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Molecular Weight and Compositional Dependence of Isotopic Blends

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ABSTRACT: The chain length and compositional dependence of the effective chi parameter, χ_s, in model isotopic polyethylene blends were determined at two different temperatures using our recently developed optimized cluster theory for polymer mixtures. χ_s was found to have a concave-up compositional dependence that decreased with increasing temperature and molecular weight, in agreement with neutron scattering measurements. A best fit to the chain length dependence of χ_s at constant temperature and composition had the form, $\chi_s = \chi_s(\infty) + D/N$, where N is the number of segments comprising the polymers. In addition, the calculated compositional dependence of χ_s could be accurately described by a simple functional form that was previously proposed to fit experimental data on isotopic blends. However, the theory underestimates the breadth of the compositional dependence reported in the literature.

I. Introduction

Structurally symmetric isotopic blends are ideal candidates for the initial investigation of the role compositional fluctuations, fluid compressibility, and local liquid packing have on the thermodynamic properties, specifically the χ parameter, χ_s, in polymer blends. Because of the weak dispersive interactions between the species present, arising from the difference in the bond polarizabilities of the C−H and C−D bonds, nearly mean field behavior is expected to be observed in these systems.[1,2] However, χ_s, determined from neutron scattering measurements by comparing the coherent scattering intensity to the RPA form of the structure factor,[1−6] is found to follow the form $\chi_s = A/T + B$, where A and B depend on composition and molecular weight.[3−6] This can be contrasted with strict Flory−Huggins mean field theory, which assumes χ_s to be a constant divided by temperature, T. Further, the compositional dependence of χ_s has been found to be influenced by the chemical structure of the polymers. Many polyolefin based isotopic blends display a concave-up compositional dependence for χ_s,[2,3,6] while mixtures of polystyrene and deuterated polystyrene exhibit a concave-down compositional dependence for χ_s.[4,6]

The inability of Flory−Huggins mean field theory to capture the behavior of χ_s observed for isotopic blends has led to a number of new theoretical approaches. Dudowicz and Freed[7−9] have developed a lattice cluster theory (LCT) that perturbatively corrects the Flory−Huggins mean field theory. This approach allows for the modeling of complex monomeric units, and fluid compressibility is incorporated through the introduction of voids on the lattice. The free energy for the system is expanded in a double perturbation expansion in the bonding constraints, expressed in terms of the powers of the inverse of the lattice coordination number ($1/z$), and the attractive energies ($\epsilon_{\alpha\gamma}/k_BT$).[7] Calculations for binary blends to second order in both parameters are in qualitative agreement with many of the features observed in isotopic blends.[7−9] However, an attempt to model the compositional dependence of χ_s in isotopic polyethylene blends,[9] using interaction energies ($\epsilon_{\alpha\gamma}$) appropriate for isotopic mixtures, did not yield the concave-up behavior observed in recent experiments.[6] Schweizer, Curro, and co-workers[10−13] have developed an off-lattice theory for polymeric systems, referred to as PRISM theory, that is based on the reference interaction site model (RISM) theory for the structure and thermodynamics of molecular fluids, developed by Chandler and Andersen.[14,15] This theory includes contributions to χ_s derived from composition fluctuations, compressibility, and local liquid packing by solving the PRISM integral equation with some closure approximation.[11] Recently, Schweizer and Singh[12] have investigated the thermodynamics of polyolefin blends using PRISM theory and have highlighted a number of interesting findings, including a breakdown of the mean field theory for random copolymer blends and large deutration swap effects in random copolymer blends; although, the compositional dependence of χ_s was not considered in those studies. PRISM calculations[13] at meltlike densities have been performed, however, on "energetically symmetric blends", which are a simplified model for isotopic blends, and concave-up compositional dependence for χ_s was found, with the compositional dependence decreasing with increasing chain length. For chains consisting of 2500 segments at a temperature (characterized by $\chi_s N = 1.9$) fairly close to the critical temperature, χ_s varied by approximately 5% over the entire concentration range.[13] This is much smaller than the relative change of χ_s with composition observed in numerous measurements on polyolefin based isotopic blends.[2−6]

