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Compressibility Effects in Neutron Scattering by Polymer Blends

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ABSTRACT: In this paper, we consider the effects of finite compressibility on the thermodynamics of polymer blends as deduced by neutron scattering. We show that, within the framework of the lattice fluid model and contrary to past conclusions by us and others, the compressibility effects are insignificant for weakly interacting blends. An explanation for the commonly observed parabolic concentration dependence of the Flory−Huggins parameter in isotopic and model polyolefin blends must therefore be sought elsewhere. A compressible interpretation is advantageous for strongly interacting blends, such as polystyrene/poly(vinyl methyl ether), because it reduces significantly the composition dependence of the interaction parameter. We note however, that, even in this case, compressibility need not be introduced into the analysis of the scattering data. The entire analysis can be conducted in terms of the Flory−Huggins model, and the results can then be reexpressed in terms of a compressible model, if that is desired.

Introduction

Small-angle neutron scattering (SANS) is a widely used method for determining the thermodynamic interactions that govern liquid-state phase behavior in polymer blends.[1] Briefly, the coherent SANS intensity profile $I(q)$ is extrapolated to forward scattering ($q = 0$). The resulting $I(0)$ is divided by the SANS contrast factor k_N to obtain the static structure factor, $S(0) = I(0)/k_N$, and finally, a parameter quantifying the interaction strength, expressed through some specific mixing model, is evaluated. The Flory−Huggins model is traditionally used, and its form and incompressible character in fact permeate the entire SANS analysis. Thus, together with the random-phase approximation, they assist the $I(q)$ extrapolation, while incompressibility provides an explicit definition for k_N and the Flory−Huggins parameter χ_{FH} quantifies the interaction strength. In the context of the model itself, χ_{FH} depends on the temperature and the polymeric species, but it is independent of the component chain lengths and volume fractions. For most blends, however, the values of χ_{FH} extracted from the SANS data are found to depend on the component volume fractions.

Among the various proposed explanations for a composition dependence in χ_{FH}, it was suggested that the assumption of incompressibility in formulating the SANS analysis might be responsible.[2,3] We recently undertook to investigate that possibility[4] with a compressible mixing model, the lattice fluid,[5] in place of the Flory−Huggins model. Others have shown that the extrapolation to obtain $I(0)$ is rather insensitive to compressibility effects (see refs 3, 6, and, most recently, 7). We have therefore focused upon the interpretation of $I(0)$. We showed that inclusion of compressibility can provide consistency between model and observations. In this paper, we extend our previous work and show that finite compressibility, at least in the lattice-fluid approximation, cannot account for the parabolic dependence of χ_{FH} on the volume fraction Φ that is observed in weakly interacting binary blends such as isotopic and polyolefin mixtures. On the other hand, we show that compressibility can account for the linear dependence of χ_{FH} on Φ in strongly interacting blends such as polystyrene/poly(vinyl methyl ether). Finally, we assert that compressibility need not be introduced into the SANS data analysis itself, that the effect of compressibility on blend thermodynamics can be introduced afterward, if desired, without significant loss of information.

Evaluation of Interactions

In our previous paper,[4] we compared the evaluation of the component interactions from the SANS forward scattering intensity of binary polymer blends by means of two models, incompressible Flory−Huggins and compressible lattice fluid. The Flory−Huggins analysis leads to the working equation

$$\frac{k_N}{I(0)} = \frac{1}{z_1\Phi_1 v_1} + \frac{1}{z_2\Phi_2 v_2} - 2\frac{\chi_{FH}}{v_0} \tag{1}$$

in which k_N is the SANS contrast factor, $I(0)$ is $(d\Sigma/d\Omega)_0$, the differential scattering cross section at zero scattering vector, z_i, Φ_i, and v_i are the monomeric units per chain, volume fraction, and volume per monomeric unit for the components, v_0 is an arbitrary reference volume, which we take as $(v_1v_2)^{1/2}$, and χ_{FH} is the Flory−Huggins interaction parameter with respect to that volume. In the Flory−Huggins model, the interaction parameter is a dimensionless exchange energy:

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

in which the $\epsilon_{ij} = E_{ij}c/kT$ are dimensionless monomer−

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monomer interaction energies, all inherently negative (attractive), and c is the number of monomeric nearest neighbors.

