Macromolecules **2000,** *33,* 6869−6877

A Theoretical Study of Isotope Blends: No Concentration Dependence of the SANS χ Parameter

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Received October 8, 1999; Revised Manuscript Received April 27, 2000

ABSTRACT: The small-angle neutron scattering (SANS) interaction parameter χ_{NS} in isotope blends almost always exhibits pronounced upward curvature when plotted as a function of concentration at any given temperature. Optimized cluster theory (OCT), which accounts for blend compressibility and for fluctuations, is used to address this effect in blends of conventional and perdeuterated polyethylene. Structure factors are calculated for symmetric systems having a concentration independent $\chi_{bare} = 2.09 \times 10^{-4}$ and chains of $N = 3290$ or $N = 8746$ monomers. When analyzed in terms of incompressible RPA approach, *exactly as done in experiments*, the model returns an interaction parameter that is practically indistinguishable from χ_{bare} for all blends concentrations between 0.01 and 0.99. Trivial departures from the energetic χ_{bare} are attributed to equation-of-state effects. These results, combined those from compressible lattice models, show clearly that compressibility has no significant role in determining the composition dependence of the interaction parameter. The experimental behavior of isotope blends cannot be ascribed to any theoretical reason (i.e., compressibility or density fluctuations) and is therefore attributed to measurement errors.

Introduction

The interaction parameter for binary blends of chemically similar polymers, i.e., polyolefin blends and isotopic blends, derived from scattering experiments is generally found to be larger in blends dilute in either component. Past theoretical work has attributed this to blend compressibility and non-mean-field concentration fluctuations. We illustrate conclusively that, when the theoretical analysis tracks the experimental treatment of scattering data, the interaction parameters are independent of composition. Since this result is separately verified by three separate models, namely the Sanchez−Lacombe model (Kumar et al.[1]), the Bethe lattice approach (Gujrati[2]), and here by optimized cluster theory, we are forced to conclude that none of the theoretical approaches adopted to this time can explain the experimental results. The composition dependence of the interaction parameter is currently not understood but derives at least in part from limitations inherent to the scattering experiment.

Critical Summary of Current Status of the Field

Small-angle neutron scattering (SANS) from binary or, in some cases, ternary polymer blends is the most valuable experimental tool for assessing interactions between dissimilar chainlike molecules. An interesting class of such systems is isotope blends, wherein the two polymers are distinguished only by the substitution of deuterium for hydrogen. Following the seminal prediction of Buckingham and Hentschel,[3] a number of experiments confirmed the presence of repulsive interactions between conventional and perdeuterated polymers. These interactions, while small by many standards, may trigger phase separation in systems of high degree of polymerization[4] and in a one-phase blend give rise to excess SANS that is represented by a positive interaction parameter χ_{NS}. Deuterium in this case provides both the nonideal free energy of mixing and the contrast for the SANS experiment. Random phase approximation (RPA) theory[5,6] is used to evaluate χ_{NS} from scattering data, subject to the following assumptions: (1) the blend is incompressible, so density fluctuations are ignored; (2) free energy of mixing in excess of that from ideal combinatorial entropy derives from binary contacts that occur with a probability $\varphi_1\varphi_2$, i.e., random mixing is assumed for the one-phase blend.

SANS experiments for a binary blend with component volume fractions φ_1 and $\varphi_2 = 1 - \varphi_1$ are analyzed to define χ_{NS} according to[7]

$$\chi_{NS} \equiv \frac{v_0}{2}\left(\frac{1}{N_1\varphi_1 v_1} + \frac{1}{N_2\varphi_2 v_2}\right) - \frac{v_0 K_N}{2I(0)} \qquad (1)$$

$I(0)$ is the experimental coherent cross-section per unit volume extrapolated to $q = 0$. Incoherent background scattering has been subtracted, a step of potential significance that is considered later in this paper. Blend components have N_i monomers per chain (weight average if polymer is not monodisperse), the monomer volumes are v_i, the reference volume is usually chosen as $v_0 = (v_1v_2)^{1/2}$, and the contrast factor is $K_N = (b_1/v_1 - b_2/v_2)^2$, where b_i are coherent scattering lengths of the monomers. The relation of χ_{NS} to blend thermodynamics depends on the concentration dependence of the free energy of mixing, the latter being normalized for thermal energy kT and the size of the reference volume element v_0. In this approach to solution theory, all nonideal contributions to the normalized free energy of

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10.1021/ma991690y CCC: $19.00

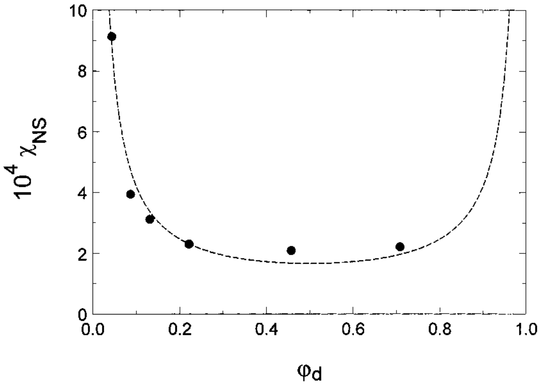

Figure 1. Interaction parameter χ_{NS} as a function of concentration for a blend of conventional and deuterated polyethylene. $N_1 = 8298$, $N_2 = N_d = 9196$, $T = 443$ K (160 °C). Data from Londono et al.[12] Dashed line is fit to $\chi_{NS} = a + b/N\varphi_1\varphi_2$, which is seen in all isotope blends,[9] and may be the consequence of systematic experimental errors.[16]

mixing are expressed as $\varphi_1\varphi_2\chi/v_0$, where χ is the *thermodynamic* interaction parameter. One should note that there are no a priori restrictions on how χ depends on temperature T, chain length N, or concentration φ. Ideal free energy of mixing is the product of $-T$ and the combinatorial entropy of the blend, reckoned on a lattice with cell volume v_0; each chain occupies N_iv_i/v_0 lattice sites. The first term of eq 1 is the second derivative of the normalized ideal free energy of mixing with respect to volume fraction φ_1. The reader is reminded that χ/v_0 and χ_{NS}/v_0 are intensive quantities, while the magnitude of either interaction parameter is proportional to the chosen reference volume v_0.