Recently, we have developed a theory[16,17] for the structure and thermodynamic properties of binary polymer blends that is a generalization of the optimized cluster theories for simple liquids and one component molecular systems.[18−21] The theory includes, in an approximate manner, fluctuation and compressibility effects, and chemical details that are responsible for local liquid packing can easily be incorporated in the theory. In ref 16, the theory was used to determine the compositional dependence of χ_s of model isotopic polyethylene mixtures at a single temperature and chain length for the two components. The predictions were found to be in reasonable agreement with the neutron scattering measurements of Londono et al.[6] Here we focus on the determination of the compositional depen-

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dence of χ_s as a function of chain length and temperature. The rest of the paper is organized as follows: In section II, the important aspects of the optimized cluster theory (OCT) of binary polymer blends are reviewed. Details of the theory were presented in two earlier publications.[16,17] The application of the OCT to isotopic polyethylene blends is described in section III and the compositional dependence of the effect SANS χ parameter, χ_s, is computed and then compared to neutron scattering measurements. Finally, the summary and conclusions are provided in section IV.

II. Theory

A. Optimized Cluster Theory of Binary Polymer Blends. For a binary mixture of two linear polymers, A and B, the OCT developed starts with the formally exact cluster expansions for the Helmholtz free energy, A, and pair correlation functions of a molecular mixture developed by Chandler and co-workers[22−24] within the interaction site formalism.[15,19] If polymers A and B have N_A and N_B interaction sites, respectively, there will be on the order of $N_A \times N_B$ independent pair correlation functions, $g_{mm'}^{(\alpha\gamma)}(|\mathbf{r}_{1,m}^{(\alpha)} - \mathbf{r}_{2,m'}^{(\gamma)}|) = h_{mm'}^{(\alpha\gamma)}(|\mathbf{r}_{1,m}^{(\alpha)} - \mathbf{r}_{2,m'}^{(\gamma)}|) + 1$, which give the intermolecular correlations between sites α and γ on polymers of type m and m′. The cluster expansions provide the various correlation functions and free energy in terms of an infinite series of diagrams involving the **f**-bonds and **s**-bonds, where **f**-bonds represent the Mayer functions

$$f_{mm'}(|\mathbf{r}_{i,m}^{(\alpha)} - \mathbf{r}_{j,m'}^{(\gamma)}|) = \exp[-\nu_{mm'}(|\mathbf{r}_{i,m}^{(\alpha)} - \mathbf{r}_{j,m'}^{(\gamma)}|)/k_B T] - 1 \quad (2.1)$$

$\nu_{mm'}(r)$ is the pair potential between sites α and γ on polymers i and j of type m and m′, respectively, and the **s**-bonds represent the various intrachain correlation functions, $\{s_{m,\alpha\beta\gamma...}^{(n/Nm)}(\mathbf{r}_{i,m}^{(\alpha)}, \mathbf{r}_{i,m}^{(\beta)}, \mathbf{r}_{i,m}^{(\gamma)}, ...)\}$, as previously defined.[16,17] The rules for constructing the diagrams in the cluster expansions were provided in one of our earlier publications.[16]

The key step in development of the optimized cluster theory (OCT) of polymer blends, is the separation of the pair potentials into the sum of a "reference potential", $\nu_{mm'}^{\circ}(r)$, which contains the harsh repulsions, and a "tail potential", $\nu_{mm'}^{tail}(r)$, that contains the more slowly varying part of the potential

$$\nu_{mm'}(r) = \nu_{mm'}^{\circ}(r) + \nu_{mm'}^{tail}(r) \quad (2.2)$$

Equation 2.2 was then used to rewrite the cluster expansions for $h_{mm'}^{(\alpha\gamma)}(r)$ and A in terms of the reference system Mayer functions, $\mathbf{f}^{\circ}$-bonds, the tail potentials, $\phi_{mm'}(r) = -\nu_{mm'}^{tail}(r)/k_B T$, and **s**-bonds. Next the *site averaging approximation*,[16] wherein the **s**-bonds were replaced by their average over all segments, was used to reduce the total number of pair correlation functions to 3 − 2 describing the correlations between like species ($h_{AA}(r)$ and $h_{BB}(r)$) and one for unlike species ($h_{AB}(r)$). A similar approximation has been employed in the PRISM theory of polymers and has been shown to accurately model the liquid structure,[10,11] even for fairly short chains.[25]