In our previous paper, we showed that the contribution of density fluctuations to $I(0)$ is negligible and also that the effect of compressibility on the contrast factor is negligible. We then developed the lattice-fluid analogue of eq 1, the result being

$$\frac{k_\mathrm{N}}{I(0)} = \frac{(1-\phi_{1\mathrm{v}})(1-\phi_{2\mathrm{v}})}{(1-\phi_\mathrm{v})^2}\frac{\Lambda}{\Gamma} \tag{3}$$

with

$$\Gamma \equiv 1 + \phi_\mathrm{v}(\mathrm{x}_1{}^2\epsilon_{11} + 2x_1x_2\epsilon_{12} + x_2{}^2\epsilon_{22}) \tag{4}$$

and

$$\Lambda = \phi_\mathrm{v}\frac{\epsilon_{11}\epsilon_{22} - \epsilon_{12}{}^2}{v_0} + \left[\frac{1+\phi_\mathrm{v}\epsilon_{22}}{z_1v_1\phi_1(1-\phi_{1\mathrm{v}})} + \frac{1+\phi_\mathrm{v}\epsilon_{11}}{z_2v_2\phi_2(1-\phi_{2\mathrm{v}})}\right] - \frac{2\chi_\mathrm{FH}}{v_0} \tag{5}$$

in which ϕ_v, $\phi_{1\mathrm{v}}$, and $\phi_{2\mathrm{v}}$ are void fractions in the blends and pure components, while v_i^*, x_i, and ϕ_i are the hard-core monomeric volume, mole fraction, and hard-core volume fraction, $(1-\phi_\mathrm{v})x_iv_i^*/(x_1v_1^* + x_2v_2^*)$, of species i. Finally, a lattice-fluid interaction parameter was defined

$$\chi_\mathrm{LF} \equiv \chi_\mathrm{FH} - \frac{\phi_\mathrm{v}}{2}(\epsilon_{11}\epsilon_{22} - \epsilon_{12}{}^2) - \frac{v_0\phi_\mathrm{v}}{2}\left(\frac{\epsilon_{11}}{z_2v_2^*\phi_2} + \frac{\epsilon_{22}}{z_1v_1^*\phi_1}\right) \tag{6}$$

These expressions differ slightly from those given in our earlier paper. A negligibly small contribution of order $1/z_1z_2$ has been omitted from the bracketed terms in eq 5, and various simplifications based on nearly identical energies and void fractions[4] have not been used here. The pure-component energies, ϵ_{11} and ϵ_{22}, the void fractions, $\phi_{1\mathrm{v}}$ and $\phi_{2\mathrm{v}}$, and the hard-core monomeric volumes, v_1^* and v_2^*, were obtained by fitting pure-component *PVT* data to the lattice-fluid equation of state, as described in the appendix of ref 4. The composition dependence of ϕ_v depends on pure-component properties through the lattice-fluid expression for mixtures:

$$\frac{Pv_0}{kT} = \frac{\phi_1{}^2\epsilon_{11}}{2} + \phi_1\phi_2\epsilon_{12} + \frac{\phi_2{}^2\epsilon_{22}}{2} - \ln\phi_\mathrm{v} - (1-\phi_\mathrm{v}) \tag{7}$$

Equations 1 and 3−6 were used in ref 4 to obtain both χ_FH and χ_LF from $k_\mathrm{N}/I(0)$ for four weakly interacting blends, one isotopic pair[8] and three model polyolefin pairs[9], and one strongly interacting blend, polystyrene and poly(vinyl methyl ether).[11] The question investigated was simply the consistency between mixing model choice and the compositional dependence of the interaction parameter that it produced when applied to SANS data. The results obtained with Flory−Huggins (eq 1), values of χ_FH that vary with component concentration, are not consistent with the composition independence implicit in that model. Although χ_LF also varies with component concentration, the variation obtained by employing eqs 3−6 is not inconsistent with the lattice-fluid model, for which χ_LF is composition dependent (see eq 6).

Table 1. Lattice-Fluid Parameters for the Pure Components

polymer	P^*, MPa	T^*, K	v^*_sp, cm^3/g
PS[a]	429	743	0.910
H97[b]	358	594	1.074
H88[b]	365	593	1.076
H78[b]	376	592	1.077
H66[b]	388	590	1.074
H52[b]	385	592	1.080
PVME[c]	353	616	0.903

[a] Polystyrene. [b] Model ethylene−butene statistical copolymers, the number indicating weight % 1-butene units. [c] Poly(vinyl methyl ether).