We are concerned with SANS experiments done with one polymer pair at fixed T and variable concentrations φ_i. The neutron scattering quantity χ_{NS} is related to the thermodynamic χ by the relation[8]

$$\chi_{NS} \equiv -\frac{1}{2}\frac{d^2(\varphi_1\varphi_2\chi)}{d^2\varphi_1} \tag{2}$$

One sees immediately that $\chi_{NS} = \chi$ if χ is independent of concentration. We emphasize that there are two related quantities that describe blend thermodynamics; χ is a direct measure of nonideal contributions to the free energy of mixing, while χ_{NS} is an experimental quantity that is related to χ by eq 2. If χ has a concentration dependence, the φ dependence of χ_{NS} is considerably larger than that of the thermodynamic χ.[8,9]

A surprising, and in many ways disturbing, result is that χ_{NS} has a pronounced concentration dependence in each of the nine SANS studies reported for isotope blends. Such behavior has been reported for one-phase mixtures of conventional and deuterated poly(ethylethylene),[10] poly(vinylethylene),[10] polystyrene,[11,12] polyethylene,[12] poly(methyl methacrylate),[13,14] polyisoprene,[14] and poly(ethylene oxide).[14] In all cases χ_{NS} changes by at least 20% (typically more than 50%) when the volume fraction of deuterated polymer φ_d is lowered/raised from 0.5 to 0.1/0.9. Excepting polystyrene, χ_{NS} *increases* for isotope blends dilute in either component; for polystyrene blends χ_{NS} decreases toward the concentration extremes. The concentration dependence of χ_{NS} in isotope blends is illustrated by a polyethylene system shown in Figure 1. Note particularly that χ_{NS} is nearly constant near the midrange of concentration and appears to diverge in the limits of $\varphi_d = 0$ or 1. We shall distinguish between diverging behavior and parabolic behavior, where χ_{NS} may curve upward (or downward) about $\varphi_d \approx 0.5$ to *finite* values at the concentration limits. A related effect is that χ_{NS} appears to depend on molecular weight as well.[12]

This unexpected concentration dependence of χ_{NS} in isotope blends has led to considerable discussion. Accepting as correct experimental results such as those in Figure 1, the implied dependence of the thermodynamic χ on φ is counterintuitive and has led to questioning the relation between scattering and thermodynamics and the SANS experiment itself. Schweizer[15] notes that eq 1 establishes χ_{NS} as the difference between two quantities that diverge as concentration of either blend component approaches zero. He attributes the divergence of χ_{NS} to errors stemming from the assumption of blend incompressibility. Crist[9] posited that the ideal entropy of mixing, which gives rise to the first term in parentheses on the right-hand side of eq 1, may be incorrect for blends below the overlap concentration φ^*. A recent analysis of the SANS experiment[16] showed that systematic errors (e.g., incorrect degree of polymerization N) will lead to either positive or negative divergence of χ_{NS} when the thermodynamic χ is independent of φ. The functional dependence of χ_{NS} when such errors are operative is illustrated by the dashed line in Figure 1. Regardless of whether the cause is inadequate theory or imperfect experiments, the nature of eq 1 is certainly conducive to χ_{NS} diverging at the concentration extremes. Care must be exercised with both experiments and theories that examine the concentration dependence of polymer blend thermodynamics.

Beyond the general arguments described above, a stream of theoretical or simulation studies has appeared during the past decade. All of these investigations have focused on nonclassical concentration fluctuations and/or compressibility, both being neglected in the RPA theory that underlies eq 1. It is not our purpose to review these analyses in detail, but the most salient points will be emphasized. The classical or mean field treatment of a solution relies on the average concentration and hence predicts that the magnitude of concentration fluctuations in the blend diverges at the instability line or spinodal. More complete descriptions of fluctuations include nonrandom mixing and gradient energies, but the region in which these refinements are important is small in blends of large N polymers.[17] Compressibility refers to the influence of unoccupied or free volume on the thermodynamic interactions between the blend components.

In each study it was assumed that the monomer–monomer interaction energies ϵ_{11}, ϵ_{22}, and ϵ_{12} are independent of blend concentration φ and temperature T. Hence, the exchange energy $\epsilon_{21} - (\epsilon_{11} + \epsilon_{22})/2$, the input for nonideal free energy of mixing, is constant as well. Models or simulations return a thermodynamic χ or scattering χ_{NS}. Comparison to the value expected from exchange energy alone is facilitated by expressing the latter as χ_{bare}:

$$\chi_{bare} = \frac{1}{2kT}(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}) \tag{3}$$

The reference quantity χ_{bare} is by definition independent of concentration and N and is inversely proportional to T. Models or simulations with a fixed χ_{bare} have been used to evaluate the thermodynamic χ or the scattering χ_{NS} (or sometimes both) for different φ_i, usually with symmetric blends having $N_1 = N_2$. At issue, of course, is how χ and χ_{NS} depend on φ_i. These studies were often done for various chain lengths and temperatures.

Nonclassical concentration fluctuations (or nonrandom mixing) have been treated by incompressible off-lattice[10,18,19] or lattice[20,21] theories. The analysis of Bates et al.[10] appears to account for χ_{NS} diverging upward in isotope blends (as in Figure 1), but that result derives from approximations that are inapplicable at low φ_i where χ_{NS} is seen to diverge. The fundamental problem with that theory is manifested as a nonzero free energy of mixing for the pure components. More recent treatments of fluctuations[19,21] have χ increasing smoothly to χ_{bare} at $\varphi_i = 0.1$ from a minimum at $\varphi_i = 0.5$. For physically realistic values ($\chi_{bare}N < 2$ and $N \geq 1000$), this change in χ is less than 1%, and χ_{NS} evaluated by eq 2 varies by less than 3% with no divergence. While fluctuations do cause a drop in χ_{NS} near the critical point, the effect is at least an order of magnitude smaller than observed and furthermore lacks the divergent character of data in Figure 1.

