends. Dudowicz and Freed[18−20] have reformulated the interpretation expression, as in eq 11, to account for compressibility. This expression is based on these authors' lattice cluster model[19] and depends on both composition and molecular weight. For the strongly interacting PSD/PVME system, the correspondence between the composition dependence of the data of Han et al.[4] and that of the prediction is reasonable.[19] However, for weakly interacting blends, the predicted composition dependence is universally parabolic with *downward* curvature,[20] in agreement only with the blend of isotopic polystyrenes.

Bidkar and Sanchez[21] have extended this approach, based on the lattice fluid model,[22] to nonzero wavevectors and find reasonable fits to experimental $I(q)$ vs q data. They also have recognized the importance of consistency between the data analysis procedure (the analysis expression) and the model interpretation (the interpretation expression). Their resulting $I(0)$ calculations predict a variation of χ with composition that is always parabolic with *upward* curvature[21] for weakly interacting blends. This is qualitative agreement with most weakly interacting blends studied experimentally but is of course inconsistent with the behavior of the PS/PSD blend.

Building on the work of Bidkar and Sanchez, we consider how both the analysis and interpretation expressions can be reformulated in a self-consistent manner for a compressible polymer blend. The effect of blend compressibility on the data analysis procedure itself has been considered only for step 1, first by Tang and Freed[23] and more recently by Bidkar and Sanchez.[21] The research of both groups suggests that, although compressibility may affect the determination of chain dimensions, the assignment of $I(0)$ is relatively unaffected. Here we accept the validity of step 1 to obtain $I(0)$[21,23] and focus on formulating steps 2 and 3 (the analysis expression) for a compressible system. We first develop a general relation between $I(0)$ and thermodynamic properties for a compressible blend. This leads to a compressible version of eq 5 in which the scattering intensity is again inversely proportional to the curvature of the Gibbs energy at fixed temperature and pressure. The general model-independent result is rigorously applicable to any compressible binary mixture.

The development of a compressible version of step 3 requires a model, and here we use the Sanchez−Lacombe lattice fluid (LF) model, which is the simplest available compressible model. The LF model is used to express the curvatuve of the Gibbs energy in terms of microscopic quantities, resulting in both a LF *analysis* expression and a LF *interpretation* expression, in which the LF interaction parameter depends on composition and molecular weight. Thus, we introduce both an alternative method of data analysis *and* an alternative interpretation of the interaction parameter. Application of both to experimental scattering data for isotopic polystyrene mixtures and polyolefin blends is then shown to provide excellent agreement between the interaction parameters obtained from the LF analysis expression and their LF interpretation.

2. Analysis of SANS Data from Compressible Blends

In this section, we develop the analysis and interpretation expressions necessary to determine an interaction parameter from SANS data for a compressible binary polymer blend. The starting point is the fact that the scattering intensity arises from fluctuations in the number of moles of each component (1 and 2) in a given sample volume. Such concentration fluctuations are related to composition derivatives of the chemical potential, expressed in terms of the independent variable set $\{T,V,\mu_i\}$ (grand canonical ensemble),[25] which is appropriate for treating open control volumes. Transforming this variable set to the experimentally appropriate set $\{T,P,n_i\}$ (isothermal−isobaric ensemble)[25] leads to an expression for the scattering intensity that is the sum of two contributions. One arises purely from fluctuations in system volume at fixed T and mole numbers of both components (density fluctuations), and the other from fluctuations in mole numbers of one of the components at fixed T, P, and mole number of the other component (concentration fluctuations). From this general expression for the scattering intensity of a compressible binary mixture, we show that the concentration fluctuation term is dependent upon a single thermodynamic quantity, the curvature of the Gibbs energy. This general expression is then tailored to the small isothermal compressibilities and excess volumes of mixing that typify polymer mixtures. Neglecting both quantities is shown to introduce negligible errors in the analysis of SANS data. Finally, the LF model is used to obtain an expression for the curvature of the Gibbs energy, leading to the desired LF versions of the analysis and interpretation expressions.

The scattering intensity of a binary blend is given by[7]

$$V\,I(0) = b_1{}^2 S_{11}(0) + b_2{}^2 S_{22}(0) + 2b_1 b_2 S_{12}(0) \tag{12}$$

where V is the sample volume. The partial structure factors represent the pairwise fluctuations of monomers in a given volume:[25,26]

$$S_{ij}(0) = \langle \delta n_i \delta n_j \rangle_{T,V,\mu j} = k_{\mathrm{B}} T \left(\frac{\partial \mu_i}{\partial n_j}\right)^{-1}_{T,V,\mu_j} \tag{13}$$

where μ_i is the chemical potential of monomer i[39] and n_j is the number of j monomers in the volume V. The derivatives at constant T, V, and μ_j can be transformed to those at constant T, P, and n_j, and the Gibbs–Duhem equation can be used to express all of these derivatives in terms of a single one.[7,27–31] Substitution of the resulting expressions for the $S_{ij}(0)$ into eq 12 leads to (see p 202 of ref 7)

$$I(0) = (b_1 n_1 + b_2 n_2)^2 \frac{k_{\mathrm{B}} T \kappa_{\mathrm{T}}}{V^2} + \frac{n_2{}^2 (b_1 \bar{v}_2 - b_2 \bar{v}_1)^2 k_{\mathrm{B}} T}{V^3 (\partial \mu_1 / \partial n_1)_{T,P,n_2}} \tag{14}$$

where the $\bar{v}_i$ are partial molar volumes and κ_{T} is the isothermal compressibility. The first term corresponds to scattering from density fluctuations exclusively[7,25] and will be denoted by $I^{\mathrm{d}}(0)$. The second term (the concentration fluctuations) is inversely proportional to pairwise mean square fluctuations at constant T, P, and n_i:[25]

$$\langle (\delta n_1)^2 \rangle_{T,P,n_2} = k_{\mathrm{B}} T \left(\frac{\partial \mu_1}{\partial n_1}\right)^{-1}_{T,P,n_2} \tag{15}$$