Shortly after ref 4 appeared, we realized that, although formally correct, its conclusions are somewhat misleading. Thus, the definition of χ_LF used in ref 4 contains an intrinsic composition dependence, so the central question—whether finite compressibility can explain the observed composition dependence of χ_LF—was obscured. Here we address that question more directly. We examine whether interpreting $I(0)$ with a compressible model leads to a parameterization of the interaction that is less sensitive to component concentration than χ_FH. We use the lattice-fluid model, but the parameter χ_LF in ref 4 is not used. Instead we use an expression relating $k_\mathrm{N}/I(0)$ directly to the cross-energy ϵ_{12}, which in the context of the lattice-fluid model should be independent of the component concentration. Thus, with all other quantities in eqs 3−5 and 7 being obtainable by independent measurements, each value of $k_\mathrm{N}/I(0)$ corresponds to a unique value of ϵ_{12}.

The energies ϵ_{11}, ϵ_{22}, and ϵ_{12} are nearly identical in magnitude, and their differences appear frequently, so it is convenient to make the substitution

$$\epsilon_{12} = -(1-\kappa)(\epsilon_{11}\epsilon_{22})^{1/2} \tag{8}$$

where κ may be interpreted as a measure of departure from the Berthelot conjecture in solubility parameter theory.[11] The result of combining eqs 3−5 with eq 8 is

$$\frac{k_\mathrm{N}}{I(0)} = \left[\frac{(1-\phi_{1\mathrm{v}})(1-\phi_{2\mathrm{v}})}{v_0(1-\phi_\mathrm{v})^2}\right] \times \frac{v_0\left[\frac{1+\phi_\mathrm{v}\epsilon_{22}}{z_1v_1\phi_1(1-\phi_{1\mathrm{v}})} + \frac{1+\phi_\mathrm{v}\epsilon_{11}}{z_2v_2\phi_2(1-\phi_{2\mathrm{v}})}\right] + \Omega}{1 - \phi_\mathrm{v}[[x_1(-\epsilon_{11})^{1/2} + x_2(-\epsilon_{22})^{1/2}]^2 - 2\kappa x_1x_2(\epsilon_{11}\epsilon_{22})^{1/2}]} \tag{9}$$

in which

$$\Omega = -[(-\epsilon_{11})^{1/2} - (-\epsilon_{22})^{1/2}]^2 - 2(\epsilon_{11}\epsilon_{22})^{1/2}\kappa + \phi_\mathrm{v}\epsilon_{11}\epsilon_{22}\kappa(2-\kappa) \tag{10}$$

Thus, ϵ_{12} is replaced by the small number κ as the fitted LF parameter. Both χ_FH and κ are dimensionless descriptions of energy differences in their respective single-parameter models; both are small and have rather similar magnitudes. The values of the lattice-fluid parameters from pure-component *PVT* data are listed in Table 1. Table 2 lists the derived blend parameters.

Table 2. Lattice Fluid Parameters for the Blends

blend[a]	temp, °C	z_1	z_2	$-\epsilon_{11}{}^b$	$-\epsilon_{22}{}^b$
HPS/DPS	160	8 700	11 500	3.432	3.421
H78/D66	27	1 285	2 030	3.947	3.927
	51			3.654	3.636
	83			3.326	3.309
	121			3.005	2.990
	167			2.691	2.677
H97/D88	27	1 600	1 610	4.041	4.027
	51			3.668	3.654
	83			3.337	3.326
	121			3.015	3.005
	167			2.700	2.691
H66/D52	83	2 030	1 510	3.315	3.320
	167			2.682	2.686
HPVME/DPS	100	19 000	5 300	3.303	3.984
	120			3.135	3.781
	130			3.057	3.687
	138			2.998	3.616

[a] Components 1 and 2 listed first and second, respectively. [b] Adjustment for isotopic effects are described in ref 4.

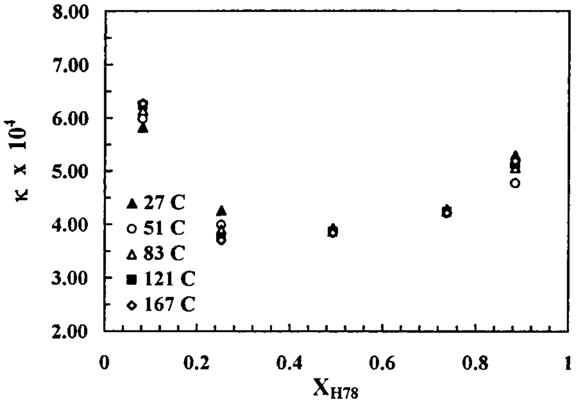

Figure 1. Variation of κ with composition for H78/D66. The symbols representing system temperatures are shown in within the figure.