Studies of compressible isotope blends without consideration of nonrandom mixing, based on simple lattice theory[22,23] or lattice fluid theory,[7,24,25] have returned discordant results. Compressible lattice models include voids or free volume as a third blend component. Throughout this paper we retain macroscopic polymer volume fractions φ_i where $\varphi_1 + \varphi_2 = 1$, realizing that the local volume fractions are scaled to account for the presence of free volume. Of interest here are compressible models for weakly interacting blends in which overall monomer density is nearly independent of φ, or, equivalently, the volume of mixing is nearly ideal. Dudowicz and Freed[23] found that χ_{NS} diverges downward (as in experiments on polystyrene isotope blends), while Bidkar and Sanchez[24] and Talyor et al.[7] had χ_{NS} diverging upward (like all other isotope blends). Downward divergence was also predicted by Hammouda in his treatment of compressible RPA theory.[26] In each case, however, the apparent concentration dependence of χ_{NS} is caused by incorrect definition of one of the two terms on the right-hand side of eq 1. Difficulties arise if the second term, which is calculated for a compressible model, is not adjusted to conform to the incompressible lattice underlying the first combinatorial entropy term in parentheses.[16] Recall that eq 1 is based on the free energy of mixing per lattice site, the volume of which includes both “hard core” and “free” volume. Compressible lattice theories calculate the free energy of mixing per monomer, but here the monomer volume is “hard core” only and is smaller than v_0 in the incompressible approach. The compressible lattice has more, smaller cells than the incompressible lattice of the same overall volume. Absent a consistent basis for the two terms, χ_{NS} from eq 1 invariably diverges at the concentration extremes and gives a false indication that compressibility alters blend thermodynamics in a significant manner. The two terms can be made commensurate, as in the most recent lattice fluid calculation of Taylor-Maranas et al.,[25] although the error in their earlier work[7] was not identified. The correct approach gave essentially no variation of χ_{NS} with φ when χ_{bare} is constant and volumes of mixing are nearly ideal. The same conclusion, that compressibility in weakly interacting blends in no way triggers a pronounced concentration dependence of χ_{NS}, was made with a general thermodynamic analysis by Kumar et al.[1] These newer findings agree with well-established statistical thermodynamic results[27−29] that scattering from density fluctuations and concentration fluctuations are separable; there is no correlation or coupling between density fluctuations and concentration fluctuations in a compressible blend, a point that is used in the present work.

The effects of fluctuations and compressibility can be combined in more comprehensive theories or in simulations. Schweizer and Curro[30,31] applied polymer reference interaction site model (PRISM) theory to the study of isotope blends and found that χ_{NS} curved upward by as much as 40% over the range $\varphi_d = 0.1-0.9$. Later studies,[32] with different model assumptions and different parameters, gave a smaller φ dependence of χ_{NS}; the effective interaction parameter increased nearly linearly by less than 5% between $\varphi = 0.5$ and $\varphi = 1$ in blends with $N \geq 1000$ and meltlike monomer densities. Dudowicz et al.[33] have applied lattice cluster theory to isotope blends. They found that χ_{NS} diverges downward (as in the unique polystyrene system), but this results from inappropriate definitions of terms in eq 1. Optimized cluster theory (OCT), a diagramatically correct integral equation theory, was employed by Melenkevitz and Curro[34] and by Melenkevitz[35] to examine isotope blends. Here χ_{NS} was observed to diverge upward at the concentration extremes, but it is shown below that the apparent φ dependence in that case is caused by incorrect definition of one of the factors in eq 1. Gujrati[2] has recently considered both fluctuations (nonrandom mixing) and compressibility with a lattice model. That work clearly demonstrates that divergence of χ_{NS} can be caused by inconsistencies in the two terms in eq 1.

The last method to be discussed is simulations that, like theories in the paragraph above, include both fluctuations and compressibility. As simulations are confined to short chains ($N = 16-128$ in the works to follow), fluctuations are expected to be important near the critical point. Constant volume lattice Monte Carlo simulations of symmetric isotope blends by Binder and coworkers showed that the thermodynamic χ[36] and the scattering χ_{NS}[37] have nearly parabolic upward curvature with no divergence. The concentration dependence of χ is reduced when T is raised above the critical temperature T_c, as predicted for fluctuation effects. Kumar[38] did an off-lattice Monte Carlo simulation of an isotope blend ($N = 25$) to obtain the thermodynamic χ at constant pressure. The same type of system ($N = 50$) was investigated at constant density with molecular dynamics by Cui et al.,[39] who evaluated the scattering quantity χ_{NS}. In these studies χ and χ_{NS} respectively were found to be small and positive, but limited precision precluded any meaningful assessments of concentration dependence.

The collection of theories and simulations described above presents a confusing picture. In an attempt to summarize, we believe that fluctuations (nonrandom mixing) lead in principle to upward curvature of the thermodynamic χ near the critical temperature T_c, but this concentration dependence (and the resulting φ dependence of χ_{NS}) is very small for blends of large N chains. Hence, fluctuations are thought not to be the cause of the behavior seen in experiments such as those in Figure 1. Compressibility is a thornier issue. Our working hypothesis is that the divergent behavior of χ_{NS} at the concentration limits reported in many theories[7,23,24,33−35] is misleading. Supporting this notion is the fact that χ and/or χ_{NS} do not diverge, although some upward curvature is apparent, in simulations,[36,37] PRISM calculations,[32] and lattice theory[2] that include compressibility.

In this paper we apply optimized cluster theory (OCT) to blends with parameters appropriate for polyethylene/deuterated polyethylene (PE/*d*-PE). The procedure is straightforward: holding χ_{bare} constant at a single temperature, concentration φ is varied over wide limits. OCT is used to evaluate $I(0)$ for the blends, which are analyzed with eq 1 to obtain χ_{NS} exactly as in experiments. The scattering quantity χ_{NS} from this OCT treatment of compressible blends equals χ_{bare} within a factor of about 10^{-3}, with no significant dependence on either concentration φ or chain length N. Hence, compressibility and nonrandom mixing, both of which are included in the model, are unambiguously shown not to be the cause of experimental results such as those in Figure 1. Other possible causes for observed behavior are considered.