It can be shown that the derivative above is related to the curvature of the Gibbs energy:

$$\left(\frac{\partial^2 g}{\partial x^2}\right)_{T,P} = \frac{N}{x_2{}^2} \left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,P,n_2} \tag{16}$$

where $N = n_1 + n_2$ is the total number of monomers and $x_i = n_i/N$ is the mole fraction of i monomers. The notation $(\partial^2 g/\partial x^2)_{T,P}$ represents any of the second derivatives of the Gibbs energy with respect to monomer mole fractions, which are equivalent for any binary mixture, as can be shown using the Gibbs–Duhem equation:

$$\left(\frac{\partial^2 g}{\partial x^2}\right)_{T,P} \equiv \left(\frac{\partial^2 g}{\partial x_1{}^2}\right)_{T,P} = \left(\frac{\partial^2 g}{\partial x_2{}^2}\right)_{T,P} = -\left(\frac{\partial^2 g}{\partial x_1 \partial x_2}\right)_{T,P} \tag{17}$$

Substituting eq 16 into eq 14 leads with rearrangement to

$$I(0) = I^{\mathrm{d}}(0) + k_{\mathrm{B}} T \left(\frac{\partial^2 g}{\partial x^2}\right)^{-1}_{T,P} \left(\frac{N}{V}\right)^3 (\bar{v}_1 \bar{v}_2)^2 \left(\frac{b_1}{\bar{v}_1} - \frac{b_2}{\bar{v}_2}\right)^2 \tag{18}$$

Equation 18 is a general result for the scattering from a compressible binary mixture. It is analogous to eq 5, which was derived for an incompressible blend, and reduces to that expression in the incompressible limit ($V/N = v_0$, $\bar{v}_i = v_i$ and $\kappa_{\mathrm{T}} = 0$) when the reference volume is $v_0 = (v_1 v_2)^{1/2}$.[32]

For polymeric mixtures, the isothermal compressibilities are small enough that $I^{\mathrm{d}}(0)$ makes a negligible contribution to the scattering intensity. The experimentally measured scattering intensity for polymer blends, as quantified by $I(0)/k_{\mathrm{N}} v_0$ (dimensionless), is of order 10^1–10^2 for strongly interacting blends[4] and of order 10^2 or more for both isotopic mixtures[9,11] and polyolefin blends.[33] From eq 14, the corresponding scattering intensity from density fluctuations can be rearranged to yield

$$\frac{I^{\mathrm{d}}(0)}{k_{\mathrm{N}} v_0} = \left[\frac{(b_1 x_1 + b_2 x_2)^2 \rho^2}{\left(\dfrac{b_1 v_0}{v_1} - \dfrac{b_2 v_0}{v_2}\right)^2}\right] \frac{v_0 k_{\mathrm{B}} T}{m^2} \kappa_{\mathrm{T}} \tag{19}$$

where $\rho = Nm/V$ g/cm^3 and m is the molecular weight per monomer. The bracketed term is of order 1, so that $v_0 k_{\mathrm{B}} T / m^2 \kappa_{\mathrm{T}}$ gives an order-of-magnitude estimate for the scattering contribution from density fluctuations. Typical values for polyolefin blends[36] are $v_0 \approx 70$ cm^3/mol, $m \approx 55$ g/mol, and $\kappa_{\mathrm{T}} \approx 10^{-3}$ MPa^{-1}. Accordingly, at near-ambient temperatures, the contribution of this term is of order 10^{-2}, i.e., 4 orders of magnitude smaller than the measured scattering intensity. The same conclusion is reached by considering the ratio of the two terms in eq 14,

$$\frac{I^{\mathrm{d}}(0)}{I(0) - I^{\mathrm{d}}(0)} = \kappa_{\mathrm{T}} \left(\frac{\partial^2 (g/v_0)}{\partial x^2}\right) \tag{20}$$

where the order of magnitude of the derivative can be estimated using the FH equation. This analysis again shows the ratio to be of order 10^{-4}, or as stated a different way, $-\chi$ must be absurdly large, i.e., of order 10^2 in order for this ratio to approach unity. Accordingly, $I^{\mathrm{d}}(0)$ is negligible for polymer blends, and the scattering intensity can be written as

$$I(0) = k_{\mathrm{B}} T \left(\frac{\partial^2 g}{\partial x^2}\right)^{-1}_{T,P} \left(\frac{N}{V}\right)^3 (\bar{v}_1 \bar{v}_2)^2 \left(\frac{b_1}{\bar{v}_1} - \frac{b_2}{\bar{v}_2}\right)^2 \tag{21}$$

Excess volumes of mixing for polymeric systems are small enough to permit the replacement of partial molar volumes by the molar volume per monomer in the pure state:

$$\bar{v}_i \approx v_i \tag{22}$$

The negligible error introduced by this approximation can be seen from the following analysis. Excess volumes of mixing for liquids often follow the form[34]

$$\frac{v^{\mathrm{E}}}{V_0} = \Phi_1 \Phi_2 \alpha(T) \tag{23}$$

Here $V_0 = n_1 v_1 + n_2 v_2$, and the $\Phi_i = (n_i v_i)/(n_1 v_1 + n_2 v_2)$ are apparent volume fractions. The partial molar volumes that result from this form are

$$\bar{v}_i = v_i[1 + (1 - \Phi_i)^2\alpha(T)] \tag{24}$$

When these expressions are substituted for the partial molar volumes in eq 21 and the result is expanded in powers of $\alpha(T)$, the scattering intensity to first order is

$$I(0) = k_B T\left(\frac{\partial^2 g}{\partial x^2}\right)^{-1}_{T,P}\left(\frac{N}{V}\right)^3 (v_1 v_2)^2\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \times \left[1 + 2\alpha(T)\frac{\left(\frac{b_1\Phi_1^{\,2}}{v_1} - \frac{b_2\Phi_2^{\,2}}{v_2}\right)}{\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)}\right] \tag{25}$$