The new cluster expansions were then reduced through a series of topological reductions to yield an approximate theory, applicable to dense systems. Diagrams in A and $h_{mm'}(r)$ involving only $\mathbf{f}^{\circ}$-bonds were completely summed, to yield the reference system free energy, A_o, and pair correlation functions $h_{mm'}^{\circ}(r)$ (i.e. a system interacting only through the reference potentials) in the expansions for A and $h_{mm'}$, respectively.[16] $\mathbf{f}^{\circ}$-bonds still remaining in the cluster expansions were then eliminated in favor of reference system correlation functions, called $\mathbf{h}^{\circ}$-bonds, by summing subsets of diagrams involved only $\mathbf{f}^{\circ}$-bonds and **s**-bonds. This step was accomplished in a diagrammatically proper fashion (i.e., sum only allowed diagrams in the various cluster expansions), by introducing the Chandler, Silbey, and Landanyi[26] decomposition of the site−site pair correlation function for molecular systems

$$h_{mm'}^{\circ}(r) = h_{mm',aa}^{\circ}(r) + h_{mm',as}^{\circ}(r) + h_{mm',sa}^{\circ}(r) + h_{mm',ss}^{\circ}(r) \quad (2.3)$$

where the definitions of the components of $h_{mm'}^{\circ}$ can be found elsewhere.[16,22]

Following the OCT developed for atomic mixtures and single component molecular systems, the cluster expansions were further reduced by summing "ring diagrams" in A involving ϕ, $\mathbf{h}^{\circ}$, and $\mathbf{s}^{(2)}$-bonds ($\mathbf{s}^{(2)}$-bonds are the average two-point intrachain correlation functions). This contribution was labeled a_{RING}. The analogous set of diagrams in $h_{mm'}(r)$ correspond to chain diagrams containing ϕ, $\mathbf{h}^{\circ}$, and $\mathbf{s}^{(2)}$-bonds which were denoted $C_{mm'}(r)$. Again to make the theory proper, $C_{mm'}(r)$ was decomposed in a manner analogous to that employed for $h_{mm'}^{\circ}$:

$$C_{mm'}(|\mathbf{r}_{1,m} - \mathbf{r}_{2,m'}|) = C_{mm',aa}(|\mathbf{r}_{1,m} - \mathbf{r}_{2,m'}|) + C_{mm',as}(|\mathbf{r}_{1,m} - \mathbf{r}_{2,m'}|) + C_{mm',sa}(|\mathbf{r}_{1,m} - \mathbf{r}_{2,m'}|) + C_{mm',ss}(|\mathbf{r}_{1,m} - \mathbf{r}_{2,m'}|) \quad (2.4)$$

where the notation is similar to that used in the decomposition of $h_{mm'}^{\circ}$.

After these steps, the cluster expansion for the free energy could be written as[16]

$$A = A_o + a_{HTA} + a_{RING} + \Delta A \quad (2.5)$$

where A_o is the free energy of the mixture interacting solely through the reference potentials, a_{RING} is the contribution to the mixture free energy from the ring diagrams, a_{HTA} is referred to as the "high temperature approximation"[19]

$$Va_{HTA} = \frac{1}{2}\sum_{mm'}\int \hat{\rho}_m \hat{\rho}_{m'} [h_{mm'}^{\circ}(|\mathbf{r}_1 - \mathbf{r}_2|) + 1] \times \phi_{mm'}(|\mathbf{r}_1 - \mathbf{r}_2|)\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (2.6)$$

where $\hat{\rho}_m$ is the segment density of polymer m and V is the system volume. ΔA, in eq 2.5, contains all other diagrams in the formally exact cluster expansion for A not included in the first three terms, and a_{RING} was determined to be[16,17]