Optimized Cluster Theory

Optimized cluster theory (OCT) has been developed for binary polymer−polymer mixtures by Melenkevitz and Curro.[34] Only a brief outline of the theory is given here. OCT starts by separating the interaction between any two sites (monomers) on different chains into a steep repulsive potential and more a slowly varying tail potential that is generally attractive. The former, assumed in the present work to be of the hard core type with characteristic distance d, is the reference potential. Of interest are the Helmholtz free energy A and the three intermolecular monomer−monomer correlation functions $h_{ij}(r)$ for chains of type i, $j = 1, 2$. OCT uses the *site averaging approximation*, where intramolecular correlations are replaced by two-point averages expressed as $s_i(r)$;[34] all chains of type i are represented by a single intramolecular correlation function $s_i(r)$, which further ignores explicit chain end effects. In the absence of tail potentials, the hard core reference potential leads to a reference free energy A^{o} and the reference correlation functions $h^{\text{o}}{}_{ij}(r)$. When the full potentials are present, the desired quantities A and $h_{ij}(r)$ are written as the sum of reference functions plus appropriate cluster perturbation expansions, expressed as infinite sums of interaction site diagrams. Furthermore, it is necessary to divide each correlation function $h_{ij}(r)$ into four terms, based on topology of the interaction diagrams.[34]

Utilized here is an integral equation theory for polymer blends that is diagramatically proper, i.e., developed through exact topological reductions of the cluster expansion for the pair correlation functions. Written in matrix form, the integral equation expresses $\hat{\mathbf{h}}(q)$, the Fourier transform of the correlation function $\mathbf{h}(r)$:[34]

$$\hat{\mathbf{h}}(q) = \hat{\mathbf{c}}(q) + \hat{\mathbf{c}}(q)\boldsymbol{\rho}\hat{\mathbf{s}}(q) + \hat{\mathbf{s}}(q)\boldsymbol{\rho}\hat{\mathbf{h}}(q) + \hat{\mathbf{c}}(q)\boldsymbol{\rho}\hat{\mathbf{h}}(q) \quad (4)$$

$\hat{\mathbf{h}}(q)$ is a symmetric 2 × 2 matrix with elements $\hat{h}_{ij}(q)$, each of which is in turn a 2 × 2 submatrix of four terms based on topology of interaction site diagrams. The matrix $\hat{\mathbf{c}}(q)$ has the same structure, and its elements are Fourier transforms of the direct correlation function $c_{ij}(r)$. Fourier transforms of the intramolecular correlations $s_i(r)$ are contained in the (block diagonal) elements of $\hat{\mathbf{s}}(q)$, and monomer number densities ρ_i are the elements of $\boldsymbol{\rho}$. Details are given in ref 35.

The solution of eq 4 requires a closure relation between $\mathbf{c}(r)$, $\mathbf{h}(r)$, and the full pair potentials, a step most readily achieved by specifying the correlation functions with respect to the reference system of hard core chains employed in the optimized cluster theory. Defining $\delta\mathbf{h}(r) = \mathbf{h}(r) - \mathbf{h}^{\text{o}}(r)$ and $\delta\mathbf{c}(r) = \mathbf{c}(r) - \mathbf{c}^{\text{o}}(r)$, where $\mathbf{h}^{\text{o}}$ and $\mathbf{c}^{\text{o}}$ are correlation function matrices for the reference system, eq 4 can be rewritten as[34]

$$\delta\hat{\mathbf{h}}(q) = \{\mathbf{I} - [\hat{\mathbf{s}}(q) + \hat{\mathbf{c}}^{\text{o}}(q) + \delta\hat{\mathbf{c}}(q)]\boldsymbol{\rho}\}^{-1}\delta\hat{\mathbf{c}}(q)\{\mathbf{I} + \boldsymbol{\rho}[\hat{\mathbf{s}}(q) + \hat{\mathbf{c}}^{\text{o}}(q)]\}\{\mathbf{I} - \boldsymbol{\rho}[\hat{\mathbf{s}}(q) + \hat{\mathbf{c}}^{\text{o}}(q)]\}^{-1} \quad (5)$$

Here $\mathbf{I}$ is the identity matrix. The closure relations establish that $\delta h_{ij}(r) = 0$ for $r < d$ (no overlap within the range of the hard core potential) and that $\delta c_{ij}(r)$ are explicit functions of the tail potentials for $r \geq d$.

With these closure relations, eq 5 is solved numerically for $\delta\hat{\mathbf{h}}(q)$ by the Picard iteration procedure to a convergence of ca. 10^{-8}. The result establishes the Fourier transforms of the three pair correlation functions $\hat{h}_{ij}(q) = \hat{h}^{\text{o}}{}_{ij}(q) + \delta\hat{h}_{ij}(q)$, which are used to write the partial structure factors of the blend:

$$S_{ij}(q) = \rho_i[1 + \hat{s}_i(q)]\delta_{ij} + \rho_i\rho_j\,\hat{h}_{ij}(q) \quad (6)$$

The reader is reminded that OCT is an approximate theory that is most accurate at high density and temperature, where the effects of short-range tail potentials are small. More complete descriptions of the theory and input parameters (pair potentials, intrachain correlation function matrix $\hat{\mathbf{s}}(q)$, reference system correlation function matrices $\hat{\mathbf{h}}^{\text{o}}(q)$ and $\hat{\mathbf{c}}^{\text{o}}(q)$) may be found in refs 34 and 35.

Application of OCT to Polyethylene Isotope Blends

Parameters are precisely those used in an earlier study[35] of the same systems. Two symmetric blends are considered, one with $N = 8746$ and the other with $N = 3290$, based on CH_2 (or CD_2) monomers that are treated as united atom entities. The large N blend corresponds to the experimental system in Figure 1, aside from a 10% difference between N_1 and N_2 in the latter. $N = 3290$ was chosen to check for chain length effects. Concentration ranges from $\varphi_2 = \varphi_{\text{d}} = 0.01{-}0.99$ (the subscript 2 is used throughout for *d*-PE). Monomer density is $\rho = 33.54$ nm^{-3}, which is based on mass density of 779.6 kg/m^3 for molten PE at $T = 430$ K and ambient pressure.[40] Hence, both monomer volumes and the reference volume are $v = v_1 = v_2 = v_0 = 0.02983$ nm^3, which neglects the ca. 0.4% contraction that might be expected in *d*-PE.[41] Intermolecular Lennard-Jones potentials for PE utilize the energy parameter (well depth divided by the Boltzmann constant k) $e_{11} = 38.7$ K and the length parameter $\sigma = 0.437$ nm;[42] the latter was used for *d*-PE as well. The potential between PE and *d*-PE monomers uses the Berthelot average $e_{12} = (e_{11}e_{22})^{1/2}$, where e_{22} was established by matching the experimental critical temperature $T_{\text{c}} = 398$ K for the PE isotope blend with $N = 8746$.[12] In this study $e_{11}/e_{22} = \lambda^2 = 1.030$, or intermolecular bonding in *d*-PE is 3% weaker than in PE. With these energies the interaction parameter is $\chi_{\text{bare}} = 2.086 \times 10^{-4}$ at $T = 443$ K.[43] The hard core diameter d is fixed at 0.390 nm for both types of chains,[42] and the intrachain correlation function $\hat{s}_i(q)$has been described previously.[35] Calculations are done at $T = 443$ K, which corresponds to $\chi_{\text{bare}}N = 0.68$ and 1.83 for $N = 3290$ and 8746, respectively.