It is evident that the error introduced by approximating the partial molar volumes with monomer volumes is of order $\Phi_i^2\alpha(T)$, or approximately v^E/V_0. Accordingly, the assumption $\bar{v}_i \approx v_i$ leads to an uncertainty in the scattering intensity, $I(0)/k_N v_0$, of order v^E/V_0, which corresponds to an uncertainty in the inverse scattering intensity, $k_N v_0/I(0)$, of order $(v^E/V_0)/[I(0)/k_N v_0]^2$. For polyolefin blends,[36] where $v^E/V_0 < 10^{-4}$ and $I(0)/k_N v_0 \approx 10^2$, this uncertainty is of order 10^{-8}, and is negligible compared to measured χ values, which are of order 10^{-3}. For strongly interacting systems, such as the PSD/PVME blends,[35] where $v^E/V_0 \approx 10^{-3}$ and $I(0)/k_N v_0 \approx 10^1 - 10^2$, the uncertainties range from 10^{-5} to 10^{-7}, depending on the temperature and composition of the sample. Values of $-\chi$ are of order $10^{-2} - 10^{-3}$ for this system, and therefore, the approximation $\bar{v}_i \approx v_i$ will not seriously compromise results even for these systems. Thus, we can safely write

$$I(0) = k_B T\left(\frac{\partial^2 g}{\partial x^2}\right)^{-1}_{T,P}\left(\frac{N}{V}\right)^3 (v_1 v_2)^2\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \tag{26}$$

where, with negligible error, the effect of compressibility for polymer blends is now contained solely in the term $(\partial^2 g/\partial x^2)_{T,P}^{-1}$.

It is often convenient to work with the Helmholtz energy, rather than the Gibbs energy. Accordingly, $(\partial^2 g/\partial x^2)_{T,P}$ can be written in terms of second derivatives of the Helmholtz energy:[21]

$$\left(\frac{\partial^2 g}{\partial x^2}\right)_{T,P} = \frac{N^3}{V}k_T A_{12} \tag{27}$$

where

$$A_{12} \equiv \left[\left(\frac{\partial^2 A}{\partial n_1^{\,2}}\right)\left(\frac{\partial^2 A}{\partial n_2^{\,2}}\right) - \left(\frac{\partial^2 A}{\partial n_1 \partial n_2}\right)^2\right]_{T,V,n_{[i]}} \tag{28}$$

and the notation $n_{[i]}$ indicates that all the n_i not involved in the differentiation are held constant. Upon substitution into eq 26, an equivalent expression for the scattering intensity is obtained:

$$I(0) = k_B T\left(\frac{1}{A_{12}\kappa_T}\right)\left(\frac{v_1 v_2}{V}\right)^2\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \tag{29}$$

To proceed further, A_{12} and κ_T must be evaluated with a compressible model. Here we use the LF model,[22] which is similar to the FH model in that it is a lattice model with random mixing, but with the incompressibility constraint relaxed by including empty lattice sites. The LF expression for the Helmholtz energy of mixing is

$$\frac{\Delta A_m}{N_T k_B T} = \phi_1\phi_2\epsilon_{12} + \phi_1^{\,2}\frac{\epsilon_{11}}{2} + \phi_2^{\,2}\frac{\epsilon_{22}}{2} + \phi_v \ln \phi_v + \frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_2}{r_2}\ln \phi_2 \tag{30}$$

where for this model $r_i = z_i v_i^*/v_0$, v_i^* is the close-packed or hard-core volume of component i, $\phi_i = N_i r_i/N_T$, and ϕ_v is the fraction of lattice sites that are empty. Note that the quantity r_i is now defined in terms of the hard-core monomer volume rather than the actual monomer volume. This definition will be employed in all further usage of r_i. N_T is the total number of lattice sites and differs from the total number of segments, N, by the number of empty lattice sites. The volume fractions ϕ_i are related to the monomer mole fractions by

$$\phi_i = \frac{(1 - \phi_v)v_i^* x_i}{v_1^* x_1 + v_2^* x_2} \tag{31}$$

The fraction of empty sites is a function of T, P, and composition and can be determined from the LF equation of state:[22]

$$\frac{P v_0}{kT} = -\frac{\phi_1^{\,2}\epsilon_{11}}{2} - \phi_1\phi_2\epsilon_{12} - \frac{\phi_2^{\,2}\epsilon_{22}}{2} - \ln \phi_v - (1 - \phi_v) \tag{32}$$

A_{12} can be evaluated with eq 30, with the result[37]

$$A_{12} = \frac{(k_B T)^2}{N_T^{\,2}\phi_v}\Lambda \tag{33}$$

in which

$$\Lambda = \frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} - 2\chi_{FH} + \phi_v(\epsilon_{11}\epsilon_{22} - \epsilon_{12}^{\,2}) + \phi_v\left(\frac{\epsilon_{22}}{r_1\phi_1} + \frac{\epsilon_{11}}{r_2\phi_2} + \frac{1}{r_1\phi_1 r_2\phi_2}\right) \tag{34}$$

The isothermal compressibility is evaluated from eq 32, with the result

$$\kappa_T = \frac{v_0}{k_B T}\phi_v\left[\frac{1}{(1 - \phi_v)^2\Gamma}\right] \tag{35}$$

in which

$$\Gamma = 1 + \phi_v(x_1^{\,2}\epsilon_{11} + 2x_1x_2\epsilon_{12} + x_2^{\,2}\epsilon_{22}) \tag{36}$$