$$a_{RING} = -\frac{1}{2}\frac{1}{(2\pi)^3}\int d\mathbf{k}(\mathrm{Tr}\{[\underline{\underline{\rho}} + \underline{\underline{\rho}}(\underline{\underline{\hat{h}}}^{o}(k) + \underline{\underline{\hat{s}}}(k))\,\underline{\underline{\rho}}]\underline{\underline{\hat{\phi}}}(k)\} + \ln \det\{\underline{\underline{I}} - [\underline{\underline{\rho}} + \underline{\underline{\rho}}(\underline{\underline{\hat{h}}}^{o}(k) + \underline{\underline{\hat{s}}}(k))\underline{\underline{\rho}}]\underline{\underline{\hat{\phi}}}(k)\}) \quad (2.7)$$

where $\underline{\underline{\rho}}$, $\underline{\underline{\hat{h}}}^{o}(k)$, $\underline{\underline{\hat{s}}}(k)$, and $\underline{\underline{\hat{\phi}}}(k)$ are matrices whose definitions are given in the next subsection. Similarly, the Fourier transform of pair correlation functions were given by

$$\hat{h}_{\mathrm{mm'}}(k) = \hat{h}^{\circ}_{\mathrm{mm'}}(k) + \hat{C}_{\mathrm{mm',aa}}(k) + \hat{C}_{\mathrm{mm',as}}(k) + \hat{C}_{\mathrm{mm',sa}}(k) + \hat{C}_{\mathrm{mm',ss}}(k) + \Delta\hat{h}_{\mathrm{mm'}}(k) \quad (2.8)$$

where the components of $\hat{C}_{\mathrm{mm'}}(k)$ can be obtained from the matrix[16]

$$\underline{\underline{\hat{C}}}(k) = (\underline{\underline{\mathrm{I}}} + \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)\ \underline{\underline{\rho}})\underline{\underline{\hat{\phi}}}(k) \times [\underline{\underline{\mathrm{I}}} - (\underline{\underline{\rho}} + \underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)\ \underline{\underline{\rho}})\underline{\underline{\hat{\phi}}}(k)]^{-1}\ (\underline{\underline{\mathrm{I}}} + \underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)) \quad (2.9)$$

Approximate expressions for A and $h_{\mathrm{mm'}}(r)$ were then obtained by neglecting ΔA and $\Delta\hat{h}_{\mathrm{mm'}}(k)$ in eqs 2.5 and 2.8, respectively. This step leads to nonzero values for the pair correlation functions, $g_{\mathrm{mm'}}(r) = h_{\mathrm{mm'}}(r) + 1$, at physically unallowed separations.[16] To correct for this deficiency, the customary procedure in optimized cluster theories is to employ the optimization scheme introduced by Andersen and Chandler.[18] When $\nu^{\circ}_{\mathrm{mm'}}(r)$ is a hard core potential,[19] characterized by the hard core diameter, $d_{\mathrm{mm'}}$, the expressions for A and $g_{\mathrm{mm'}}(r)$ should not be affected by the value of the tail potentials in the hard core region, $r < d_{\mathrm{mm'}}$. $g_{\mathrm{mm'}}(r)$ can be made zero for $r < d_{\mathrm{mm'}}$ by adjusting the values of the tail potentials for $r < d_{\mathrm{mm'}}$.[16,18]

The form of the OCT presented here could be used to solve for the structure and thermodynamics of polymer blends. However, for the structurally symmetric polymer blends considered in the present investigation, it is computationally more convenient to exploit the equivalence of OCT with a set of diagrammatically proper integral equations. Details on the development of the diagrammatically proper integral equation for polymer mixtures are provided in the next subsection.