A. RPA Analysis. Equation 6 is used to evaluate the OCT partial structure factors $S_{ij}(q)$ at $q = 0$, and these

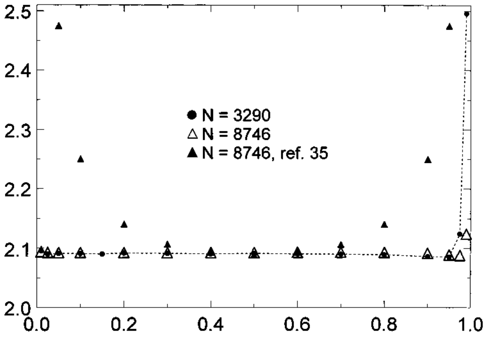

Figure 2. Apparent interaction parameter χ_{app} from eq 8 for OCT isotope blends at $T = 443$ K ($\chi_{bare} = 2.086 \times 10^{-4}$). Dashed line connecting the points for $N = 3290$ is to guide the eye. Solid triangles (▲) are earlier OCT results for $N = 8746$;[35] see text for significance.

define the scattering intensity at $q = 0$:

$$I_{OCT}(0) = b_1^{\,2}S_{11}(0) + 2b_1b_2S_{12}(0) + b_2^{\,2}S_{22}(0) \quad (7)$$

Scattering lengths are $b_1 = -0.083$ and $b_2 = 1.996$ (10^{-12} cm) for CH_2 and CD_2, respectively. $I_{OCT}(0)$ is evaluated for blends of specified $\varphi_d = \varphi_2$ and substituted into eq 1, which is simplified because all volumes are equal to v:

$$\chi_{app} \equiv \frac{1}{2N\varphi_1\varphi_2} - \frac{vK_N}{2I_{OCT}(0)} \quad (8)$$

This apparent interaction parameter is labeled χ_{app} for reasons that will become clear below. Results are presented graphically in Figure 2, where it is evident that χ_{app} is for the most part constant, independent of both φ_d and N. Note furthermore that χ_{app} is very close to $\chi_{bare} = 2.086 \times 10^{-4}$. Also included in Figure 2 are results from a previous OCT study of precisely the same $N = 8746$ blend.[35] In that work the monomer volumes v_1 and v_2 and reference volume v_0 were mistakenly set at $\pi d^3/6 = 0.03106$ nm^3 (based on hard core diameter d), which is larger than the monomer volume used here. This discrepancy reduces the second term on the right side of eq 8 by 4% and led to the misleading upward divergence of χ_{app}. While not shown in Figure 2, χ_{app} from the previous OCT work was about 10% larger for the $N = 3290$ blends, a related artifact that vanishes when proper volumes are used. Those earlier, incorrect results are included to emphasize the sensitivity of $\chi_{NS}(\varphi)$ to a systematic error in either of the two terms on the right-hand side of eq 1. The same sort of inconsistency is the cause of extreme φ dependence of χ_{NS} reported in other treatments of compressible systems.[7,23−26,38]

Returning to the present results, there is an abrupt increase in χ_{app} as φ_d approaches 1, which is more conspicuous in the low N blend. Barely evident in Figure 2 are very small increases of the same sort as φ_d approaches 0. The reason for this *asymmetric* φ dependence of χ_{app} is that $I_{OCT}(0)$ has contributions from both concentration fluctuations, which are related to χ, and density fluctuations. In eq 1 it is assumed that the intensity $I(0)$ is exclusively from concentration fluctuations, which is not the case for eq 5 that employs $I_{OCT}(0)$. For a compressible blend at pressure P and temperature T the intensity at $q = 0$ is given by[1,28]

$$I_{OCT} = I_{den} + I_{conc} \quad (9a)$$

$$I_{den} = \langle b\rangle^2\rho^2kT\beta \quad (9b)$$

$$I_{conc} = \frac{\rho^3kT\bar{v}_1^{\,2}\bar{v}_2^{\,2}K'_N}{[\partial^2g_m/\partial x_1^{\,2}]_{T,P}} \quad (9c)$$

Here the suffix (0) has been omitted for simplicity. Intensity from density fluctuations, I_{den}, is proportional to the average scattering length $\langle b\rangle = x_1b_1 + x_2b_2$ and to the isothermal compressibility β of the blend with monomer *mole fractions* x_1 and $x_2 = 1 - x_1$. Concentration fluctuations give rise to I_{conc}, which is written in terms of partial monomer volumes $\bar{v}_i$ and the second derivative of the Gibbs free energy of mixing (per monomer) g_m with respect to x_1. The average monomer density ρ conforms to $1/\rho = x_1\bar{v}_1 + x_2\bar{v}_2$, and the contrast factor is now $K'_N = (b_1/\bar{v}_1 - b_2/\bar{v}_2)^2$.