Substitution of eqs 33 and 35 in eq 29 leads to

$$I(0) = \frac{[(1 - \phi_v)v_1 v_2]^2}{v_0^{\,3}}\left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2\frac{\Gamma}{\Lambda} \tag{37}$$

It is now necessary to choose which terms in Λ we wish to determine from a SANS experiment. These terms will be our "χ" as determined from the LF model. One choice would be to determine χ_{FH} only; another choice would be to determine those terms which are nonzero only for interacting systems. We have chosen, in analogy with the FH analysis, to determine the sum of all terms except those that arise from the combinatorial entropy, $1/r_1\phi_1 + 1/r_2\phi_2$. In this case, the LF interaction parameter in terms of microscopic parameters (the LF interpretation expression) is given by

$$\chi_{\rm LF} = \chi_{\rm FH} - \frac{\phi_{\rm v}}{2}(\epsilon_{11}\epsilon_{22} - \epsilon_{12}{}^{2}) - \frac{\phi_{\rm v}}{2}\left(\frac{\epsilon_{22}}{r_1\phi_1} + \frac{\epsilon_{11}}{r_2\phi_2} + \frac{1}{r_1\phi_1 r_2\phi_2}\right) \quad (38)$$

and

$$\Lambda = \frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} - 2\chi_{\rm LF} \quad (39)$$

The pure component monomer volumes which appear in eq 37 are represented in the LF model by

$$v_i = \frac{v_i^*}{1 - \phi_{i\rm v}} \quad (40)$$

Substituting eqs 39 and 40 in eq 37, simplifying, and for convenience assigning the reference volume as

$$v_0 = (v_1^* v_2^*)^{1/2} \quad (41)$$

we arrive finally at

$$\frac{\chi_{\rm LF}}{v_0} = \frac{1}{2}\left[\frac{1}{v_1^* z_1\phi_1} + \frac{1}{v_2^* z_2\phi_2} - \left(\frac{1 - \phi_{\rm v}}{(1 - \phi_{1\rm v})(1 - \phi_{2\rm v})}\right)^2 \frac{\Gamma k_{\rm N}}{I(0)}\right] \quad (42)$$

where

$$k_{\rm N} = \left(\frac{b_1(1 - \phi_{1\rm v})}{v_1^*} - \frac{b_2(1 - \phi_{2\rm v})}{v_2^*}\right)^2 = \left(\frac{b_1}{v_1} - \frac{b_2}{v_2}\right)^2 \quad (43)$$

The set of eqs 42 and 38 are the analysis and interpretation expressions for the SANS-determined LF interaction parameter, $\chi_{\rm LF}$. Equation 42 is the LF analog to eq 7, and eq 38 is the LF analog to eq 8. It is apparent from the LF interpretation expression that $\chi_{\rm LF}$ will be a function of both composition and molecular weight.

For weakly interacting systems, the LF analysis expression can be simplified further because the following are excellent approximations:

1. The properties of the pure components are similar: $\epsilon_{11} \approx \epsilon_{22}$, $v_1 \approx v_2$, so that $\phi_i = (1 - \phi_v)x_i$, and $\phi_{1\rm v} \approx \phi_{2\rm v} \approx \phi_{\rm v}$.

2. The Berthelot conjecture describes the cross energy term[34]

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2} \quad (44)$$

The first simplification leads to a familiar form for the relationship between the interaction parameter and the scattering intensity. The approximation $\phi_{1\rm v} \approx \phi_{2\rm v} \approx \phi_{\rm v}$ results in

$$\frac{\chi_{\rm LF}}{v_0} = \frac{1}{2}\left[\frac{1}{v_1^* z_1\phi_1} + \frac{1}{v_2^* z_2\phi_2} - \frac{\Gamma k_{\rm N}^*}{I(0)}\right] \quad (45)$$

where

$$k_{\rm N}^* = \left(\frac{b_1}{v_1^*} - \frac{b_2}{v_2^*}\right)^2 \quad (46)$$

and the approximation $\phi_i = (1 - \phi_v)x_i$ allows eq 45 to be written in terms of the observable properties v_i, x_i, and $k_{\rm N}$:

$$\frac{\chi_{\rm LF}}{v_0} = \frac{1}{2(1 - \phi_v)^2}\left[\frac{1}{v_1 z_1 x_1} + \frac{1}{v_2 z_2 x_2} - \frac{\Gamma k_{\rm N}}{I(0)}\right] \quad (47)$$

Equation 47 is the LF analysis expression for weakly interacting systems. This equation, together with eq 38, forms the set of LF analysis and interpretation expressions, specialized to weakly interacting systems. Notice that $\Gamma \rightarrow 1$ when $\phi_{\rm v} \rightarrow 0$, so that eq 7 as well as eq 8 is recovered in the incompressible limit.

The second simplification (eq 44) affects the quantity Γ, which becomes $1 + \phi_{\rm v}(x_1\epsilon_{11}{}^{1/2} + x_2\epsilon_{22}{}^{1/2})^2$, and thus a function of pure component properties only. In blends where $\epsilon_{11} \approx \epsilon_{22} \equiv \epsilon$ as well, $\Gamma \approx 1 + \phi_{\rm v}\epsilon$. These simplifications have important practical significance in the use of eq 47 to analyze SANS data for weakly interacting systems. The only quantities in eq 47 that are not directly observable are $\phi_{\rm v}$ and Γ. For weakly interacting systems, both $\phi_{\rm v}$ and Γ are essentially independent of blend composition and their values can be determined by *PVT* measurements on the pure components.

3. Application to Weakly Interacting Blends

In this section, we apply the LF analysis and interpretation expressions developed in section 2 to three polyolefin blends,[12] H78/D66, H66/D52, and H97/D88, and to PS/PSD mixtures.[11] We use the LF analysis expression for weakly interacting systems (eq 47) to determine $\chi_{\rm LF}$ from $I(0)$ and compare the result with the LF interpretation expression (eq 38).