B. Equivalent Diagrammatically Proper Integral Equations. Another method for predicting the structure and thermodynamics of polymer mixtures is to develop a diagrammatically proper integral theory for the system pair correlation functions. Chandler, Silbey, and Ladanyi (CSL)[26] developed an integral equation theory for single component molecular systems that is based on the topological reduction of the formally exact cluster expansions for the pair correlation functions. Their approach was to define the total direct correlation function between sites α and γ on different molecules, $c^{(\alpha\gamma)}(r)$, as the sum of all nodeless diagrams in the cluster expansion for the total correlation function $h^{(\alpha\gamma)}(r)$. $c^{(\alpha\gamma)}(r)$ was introduced to reduce the expansions for $h^{(\alpha\gamma)}(r)$ into the sum of chain diagrams involving the direct correlation functions and the various intramolecular correlation functions, $s^{(2/N_{\mathrm{m}})}_{\mathrm{m},\alpha\gamma}(r)$.[26] In order to make this reduction diagrammatically proper, Chandler et al. had to decompose $h^{(\alpha\gamma)}(r)$ into the four components, $h^{(\alpha\gamma)}_{\mathrm{aa}}(r)$, $h^{(\alpha\gamma)}_{\mathrm{as}}(r)$, $h^{(\alpha\gamma)}_{\mathrm{sa}}(r)$, and $h^{(\alpha\gamma)}_{\mathrm{ss}}(r)$ as described in the last subsection. It also proved necessary in their development to decompose $c^{(\alpha\gamma)}(r)$ into four parts, $c^{(\alpha\gamma)}_{\mathrm{aa}}(r)$, $c^{(\alpha\gamma)}_{\mathrm{as}}(r)$, $c^{(\alpha\gamma)}_{\mathrm{sa}}(r)$, and $c^{(\alpha\gamma)}_{\mathrm{ss}}(r)$, where the subscripts on components of $c^{(\alpha\gamma)}(r)$ have the same meaning as discussed for $h_{\mathrm{mm'}}$. With this decomposition for $c^{(\alpha\gamma)}(r)$ and $h^{(\alpha\gamma)}(r)$, Chandler et al. were able to derive a set of integral equations for the four components of $h^{(\alpha\gamma)}(r)$.[26]

It is straightforward to extend this approach to molecular mixtures. For the binary mixture of two linear homopolymers described above, after applying the site averaging approximation, the Fourier transform of corresponding CSL equations is given by

$$\underline{\underline{\hat{\mathrm{h}}}}(k) = \underline{\underline{\hat{\mathrm{c}}}}(k) + \underline{\underline{\hat{\mathrm{c}}}}(k)\underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{s}}}}(k) + \underline{\underline{\hat{\mathrm{s}}}}(k)\underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{h}}}}(k) + \underline{\underline{\hat{\mathrm{c}}}}(k)\underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{h}}}}(k) \quad (2.10)$$

where the matrices $\underline{\underline{\hat{\mathrm{h}}}}(k)$, $\underline{\underline{\hat{\mathrm{c}}}}(k)$, and $\underline{\underline{\rho}}$ are given by

$$\underline{\underline{\hat{\mathrm{h}}}}(k) = \begin{bmatrix} \underline{\underline{\hat{\mathrm{h}}}}_{\mathrm{AA}}(k) & \underline{\underline{\hat{\mathrm{h}}}}_{\mathrm{AB}}(k) \\ \underline{\underline{\hat{\mathrm{h}}}}_{\mathrm{BA}}(k) & \underline{\underline{\hat{\mathrm{h}}}}_{\mathrm{BB}}(k) \end{bmatrix} \quad \text{with submatrices}$$

$$\underline{\underline{\hat{\mathrm{h}}}}_{\mathrm{mm'}}(k) = \begin{bmatrix} \hat{h}_{\mathrm{mm'aa}}(k) & \hat{h}_{\mathrm{mm'as}}(k) \\ \hat{h}_{\mathrm{mm'sa}}(k) & \hat{h}_{\mathrm{mm'ss}}(k) \end{bmatrix} \quad (2.11)$$

$$\underline{\underline{\hat{\mathrm{c}}}}(k) = \begin{bmatrix} \underline{\underline{\hat{\mathrm{c}}}}_{\mathrm{AA}}(k) & \underline{\underline{\hat{\mathrm{c}}}}_{\mathrm{AB}}(k) \\ \underline{\underline{\hat{\mathrm{c}}}}_{\mathrm{BA}}(k) & \underline{\underline{\hat{\mathrm{c}}}}_{\mathrm{BB}}(k) \end{bmatrix} \quad \text{with}$$