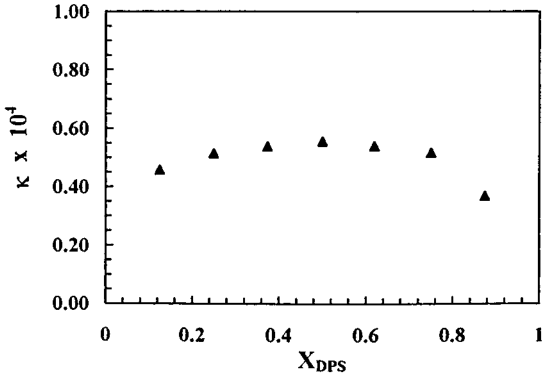

Figure 2. Variation of κ composition for PS/DPS at 160 °C.

The results of applying eq 9 to $k_N/I(0)$ data at each blend composition and temperature for the weakly interacting model polyolefin blend H78/D66 are shown in Figure 1 as κ vs x_{H78} at five temperatures. The results at 160 °C for the weakly interacting isotopic polystyrene blend HPS/DPS are shown in Figure 2. In both cases, the variation of κ with component concentration is virtually identical to the corresponding variation of χ_{FH}. Thus, although χ_{FH} and κ are numerically different and also change differently with temperature, the ratio χ_{FH}/κ for each component pair at each temperature varies by less than ±3% across the entire range of compositions. The same behavior is found for the other weakly interacting blends, H97/D88 and H66/D52.

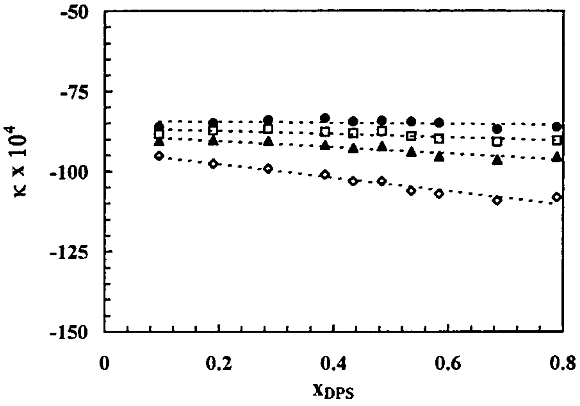

Figure 3. Variation of κ with composition for DPS/PVME. Closed circles: $T = 183$ °C. Closed triangles: $T = 120$ °C. Open diamonds: $T = 100$ °C. The dashed lines are best linear fits to the data.

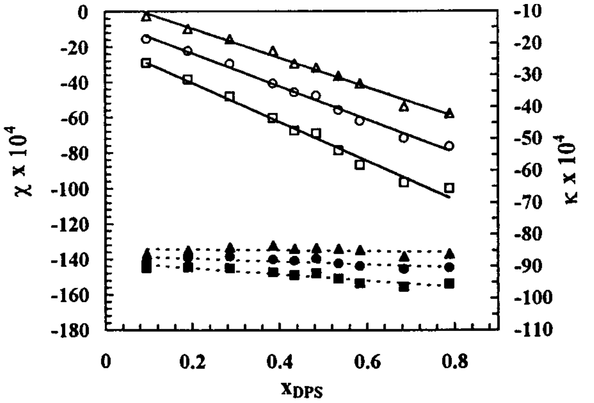

Figure 4. χ_{FH} and κ as a function of composition for DPS/PVME. The lines are best linear fits to the data. Open symbols with solid lines: χ_{FH}. Solid symbols with dashed lines: κ. Triangles: $T = 120$ °C. Circles: $T = 130$ °C. Squares: $T = 138$ °C.

These results for weakly interacting blends indicate that nothing is gained by employing a compressible model to parameterize the interactions. The clear implication is that finite compressibility is unrelated to the parabolic compositional dependence of χ_{FH} in weakly interacting blends.

The variation of κ with component concentration for the strongly interacting pair, polystyrene/poly(vinyl methyl ether), is shown at four temperatures in Figure 3. At the two highest temperatures (138 °C and 130 °C), κ is practically independent of composition, in excellent accord with the expected composition independence of ϵ_{12} for the lattice fluid. A weak linear variation of κ with concentration appears at the third temperature (120 °C), while the overall fit has become rather poor at the lowest temperature (100 °C). The Flory–Huggins and lattice-fluid interpretations are compared for the three highest temperatures in Figure 4. The variation of $(\chi_{FH})_{SANS}$ with composition is much greater than that of κ. An improvement in consistency resulting from a compressible interpretation, i.e., a significant reduction in parameter variation, is clearly evident in this strongly interacting case.