Omitting the term of order $1/r^2$ in eq 38, the LF interpretation expression consists of three contributions:

$$\chi_{\rm LF} = \chi_{\rm FH} + \frac{\phi_{\rm v}}{2}\epsilon_{11}\epsilon_{22}(\lambda^2 - 1) - \frac{\phi_{\rm v}}{2}\left(\frac{\epsilon_{22}}{r_1\phi_1} + \frac{\epsilon_{11}}{r_2\phi_2}\right) \quad (48)$$

in which we have used $\lambda = \epsilon_{12}/(\epsilon_{11}\epsilon_{22})^{1/2}$. The only term that is dependent on composition for weakly interacting blends is the last term on the right-hand side. Accordingly, we expect that the LF interaction parameter for weakly interacting blends will be an approximately parabolic function of composition:

$$\chi_{\rm LF}^{\rm w} \approx A_{\rm w}(T) - \frac{\phi_{\rm v}}{2}\left(\frac{\epsilon_{22}}{r_1\phi_1} + \frac{\epsilon_{11}}{r_2\phi_2}\right) \quad (49)$$

where $A_{\rm w}(T)$ is independent of composition. Moreover, all the energy terms, being attractive, are negative in sign, so that the curvature predicted is universally upward. The magnitude of the curvature is dependent upon the chain lengths of both components and decreases as the chain lengths increase, eventually becoming zero in the infinite chain limit. The effect of this chain length dependence for a given system, since it is proportional to $1/r_i$, will be small unless the r_i for the system vary greatly.

Illustrated in Figure 1 as functions of composition are both the prediction for $\chi_{\rm LF}$ from the LF interpretation expression (eq 38) and the $\chi_{\rm LF}$ assigned from experimental scattering data, $I(0)$, using the LF analysis expression (eq 47) for the H78/D66 blend. For reference, the result of analyzing the scattering data with the FH analysis expression (eq 7) is also shown. The param-

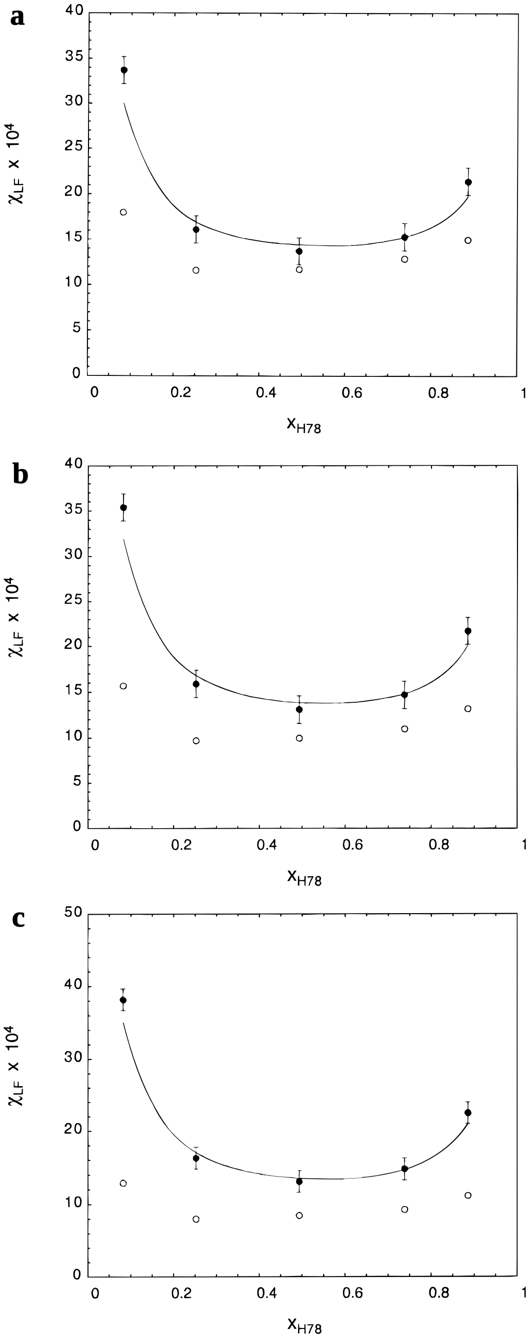

Figure 1. LF interaction parameter for H78/D66: (a) 83 °C; (b) 121 °C; (c) 167 °C. Solid symbols: data analyzed with LF analysis expression (eq 47). Open symbols: data analyzed with FH analysis expression (eq 7). Curve: prediction of LF interpretation expression (eq 38).

Table 1. System Parameters for Blend Components

blend	temp (°C)	z_1	z_2	ϵ_{11}	ϵ_{22}	$(1 - \lambda) \times 10^4$
PS(2)/PSD(1)	160	11500	8700	−3.4210	−3.4319	0.58
H78(2)/D66(1)	27	2030	1285	−3.9267	−3.9467	4.30
H78(2)/D66(1)	51	2030	1285	−3.6358	−3.6543	4.30
H78(2)/D66(1)	83	2030	1285	−3.3090	−3.3258	4.30
H78(2)/D66(1)	121	2030	1285	−2.9898	−3.0051	4.30
H78(2)/D66(1)	167	2030	1285	−2.6773	−2.6910	4.30
H97(2)/D88(1)	51	1610	1600	−3.6543	−3.6667	3.50
H97(2)/D88(1)	83	1610	1600	−3.3258	−3.3371	3.50
H97(2)/D88(1)	121	1610	1600	−3.0051	−3.0152	3.50
H97(2)/D88(1)	167	1610	1600	−2.6910	−2.7000	3.50
H66(2)/D52(1)	83	1510	2030	−3.3202	−3.3146	4.30
H66(2)/D52(1)	167	1510	2030	−2.6864	−2.6818	4.30