$$\underline{\underline{\hat{\mathrm{c}}}}_{\mathrm{mm'}}(k) = \begin{bmatrix} \hat{c}_{\mathrm{mm'aa}}(k) & \hat{c}_{\mathrm{mm'as}}(k) \\ \hat{c}_{\mathrm{mm'sa}}(k) & \hat{c}_{\mathrm{mm'ss}}(k) \end{bmatrix} \quad (2.12)$$

$$\underline{\underline{\rho}} = \begin{bmatrix} \underline{\underline{\rho}}_{\mathrm{A}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\rho}}_{\mathrm{B}} \end{bmatrix} \quad \text{with} \quad \underline{\underline{\rho}}_{\mathrm{m}} = \begin{bmatrix} \hat{\rho}_{\mathrm{m}} & \hat{\rho}_{\mathrm{m}} \\ \hat{\rho}_{\mathrm{m}} & 0 \end{bmatrix} \quad (2.13)$$

In eq 2.13, $\hat{\rho}_{\mathrm{m}}$ is the site density of polymer m, and $\underline{\underline{0}}$ is a 2 × 2 null submatrix. The matrix $\underline{\underline{\hat{\mathrm{s}}}}(k)$ in eq 2.10 is given by

$$\underline{\underline{\hat{\mathrm{s}}}}(k) = \begin{bmatrix} \underline{\underline{\hat{\mathrm{s}}}}_{\mathrm{A}}(k) & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\hat{\mathrm{s}}}}_{\mathrm{B}}(k) \end{bmatrix} \quad \text{with} \quad \hat{\mathrm{s}}_{\mathrm{m}}(k) = \begin{bmatrix} 0 & 0 \\ 0 & \hat{\mathrm{s}}_{\mathrm{m}}(k) \end{bmatrix} \quad (2.14)$$

where $\hat{\mathrm{s}}_{\mathrm{m}}(k)$ is the average two-point intrachain correlation function

$$\hat{s}_{\mathrm{m}}(k) = \frac{1}{N_{\mathrm{m}}}\sum_{\alpha,\gamma}^{N_{\mathrm{m}}}(1 - \delta_{\alpha\gamma})\ \hat{s}^{(2/\mathrm{Nm})}_{\mathrm{m},\alpha\gamma}(k)/\hat{\rho}_{\mathrm{m}} \quad (2.15)$$

In order to solve eq 2.10 for the components of the total correlation function matrix, a closure relation, relating the components of the correlation function matrices, $\underline{\underline{\mathrm{c}}}(r)$ and $\underline{\underline{\mathrm{h}}}(r)$, and the pair potentials are required.

To develop a diagrammatically proper integral equation theory from eq 2.10 that is equivalent to the OCT discussed in section II.A., eq 2.10 was first used to determine the correlation functions with respect to the reference system of hard core chains. Defining $\delta\underline{\underline{\hat{\mathrm{h}}}}(k) = \underline{\underline{\hat{\mathrm{h}}}}(k) - \underline{\underline{\hat{\mathrm{h}}}}{}^{\circ}(k)$, $\delta\underline{\underline{\hat{\mathrm{c}}}}(k) = \underline{\underline{\hat{\mathrm{c}}}}(k) - \underline{\underline{\hat{\mathrm{c}}}}{}^{\circ}(k)$, and $\underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k) = \underline{\underline{\hat{\mathrm{h}}}}{}^{\circ}(k) + \underline{\underline{\hat{\mathrm{s}}}}(k)$, where $\underline{\underline{\hat{\mathrm{h}}}}{}^{\circ}(k)$ and $\underline{\underline{\hat{\mathrm{c}}}}{}^{\circ}(k)$ are the Fourier transforms of the correlation function matrices for the reference system, eq 2.15 can be rewritten as

$$\delta\underline{\underline{\hat{\mathrm{h}}}}(k) = (\underline{\underline{\mathrm{I}}} + \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)\ \underline{\underline{\rho}})\delta\underline{\underline{\hat{\mathrm{c}}}}(k)[\underline{\underline{\mathrm{I}}} - (\underline{\underline{\rho}} + \underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)\ \underline{\underline{\rho}})\delta\underline{\underline{\hat{\mathrm{c}}}}(k)]^{-1}\ (\underline{\underline{\mathrm{I}}} + \underline{\underline{\rho}}\ \underline{\underline{\hat{\mathrm{H}}}}{}^{\circ}(k)) \quad (2.16)$$