The asymmetric increase in χ_{app} near the concentration limits in Figure 2 can be understood in qualitative terms with the aid of eq 9. I_{den} increases with $\langle b\rangle^2$ by a factor of nearly 600 between PE ($\varphi_d = 0$) and *d*-PE ($\varphi_d = 1$) because $b_2 = 24|b_1|$. Scattering from concentration fluctuations, I_{conc}, on the other hand, is zero in the pure components and has a maximum at $\varphi_d = 0.5$. Hence, $I_{OCT} = I_{den} + I_{conc}$ is a good approximation of I_{conc} at intermediate concentrations, and $\chi_{app} \approx \chi_{bare}$. When φ_d approaches either limit, I_{conc} approaches zero as $\varphi_1\varphi_2$, and the total scattering I_{OCT} is increasingly contaminated by I_{den}, much more so for $\varphi_d \approx 1$. Because $I_{OCT} > I_{conc}$, eq 8 gives χ_{app} that is too large, and the effect is greater for the low N blend that has smaller I_{conc}. Regardless, it is clear from Figure 2 that the RPA analysis for a fully compressible system returns a measure of the interaction parameter that is quite close to χ_{bare} over most of the concentration range. A more detailed study requires separation of I_{OCT} into its components I_{den} and I_{conc}.

B. Thermodynamic Analysis of I_{OCT}. Compressibility has two effects on the scattering I_{OCT}. The obvious one is the presence of density fluctuations that lead to I_{den}. Furthermore, it is possible that compressibility (the presence of "voids" or free volume) influences the functional form of g_m, i.e., the thermodynamics of mixing. To examine such an effect, we replace the total intensity I_{OCT} in eq 5 by I_{conc}, which comes from concentration fluctuations only:

$$\chi_{NS} \equiv \frac{1}{2N\varphi_1\varphi_2} - \frac{\rho^3\bar{v}_1^{\,2}\bar{v}_2^{\,2}K'_N}{2I_{conc}} \quad (10)$$

The second term is simply $^1/_2(\partial^2g_m/kT)/\partial x_1^2$ (see eq 9c), while the first term is the incompressible analogue for an ideal blend. It is important to note that each term is based on free energy of mixing per monomer unit having volume $v = 1/\rho$. A misleading divergence of χ_{NS} will be seen if the same basis is not used for the two terms, as evident in Figure 2.

For a particular blend with volume fractions φ_1 and $\varphi_2 = 1 - \varphi_1$, OCT returns the three partial structure factors S_{ij} that establish the total intensity I_{OCT} (eq 7). At this point we employ the treatment of scattering from a binary, compressible blend presented by Higgins and Benoît,[28] which in fact leads to eq 9. The three S_{ij} are used to evaluate the compressibility as $kT\beta$ and the partial monomer volumes $\bar{v}_1$ and $\bar{v}_2$ as described in

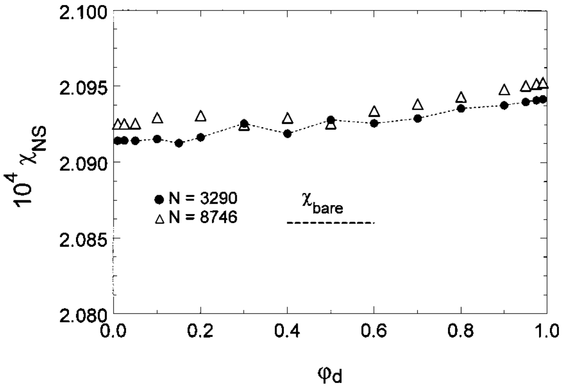

Figure 3. Interaction parameter χ_{NS} from eq 10 for OCT isotope blends at $T = 443$ K ($\chi_{bare} = 2.086 \times 10^{-4}$). Dashed line connecting the points for $N = 3290$ is to guide the eye.

Appendix A. Compressibility leads directly to I_{den} (eq 9b), which is then used to reckon the scattering from concentration fluctuations as $I_{conc} = I_{OCT} - I_{den}$. Results for the scattering quantity χ_{NS} from eq 10 are plotted in Figure 3. Realizing that the ordinate in this figure extends only 1%, the interaction parameter for these compressible blends is essentially constant, with no indication whatever of divergence at either concentration extreme, and only slightly larger (0.3%) than χ_{bare}. Be aware that convergence errors lead to some noise at this level of precision.

Nevertheless, it appears that χ_{NS} increases systematically with φ_d and is larger for $N = 8746$ than for $N = 3290$. Each of these changes is less than 0.13% (relative) and is attributed to subtle equation of state effects that also raise χ_{NS} slightly above χ_{bare}. Absolute compressibility from OCT is reasonable, some 50% below the experimental $\beta = 11 \times 10^{-10}$ m^2/N for conventional PE at 443 K.[44] The calculated compressibility is ~5% larger in blends with greater φ_d and smaller N, which parallels the behavior of χ_{NS}. It is reasonable that equation-of-state effects are more evident in more compressible systems.

We formulated the problem with actual scattering lengths b_1 and b_2 for CH_2 and CD_2, respectively. Changing these parameters obviously affects intensities I_{OCT} (eq 7), I_{den} (eq 9b), $I_{conc} = I_{OCT} - I_{den}$, and the contrast factor K'. But χ_{NS} (eq 10) is independent of scattering length, as it should be.

Discussion

The primary result developed here is that the SANS experiment should give an excellent measure of the thermodynamic χ in a compressible blend, at least for the standard test case where χ_{bare} is independent of concentration. Compressibility presents no difficulty when $I(0)$ is analyzed in the incompressible RPA format. Model results in Figure 2 do contain a spurious contribution from density fluctuations that causes χ_{app} to rise *asymmetrically* at the concentration extremes, but that sort of behavior is never seen in experimental χ_{NS} for isotope blends. The scattering contribution from density fluctuations is not observable in liquids (or glasses) because it is masked by stronger SANS incoherent "background" intensity, which comes primarily from hydrogen. It is an easy exercise to show that incoherent scattering is at least an order of magnitude larger than I_{den} for the blends in Figure 1, and the same applies to other isotope blends. In all cases experimental $I(0)$ are corrected for incoherent background in a manner which simultaneously removes the smaller I_{den}.[45] These corrected experimental $I(0)$, which are used in eq 1 to determine χ_{NS}, are not affected by blend compressibility. We are left with the inescapable conclusion that compressibility does not account for the pronounced concentration dependence of χ_{NS} in Figure 1 and in other experiments on isotope blends.[10-14]

Why are the data in Figure 1 so different from the OCT results in Figure 3? Two possible answers will be considered. The first is that the thermodynamic χ (for instance the exchange energy or χ_{bare}) has a real concentration dependence that gives rise to $\chi_{NS}(\varphi)$ through eq 2. Furthermore, if the data in ref 12 are considered to be accurate representations of the thermodynamics in PE/*d*-PE blends, then the concentration-dependent χ decreases at larger N. It was noted earlier[9,12] that the φ, N, and T dependencies of χ_{NS} are consistent with a positive contribution to the free energy of mixing that is entropic in nature. Beyond this general observation, we can propose no cause for a genuine concentration dependence of χ when χ_{bare} is constant.