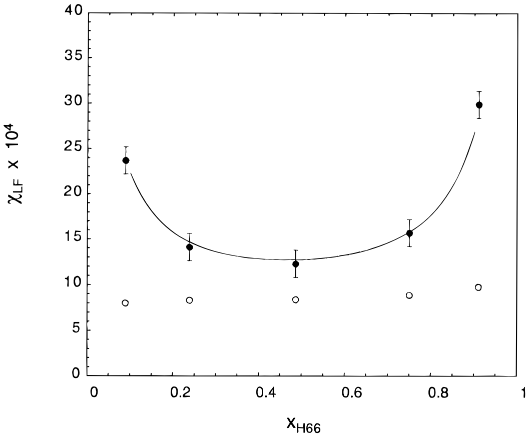

Figure 2. LF interaction parameter for H66/D52 at 167 °C. Solid symbols: data analyzed with LF analysis expression (eq 47). Open symbols: data analyzed with FH analysis expression (eq 7). Curve: prediction of LF interpretation expression (eq 38).

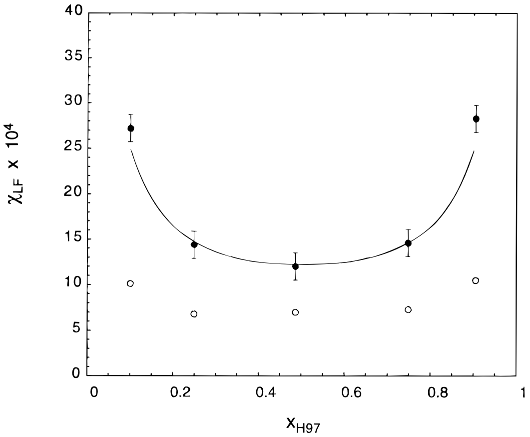

Figure 3. LF interaction parameter for H97/D88 at 167 °C. Solid symbols: data analyzed with LF analysis expression (eq 47). Open symbols: data analyzed with FH analysis expression (eq 7). Curve: prediction of LF interpretation expression (eq 38).

eters ϵ_{11} and ϵ_{22} were assigned by fitting *PVT* data on the pure components to the LF equation of state. The procedure is described in the Appendix, and the parameters at each temperature are given in Table 1. Note that ϵ_{11} and ϵ_{22}, as defined earlier, are inversely proportional to temperature, so $\epsilon_{11}T$ and $\epsilon_{22}T$ are the temperature-independent quantities. The only adjustable parameter which has been used to fit the data is λ. Note that a single temperature- and composition-independent value for this parameter describes the composition dependence of χ_{LF} at all five temperatures. The results for three temperatures are plotted in Figure 1, and the agreement between the prediction of the LF interpretation expression and the data analyzed with the LF analysis expression is uniformly good. The results from application of the same procedure to the H66/D52 and H97/D88 blends are shown in Figures 2 and 3. Although plotted here only at one temperature, χ_{LF} at all temperatures is again well described by the choice of a single fitting parameter λ that is independent of both temperature and composition.

Figure 4 shows the composition dependence of χ_{LF} obtained for the PS/PSD blend. Notice here that application of the LF analysis expression (eq 47) results in upward curvature, rather than the downward cur-

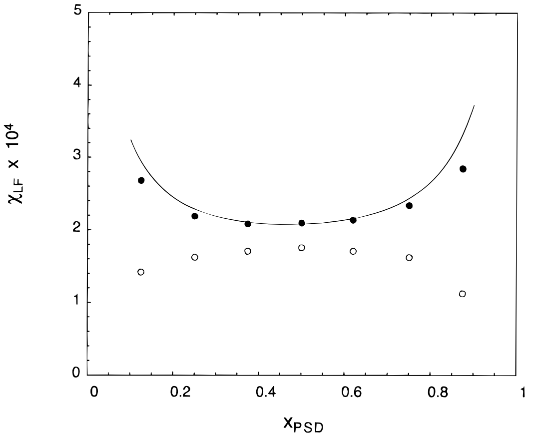

Figure 4. LF interaction parameter for PS/PSD at 160 °C. Solid symbols: data analyzed with LF analysis expression (eq 47). Open symbols: data analyzed with FH analysis expression (eq 7). Curve: prediction of LF interpretation expression (eq 38).

Table 2. Lattice Fluid Parameters for Blend Components

sample	P^* (MPa)	T^* (K)	$v_{sp}^* = 1/\rho^*$ (cm^3/g)	s^2 (mPa^2)
PS	429	743	0.9102	3
H97	358	594	1.0735	9
H88	365	593	1.0755	9
H78	376	592	1.0768	
H66	388	590	1.0744	8
H52	385	592	1.0797	8

Table 3. Composition Dependence of Γ for Weakly Interacting Blends

x_{H78}	H78/D66 83 °C	H78/D66 121 °C	H78/D66 167 °C	H97/D88 167 °C	H66/D52 167 °C	PS/DPS 160 °C
0.1	0.6321	0.5816	0.5246	0.5272	0.5260	0.6495
0.2	0.6323	0.5818	0.5249	0.5274	0.5259	0.6493
0.3	0.6326	0.5820	0.5251	0.5275	0.5258	0.6492
0.4	0.6328	0.5823	0.5254	0.5277	0.5257	0.6490
0.5	0.6330	0.5825	0.5256	0.5279	0.5256	0.6489
0.6	0.6333	0.5828	0.5259	0.5281	0.5255	0.6487
0.7	0.6336	0.5831	0.5262	0.5283	0.5255	0.6486
0.8	0.6338	0.5836	0.5265	0.5284	0.5254	0.6484
0.9	0.6341	0.5836	0.5268	0.5286	0.5253	0.6483

vature obtained using the FH analysis expression (eq 7), so that there is qualitative similarity between the composition dependence of χ_{LF} among all weakly interacting systems. However, the important point is not the *type* of curvature obtained with the LF analysis expression, but rather its consistency with the LF interpretation expression. The LF model and the terms we have chosen to include in the definition of χ_{LF} (eq 38) dictate universal upward curvature for weakly interacting blends, and the values generated from $I(0)$ data with the corresponding analysis expression (eq 47) are consistent with that requirement. Other definitions for χ_{LF} would simply dictate other features for self-consistency. What is notable, regardless of the interaction parameter definition, is that a good fit of SANS data is achieved with only pure component quantities and a single, pair-specific and composition-independent parameter λ.