Discussion

We have shown that, in the lattice-fluid approximation at least, the effect of compressibility on the analysis of $k_N/I(0)$ for weakly interacting blends, such as isotopic and polyolefin mixtures, is negligible. The interaction parameter, of course, varies in magnitude from one model to another, but the rather peculiar parabolic variation of the SANS-derived interaction parameter with composition must have some origin other than compressibility.

Some suspicion about the reality of the parabolic dependence seems appropriate in view of the results of Scheffold *et al.*[12] They measured coexistence curves for several model polyolefin blends, including some having a parabolic variation in $(\chi_{FH})_{SANS}$,[9] and were able to reproduce the observed phase boundaries quantitatively with the Flory–Huggins model and values of χ_{FH} that vary linearly with concentration. The phase equilibria and SANS intensity depend on the Gibbs energy density in rather different ways, but the linear and parabolic forms nevertheless cannot both be correct. We have explored the possibility of non-thermodynamic causes, one being errors or unanticipated variations in the absolute SANS calibration. Parabolic variations in the (apparent) values of $(\chi_{FH})_{SANS}$ could indeed be a signature of erroneous calibration, but variable errors ranging from 25% to 40% and more would be required to explain the observed behavior, and this seems implausible. Another possibility is that the experimental uncertainties in obtaining values of $k_N/I(0)$ at the concentration extremes are being underestimated and that the parabolic form is merely a result of systematic extrapolation errors. Such possibilities and others should no doubt be explored further, but meanwhile, the origin and reality of the parabolic concentration dependence must be considered an open question.

The admittedly limited results here indicate that, for SANS results on strongly interacting blends, there are benefits to be gained from a compressible interpretation. The results for the PS/PVME system suggest that, over some range of temperatures at least, the lattice-fluid model parameter ϵ_{12} is essentially independent of component concentration, as the model itself requires. The implication is that $(\chi_{FH})_{SANS}$, as obtained with the Flory–Huggins model, varies significantly with concentration because of finite compressibility, an effect that the lattice-fluid model manages to handle properly. Parenthetically, we wish to point out that a compressible interpretation of $k_N/I(0)$ offers advantages for all blends, whether strongly or weakly interacting. For example, an estimate for the excess volume v_e/v, the fractional change in volume on mixing, is the automatic byproduct of any complete compressible model. For the lattice-fluid model,

$$\text{PS/PVME} \quad \left(\frac{v_e}{v}\right)_{x=0.5} = -4.8 \times 10^{-3} \quad \text{(model prediction, 120 °C)}$$

$$\left(\frac{v_e}{v}\right)_{x=0.5} = -2.8 \times 10^{-3} \quad \text{(observed,}^{13}\text{ 50 °C)}$$

$$\text{H78/D66} \quad \left(\frac{v_e}{v}\right)_{x=0.5} = +6.5 \times 10^{-5} \quad \text{(model prediction, 120 °C)}$$

$$\left(\frac{v_e}{v}\right)_{x=0.5} < 10^{-3} \quad \text{(observed,}^{14}\text{ 23 °C)}$$

The values of v_e/v for lattice fluids would appear to be at least qualitatively correct for both weakly and strongly interacting pairs. They are inaccurate quantitatively but perhaps no worse than the predictions of other analytically tractable compressible models.

Finally, we wish to comment more generally on the analysis of SANS data for compressible blends. Benoit[15] has emphasized the independence of the density and composition fluctuations that govern coherent scattering, and as noted previously,[4] there seems to be general agreement that compressibility *per se* does not seriously compromise the extrapolation of coherent SANS intensity to obtain $I(0)$. We showed previously that the coherent SANS intensity from density fluctuations is ordinarily negligibly small for blends compared with that from concentration fluctuations and that the SANS contrast factor k_N is insensitive to blend compressibility.[4] Accordingly, $k_N/I(0)$ should reflect only the mixing thermodynamics, which can therefore be parameterized to express the interactions by any number of reasonable models, compressible or incompressible. This could be accomplished beginning, for example, with eq 26 in ref 4. Using the Flory–Huggins model to express the interactions in terms of $(\chi_{FH})_{SANS}$ does no harm, since those values can always be converted to equivalent measures of interaction strength in some other one-parameter model, as we have done here for the lattice fluid. Thus, fortunately, it is unnecessary to introduce compressibility at an early stage in the SANS data analysis in order to gain the benefit of interpretations based on a compressible model for the thermodynamics.

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