The second answer is based on experimental shortcomings. Returning to eq 1, be reminded once again that χ_{NS} is defined by the difference between two terms, each of which diverges as the concentration limits are approached. In an experiment, as opposed to a theory or simulation, these terms are subject to uncertainties. The first term reflecting the ideal entropy of mixing requires absolute degrees of polymerization, N_1 and N_2, which are accurate to about ±5%. The second term involves $I(0)$, which is based on absolute calibration of the SANS instrument and extrapolation to $q = 0$ of background corrected intensities. Instrument calibration is also accurate to about ±5%.[10] Background subtraction is sample specific, being more of an issue with blends of low N and low φ_i that have small I_{conc}. Now any experimental concentration series with a pair of polymers likely has incorrect N_1, N_2, and $I(0)$. Such unavoidable *systematic* errors lead to $\chi'_{NS}(\varphi)$ from eq 1 that diverges upward or downward at the concentration limits when the thermodynamic χ (or energetic χ_{bare}) is constant.[16] We use the modified symbol χ'_{NS} to emphasize that the apparent concentration dependence of the SANS result does not necessarily reflect blend thermodynamics. The functional form is $\chi'_{NS} = a + b/N\varphi_1\varphi_2$, which captures the experimental behavior as illustrated by the dashed line in Figure 1, and further accounts for the N dependence that is seen when the experimental χ_{NS} is concentration-dependent.[16] Divergence is upward ($b > 0$) for N_i too small or $I(0)$ too large and is less pronounced for large N.

As any SANS experiment is prone to systematic errors that cause exactly the sort of concentration dependence and N dependence displayed by χ_{NS} in isotope blends, it is tempting to write off $\chi_{NS}(\varphi,N)$ as an experimental artifact. Attractive as this idea is, two difficulties follow. First, χ_{NS} is upward curving in seven of the nine studies of isotope blends; only PS/*d*-PS has χ_{NS} diverging downward.[11,12] Add to this list similar upward curvature (apparently following $\chi_{NS} = a + b/N\varphi_1\varphi_2$) in weakly interacting blends of structurally different polyolefins, one of which is deuterated.[46-48] The only exception is the concentration independent χ_{NS} reported by Lin et al.[49] for blends of two short-chain branched polyolefins. A summary of experimental $\chi_{NS}(\varphi)$ is presented in Appendix B. Attributing $\chi_{NS}(\varphi)$ to experimental errors leads to the unsettling corollary that, more than 90% of the time, measured degrees of polymerization are too small or that improper calibration leads to $I(0)$ that is too large. While this situation is not impossible, one would anticipate a roughly equal number of examples of upward and downward curvature. Beyond the inference that systematic errors made by different experimenters are almost always of the same type, there is the second issue of their magnitude. The concentration dependence of χ_{NS} in Figure 1 implies that the apparent N_i must be 33% below their true values, or the apparent intensity $I(0)$ must be 50% too large. Intensity calibration is not in error by anything approaching 50%. Molecular weights were determined by size exclusion chromatography on the PE and *d*-PE components,[12] and a 33% error in the weight-average quantities is outside the expected accuracy range. This example is extreme; the more recent work of Krishnamoorti[14] on three isotope blends shows upward curvature that can be accounted for by combined measurement errors of less than 10%,[16] which is of the order expected.

Conclusions

The present OCT study incorporates realistically large chains, nonclassical fluctuations, and compressibility. Furthermore, results are interpreted exactly as experimental SANS intensities to probe the relation between scattering and blend thermodynamics. These elements are combined for the first time in this theoretical investigation. For symmetric isotope blends in which the repulsive exchange energy or χ_{bare} is independent of φ and N, OCT returns χ_{NS} that is sensibly identical to χ_{bare} at all concentrations for the two values of N considered here.

Many polymer scientists are justifiably perplexed by the wide variety of results from theories and simulations of isotope blends described in the critical summary. And here we report that χ_{NS} is constant, a yet different result. This new finding should be justified in relation to other work. Remember that experiments nearly always indicate positive divergence of χ_{NS}, as in Figure 1.

Nonclassical fluctuations (nonrandom mixing) do, as mentioned earlier, cause the thermodynamic χ and the scattering χ_{NS} to fall below χ_{bare} near the critical point, an effect proportional to $1/N$. While that behavior is *qualitatively* similar to data in Figure 1, we agree with Singh et al.[32] that realistic treatments of fluctuations lead to changes much smaller than those observed experimentally. Furthermore, $\chi_{NS}(\varphi)$ from fluctuations never diverges at the concentration extremes. OCT gives no observable upward curvature of χ_{NS} (Figure 3) for the chain lengths and density used here, meaning that classical or mean field behavior is reflected in the present cases, though fluctuation effects are seen for shorter chains.[50] It is misleading to imply[10,19,20] that fluctuations are responsible for the observed $\chi_{NS}(\varphi,N)$ in isotope blends that have large N.

We have also demonstrated that compressibility is in no fundamental way responsible for the divergence of χ_{NS} seen in experiments. OCT structure factors, analyzed with the incompressible entropy term (see eq 8), give χ_{NS} within 0.3% of χ_{bare}. Compressibility has been particularly troublesome with lattice theories, where the reference or monomer volume is different from that in the first (incompressible) term of eq 1. We return to our earlier statement that the structure of eq 1 leads to *apparent* divergence of χ_{NS} if the two terms, the first coming from the ideal free energy of mixing and the second from the total free energy of mixing, are not reckoned on the same basis. Gujrati[2] has made the same point in his most recent paper. However, it is not difficult to put the two terms on the same footing. Then one is perfectly justified to interpret the scattering of a compressible system, be it experimental, theoretical, or simulated, with the incompressible term in eq 1. Note that the incompressible or RPA basis is the only one accessible to experimentalists.