The composition dependencies of the auxiliary functions Γ and ϕ_v are given in Tables 3 and 4. The value of ϕ_v at each composition was determined by solving eq 32. The value of Γ at each composition was calculated from eq 36. As anticipated in section 2 for weakly interacting systems, both Γ and ϕ_v are essentially independent of composition.

Table 4. Composition Dependence of ϕ_v for Weakly Interacting Blends

x_{H78}	H78/D66 83 °C	H78/D66 121 °C	H78/D66 167 °C	H97/D88 167 °C	H66/D52 167 °C	PS/PSD 160 °C
0.1	0.1111	0.1399	0.1775	0.1756	0.1765	0.1021
0.2	0.1110	0.1398	0.1773	0.1755	0.1766	0.1022
0.3	0.1109	0.1396	0.1771	0.1754	0.1766	0.1023
0.4	0.1108	0.1395	0.1770	0.1753	0.1767	0.1024
0.5	0.1106	0.1393	0.1768	0.1752	0.1768	0.1025
0.6	0.1105	0.1391	0.1766	0.1751	0.1768	0.1025
0.7	0.1103	0.1390	0.1764	0.1749	0.1769	0.1026
0.8	0.1102	0.1388	0.1762	0.1748	0.1769	0.1027
0.9	0.1101	0.1386	0.1760	0.1746	0.1770	0.1028

We have also applied the LF analysis and interpretation expressions to the strongly interacting blend PSD/PVME. The LF analysis expression does not alter the composition dependence of χ_{LF} relative to that obtained from the FH analysis expression; the effect is simply to rescale χ. The fits that we obtain from the LF interpretation expression do not improve upon those reported for PSD/PVME in ref 19. In order to obtain a reasonable fit to the data at all temperatures, the adjustable parameter, $\epsilon_{12}T$ or λ, must be allowed to vary with temperature, although it is still composition-independent. The fits to all of the weakly interacting blends, achieved with a single pair-specific parameter for all temperatures, are superior to those obtained for the strongly interacting PSD/PVME blend. Perhaps this is because weakly interacting systems conform more closely to the random mixing assumption of the model.

It is evident from these examples that describing compressible systems by a single, composition-independent energetic parameter is not possible. However, they can be described by the three composition-independent parameters, $\epsilon_{11}T$, $\epsilon_{22}T$, and λ. For weakly interacting systems, all three parameters are also temperature-independent. Both $\epsilon_{11}T$ and $\epsilon_{22}T$ can be determined by *PVT* measurements on the pure components, and the remaining mixture parameter, λ, by fitting SANS data. This has already been suggested by Bidkar and Sanchez.[21] We prefer to use $1 - \lambda$ for the mixture parameter because the value of λ is so near unity for polymer blends. For weakly interacting systems, $1 - \lambda$ appears to be a positive, blend-specific constant, independent of temperature and composition, as illustrated in Table 1. For strongly interacting systems, we have found $1 - \lambda$ to be negative and independent of composition, but mildly dependent on temperature. Pure component *PVT* data and the determination of $1 - \lambda$ from SANS experiments thus provides a complete description of the thermodynamics for polymer blends that obey the LF model, just as χ_{FH} alone provides a complete description for blends that obey the FH model.

4. Concluding Remarks

This paper describes a general procedure for the analysis and interpretation of small-angle neutron scattering data from compressible polymer blends. The relationship between the thermodynamic properties of the blend and the experimental observable, the coherent scattering intensity at zero wavevector, is derived through statistical-mechanical fluctuation theory. Being model-independent, this relationship is applicable to any binary mixture, compressible or incompressible.

Specializing to polymeric liquids, we make two simplifying assumptions and show that they introduce only negligible errors. First, the scattering from density fluctuations alone is neglected. The resulting expression for the coherent SANS intensity is inversely proportional to a single thermodynamic quantity, the curvature of the Gibbs energy. It is thus possible to separate the desired thermodynamic information from the contrast necessary to make the experimental measurements. Second, excess volumes of mixing are neglected. We show that although the compressible nature of the blend must be accounted for implicitly through the Gibbs energy curvature, excess volumes of mixing *per se* do not significantly affect the analysis of SANS data.

We then use the lattice fluid (LF) model to derive an explicit relationship between the SANS intensity and the characteristic parameters of a compressible blend. This result is in turn used to define an interaction parameter χ_{LF}, obtainable from SANS data and a function of the three characteristic blend parameters. Two can be determined by fits to pure component *PVT* data; the third is pair-specific and obtainable by fits of the SANS data. We apply these results to the scattering data for weakly interacting systems, polyolefin blends and isotopic mixtures, and find that they accurately and self-consistently describe the observed temperature and composition dependence of χ_{LF}. More importantly, however, the description of the interactions from SANS data is consistent with the LF model itself, and for each system we have investigated, all three microscopic energetic parameters are, within the errors, independent of both temperature and composition.