If the following closure relations

$$\delta h_{\mathrm{mm',aa}}(r) = \delta h_{\mathrm{mm',as}}(r) = \delta h_{\mathrm{mm',sa}}(r) = \delta h_{\mathrm{mm',ss}}(r) = 0 \quad \text{for } r < d_{\mathrm{mm'}}$$

and

$$\delta c_{\mathrm{mm',aa}}(r) = \phi_{\mathrm{mm',aa}}(r) \quad \text{for } r \geq d_{\mathrm{mm'}}$$

$$\delta c_{\mathrm{mm',as}}(r) = \delta c_{\mathrm{mm',sa}}(r) = \delta c_{\mathrm{mm',ss}}(r) = 0 \quad \text{for } r \geq d_{\mathrm{mm'}} \quad (2.17)$$

are used to solve eq 2.16, it can be demonstrated that the diagrams summed in $\delta\underline{\underline{\hat{\mathrm{h}}}}(k)$ are identical to those included in $\underline{\underline{\hat{C}}}(k)$ of the optimized cluster theory.[16] Finally, by extending the method of Høye and Stell[28] to the current problem, it is also possible to verify that the free energy obtained from the solution of eqs 2.5 through

2.7 is identical to that provided from the OCT, provided the matrix $\underline{\underline{\hat{\phi}}}(k)$ is identified with $\delta\underline{\underline{\hat{c}}}(k)$.[16,17] Note that the inputs to the theory are the pair potentials, the two-point intrachain correlation functions, and the reference system correlation function matrix, $\underline{\underline{\hat{h}}}^{\circ}(k)$. The OCT should accurately describe the liquid structure and thermodynamics at high densities, where the effect of the tail potential does not alter the liquid structure significantly over that of the reference system. For atomic fluids, the convergence of the analogous cluster expansions has been examined, and it was shown,[18] for a short ranged tail potentials, that the OCT is correct in the limit of high density and/or high temperature. A similar analysis for the polymer OCT, employed here and developed in our earlier work,[16,17] would also demonstrate an increase in accuracy of the theory with increasing density and temperature—by construction (through eq 2.6) the theory reproduces the correct high temperature limit. The calculations for the isotopic polyethylene mixtures presented here are for dense melts; therefore, the OCT should accurately describe the system thermodynamics. A check of the system correlation functions, $g_{\mathrm{mm}'}(r)$, against the reference system correlation functions verified that the structure did not change significantly with respect to the reference system. However, systematic errors are introduced into any OCT calculations which employ reference system correlation functions determined from some approximate theory, as was done in the present study.

In the next section, the theory is applied to model isotopic polyethylene mixtures to determine the effective χ parameter, χ_s, as a function of composition, chain length, and temperature. Equations 2.16 and 2.17 were solved using the Picard iteration method[19] over 8192 equally spaced points in both real space and Fourier space. The grid spacings were 0.1 Å in real space and 3.8349×10^{-3} Å^{-1} in Fourier space.

C. Model for Isotopic Polyethylene Mixtures. Details of the model used for the isotopic polyethylene mixture were presented previously.[16] The CH_2 (H) and CD_2 (D) groups were represented by spherical sites with hard core diameter, d. We ignored the small size difference between the two repeat units that occurs with deuteration. The distance between the centers of adjacent sites on the chains, a, was taken to be the carbon−carbon bond distance, 1.54 Å. The total site density in the mixtures, $\hat{\rho}_T$, was fixed at 0.03354 Å^{-3}. This corresponds to a melt density of 0.7796 g/cm^3 at $T = 430$ K and ambient pressure.[6] We neglected the slight variation of $\hat{\rho}_T$ over the temperature range considered here and used this value for all calculations. The number of segments comprising the normal and perdeuterated chains were taken to be equivalent (i.e. $N_H = N_D = N$) for all the calculations reported here, since the solution of eqs 2.16 and 2.17 are much more computationally intensive when structural asymmetries are introduced.