Sometimes overlooked is the fact that the scattering χ_{NS} does not equal the thermodynamic χ when the latter is concentration dependent (eq 2). These two measures of nonideal free energy of mixing have different concentration dependencies. The OCT results in Figure 3 indicate that χ_{NS} increases linearly by 0.12% over the entire concentration range, which implies that the thermodynamic χ changes by less than 0.05% in this model.

In contrast to OCT results, experiments on isotope and polyolefin blends lead to χ_{NS} that increases by ca. 50% when φ_d is changed from 0.5 to 0.1 or 0.9. We conclude that results such as those shown in Figure 1 are the result of measurement errors that lead to apparent concentration dependence of χ_{NS}. In fact, one should expect divergence of the sort $\chi'_{NS} = a + b/N\varphi_1\varphi_2$ from inevitable experimental uncertainties. The reason why the curvature is nearly always in the same direction ($b > 0$) is not known.

We end this presentation by reiterating that the present OCT study of polymer blends gives no unexpected effects due to compressibility and/or nonclassical concentration fluctuations. Interactions are described to within a factor of about 10^{-3} by mean field concepts. For isotope blends and, by inference, other weakly interacting blends, the incompressible RPA format for analyzing background corrected SANS data should yield an excellent measure of χ_{bare}. Experimental uncertainties are the most likely causes for the apparent concentration dependence of χ_{NS}; the nature of eq 1 requires a nearly perfect experiment to determine the true $\chi_{NS}(\varphi,N)$. Nevertheless, the quantity $\chi_{NS}N$ derived from SANS experiments for which $\varphi_d \approx 0.5$ is reliable because the two terms in eq 1 are large. Assuming N is known with reasonable certainty, the resulting $\chi_{NS}(\varphi{=}0.5)$ can be associated with the concentration-independent thermodynamic χ. Precisely this scheme has been used to generate Flory–Huggins binodals for analyses of deeply quenched two-phase polyolefin blends. Quantitative agreement between observed and calculated volume fractions[51] and coarsening rates[52] confirms the notion that χ is independent of concentration and chain length in weakly interacting polymer blends.

Acknowledgment. The authors are indebted to J. G. Curro, K. F. Freed, and P. Gujrati for helpful discussions and correspondence. R. Krishnamoorti is thanked for sharing recent SANS data on isotope blends. S.K.K. acknowledges financial support from the National Science Foundation (DMR-9804327).

Appendix A

The partial structure factors S_{11}, $S_{12} = S_{21}$, and S_{22} at $q = 0$ are evaluated for a compressible blend at constant volume. We wish to convert these results to constant pressure, which corresponds to experiment. To this end we rearrange eq 7.42 of ref 28 to obtain

$$kT\beta = \frac{1}{\rho^2}\frac{S_{11}S_{22} - S_{12}^{\ 2}}{x_2^{\ 2}S_{11} - 2x_1x_2S_{12} + x_1^{\ 2}S_{22}} \qquad (A1)$$

$$\frac{\bar{v}_2}{\bar{v}_1} = \frac{S_{11} - x_1^{\,2}\rho^2 kT\beta}{x_1 x_2 \rho^2 kT\beta - S_{12}} \tag{A2}$$

Individual partial monomer volumes are established with relation to overall monomer density:

$$\bar{v}_2 = \frac{1}{\rho}\frac{1}{x_2 + x_1(\bar{v}_1/\bar{v}_2)} \tag{A3}$$

In the limit of an incompressible blend, $S_{11} = S_{22} = -S_{12}$; hence $kT\beta = 0$, $\bar{v}_2/\bar{v}_1 = 1$, and $\bar{v}_2 = 1/\rho$.

Appendix B

Figure 4 summarizes the concentration dependence of χ_{NS} for isotope blends, and Figure 5 presents the same information for weakly interacting blends. Abscissa is the date of publication. The dashed lines are estimates of concentration dependence based on systematic errors of ±10%.

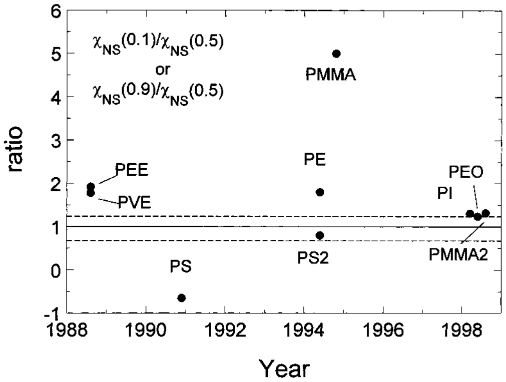

Figure 4. Ratio of χ_{fNS} at $\varphi = 0.1(0.9)$ to that at $\varphi = 0.5$ for isotope blends. Data for poly(ethylethylene) and poly(vinylethylene) from ref 10; polystyrene from ref 11; polyethylene and polystyrene2 from ref 12; poly(methyl methacrylate) from ref 13; polyisoprene, poly(ethylene oxide), and poly(methyl methacrylate)2 from ref 14. Polystyrene results are for incorrect molecular weights; when corrected, ratio is the same as for polystyrene2.[16]

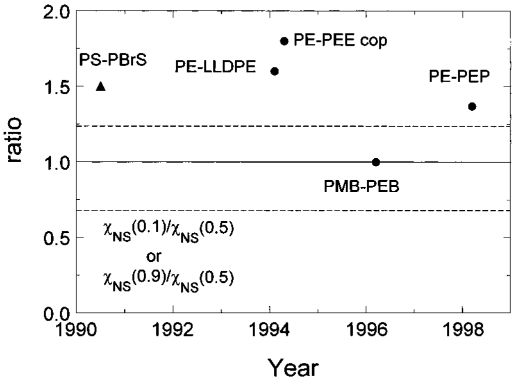

Figure 5. Ratio of χ_{fNS} at $\varphi = 0.1(0.9)$ to that at $\varphi = 0.5$ for weakly interacting blends. Data for polystyrene–poly(styrene-*co*-bromostyrene) is from X-ray scattering.[53] SANS results for blends have one of the components deuterated. Polyethylene–linear low-density polyethylene from ref 46; different poly(ethylene-*co*-ethylethylene) random copolymers from ref 47; poly(methylbutylene)–poly(ethylbutylene) from ref 49; polyethylene–poly(ethylenepropylene) from ref 48.

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MA991690Y