Since the effect of compressibility in weakly interacting polymer blends appears to be rather significant, it seems likely that interpretations with other compressible models will be undertaken. It also seems likely that, for practical reasons, the initial analysis of SANS data will continue to employ the incompressible Flory–Huggins model. For these reasons, we suggest that SANS studies include tabulations of $I(0)$ in order to provide a model-free starting point for the analysis of compressibility effects.

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Appendix: Determination of LF Parameters

For the work presented here, we require the LF parameters for four blend systems, PS/PSD, H78/D66, H97/D88, and H66/D52. The LF parameters, P^*, T^*, and $v^* = 1/\rho^*$, are determined from *PVT* data for the pure components obtained from Dr. D. Walsh and Dr. G. T. Dee at DuPont. These data are fit to the LF equation of state:[38]

$$\left(\frac{\rho}{\rho^*}\right)^2 + \frac{P}{P^*} + \frac{T}{T^*}\left[\ln\left(1 - \frac{\rho}{\rho^*}\right) + \frac{\rho}{\rho^*}\right] = 0 \qquad (50)$$

using a nonlinear least squares formulation,

$$\min s^2 = \frac{\sum_{i=1}^{N}[P_{i,\mathrm{data}} - P_{i,\mathrm{fit}}]^2}{N - 3} \qquad (51)$$

where N is the number of data points. To minimize the error in the fit, we selected blocks of data; $T = 120-220$ °C and $P = 10-50$ MPa for PS, and $T = 50-150$ °C and $P = 10-100$ MPa for the polyolefins. The parameters found by this procedure are given in Table 2.

The value used in fitting the SANS data, ϵ_{ii}, is related to T^* by $\epsilon_{ii} = -2T_i^*/T$.[38] For the polyolefin blends, in the EB copolymer series, data are available on the effect of deuteration for H08. We have estimated the parameters for D*xx* by

$$\Pi(\mathrm{D}xx) = \Pi(\mathrm{H}xx)\frac{\Pi(\mathrm{D08})}{\Pi(\mathrm{H08})} \qquad (52)$$

where Π represents the parameter of interest. *PVT* data on H78 was not available so its parameters were estimated based on interpolation between the H88 and H66 parameters. The value of each cross energy term, ϵ_{ij}, is assigned such that the calculated value for χ_{LF} matches the SANS data at the data point nearest $x = 0.5$. *PVT* data on deuterated PS were not available. Here we adopt the ratio, $\Pi(\mathrm{PS})/\Pi(\mathrm{PSD})$, used in ref 20. The value of the cross energy term is again treated as an adjustable parameter.

List of Symbols

N	number of chain segments in system
N_i	number of chains of type i
z_i	degree of polymerization of component i
n_i	number of monomers of type i in system; z_iN_i
v_i	volume per monomer of component i
v_0	arbitrary reference volume
V	total system volume
r_i	number of lattice sites occupied by an i chain
Φ_i	observable or incompressible volume fraction of component i; $n_iv_i/\sum n_iv_i = z_iv_iN_i/\sum z_iv_iN_i = r_iv_0N_i/\sum r_iv_0N_i = r_iN_i/N$
k_{B}	Boltzmann's constant
E_{ij}	attractive interaction between components i and j
T	system temperature
ϵ_{ij}	dimensionless energetic interaction between segments i and j; $zE_{ij}/k_{\mathrm{B}}T$
χ_{FH}	interaction parameter defined by Flory–Huggins theory; $\epsilon_{12} - {}^1/_2(\epsilon_{11} + \epsilon_{22})$
ΔG_{m}	Gibbs energy of mixing
g	intensive Gibbs energy of mixing; $\Delta G_{\mathrm{m}}/N$
$I(0)$	scattering intensity per unit sample volume and subtended scattering angle, cm^{-1}
b_i	coherent scattering length of a monomer of type i
q	scattering vector; $4\pi/\lambda_n \sin(\theta/2)$
λ_n	wavelength of incident radiation
θ	angle of the scattering event
$S(0)$	structure factor, dimensionless
k_{N}	scattering contrast factor, cm^{-4}; $(b_1/v_1 - b_2/v_2)^2$
χ	interaction parameter derived from SANS data via the Flory–Huggins free energy expression
χ^{s}	value of χ at the spinodal line
$A_{\mathrm{s}}(T)$, $B_{\mathrm{s}}(T)$	Coefficients describing the composition dependence of χ for strongly interacting systems

$A_w(T)$, $B_w(T)$	coefficients describing the composition dependence of χ for weakly interacting systems
$S_{ij}(0)$	partial structure factors; see eq 13 for definition
δn_i	Variation of n_i away from its equilibrium value
μ_i	chemical potential of a monomer of type i
κ_T	isothermal compressibility
$\bar{v}_i$	partial molar volume of an i monomer
$I^d(0)$	scattering intensity from density fluctuations
x_i	mole fraction of i monomers; n_i/N
ρ	system density
m	molecular weight per monomer
v^E	excess volume of mixing
V_0	system volume for $v^E = 0$
$\alpha(T)$	temperature-dependent coefficient for v^E
A_{12}	energetic term comprised of composition derivatives of the Helmholtz energy; see eq 28 for definition
ΔA_m	extensive Helmholtz energy of mixing
N_T	total number of lattice sites
ϕ_i	compressible volume fraction of component i; r_iN_i/N_T
ϕ_v	fraction of empty lattice sites or void fraction
v_i^*	close-packed or hard-core monomer of component i
P	system pressure
Λ, Γ	energetic parameters; see eqs 34 and 36 for definitions
χ_{LF}	interaction parameter determined from SANS data via compressible analysis using the LF model
ϕ_{iv}	void fraction in pure component i
k_N^*	contrast factor defined in terms of hard-core volumes; see eq 46
λ	Berthelot scaling coefficient; $\epsilon_{12}/(\epsilon_{11}\epsilon_{22})^{1/2}$
ρ^*, T^*, P^*	fitting parameters in the LF equation of state

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