The various two-point intrachain correlation functions, $s_{\mathrm{m},\alpha\gamma}^{(2/N_\mathrm{m})}(r)$, in $\hat{s}_\mathrm{m}(k)$ of eq 2.15, were approximated by a model previously employed in the calculation of the structure factor[29] and equation of state[30] in polyethylene melts. For sites separated by five bonds or less ($|\alpha - \beta| \leq 5$), $s_{\mathrm{m},\alpha\gamma}^{(2/N_\mathrm{m})}(r)$ was determined from an exact RIS calculation with the “pentane effect” included. For bonds separated by more than five bonds, the Koyama semiflexible chain model[31] was utilized, where the second and fourth moments of the vector distance between sites α and γ, $\langle R_{\alpha\gamma}^2\rangle$ and $\langle R_{\alpha\gamma}^4\rangle$ respectively, were specified from RIS calculations on polyethylene chains. Further details of this model and the parameters used in this part of the calculation can be found elsewhere.[16] The temperature, T, was fixed at 430 K for the RIS calculations. We expect this to have only a small effect on the compositional dependence χ_s over the temperature range considered, since the root mean squared radius of gyration, R_g, of the chains change by only approximately 2% over $T = 430$ K to $T = 473$ K.

Lennard−Jones potentials were used to model the interactions between pairs of sites on different chains

$$\nu_{\mathrm{mm}'}^{\mathrm{LJ}}(r) = 4\epsilon_{\mathrm{mm}'}\left[\left(\frac{\sigma_{\mathrm{mm}'}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{mm}'}}{r}\right)^{6}\right] \qquad (2.18)$$

where $\epsilon_{\mathrm{mm}'}$ and $\sigma_{\mathrm{mm}'}$ are the well-depth and position where the potential is zero for interactions species m and m′ respectively. To transform eq 3.1 into the form required by the optimized cluster theory, the Barker−Henderson (BH) approximation was implemented.[32] This leads to

$$\nu_{\mathrm{mm}'}^{\mathrm{tail}}(\mathrm{r}) = \nu_{\mathrm{mm}'}^{\mathrm{LJ}}(\mathrm{r}) \qquad (2.19)$$

while the hard core diameter, d, was fixed at 3.90 Å, which was the value estimated from previous theoretical calculations of the structure factor of homopolymer polyethylene melt at $T = 430$ K using PRISM theory. This value of d has been shown to be consistent with geometric calculations of the volume of a single CH_2 group. Strictly speaking, within the BH approximation, d should depend on temperature and the use of a single d would likely break down if a wide range of temperatures were considered. However, we limited the present calculations to $T = 443$ and 473 K and leave the temperature dependence of d for future work.

For the parameters describing the interactions between the other species in the blend, we made the following approximations: First, the small variation in the position of the position of the bottom of the potential well, associated with replacing the hydrogen with deuterium, was ignored, and σ_{DD} was set equal to σ_{HH}. The Lorentz−Berthelot combination rules[19] were then used to specify the parameters describing the interactions between the CH_2 and CD_2 sites. This results in setting $\sigma_{HD} = \sigma_{HH}$ and having the well depth parameters related by

$$\epsilon_{HD} = (\epsilon_{HH}\epsilon_{DD})^{1/2} \qquad (2.20)$$

This approximation is expected to accurately describe isotopic mixtures where the difference in interaction energies between the various components derives principally from the difference in the bond polarizabilities.[1] Again, to minimize the number parameters in the model, we also used the values $\epsilon_{HH} = 38.7$ K and $\sigma_{HH} = 4.37$ Å obtained for the calculations on polyethylene melts at 430 K.[24,25] This left only one parameter, ϵ_{DD} or ϵ_{HD}, undetermined in the model. This parameter was determined by adjusting ϵ_{DD} such that the critical temperature, T_c, predicted by OCT matched the value from neutron scattering measurements with $N = 8746$ and $\phi_D = 0.5$.[16]

In section III, results are presented for mixtures at $T = 443$ and 473 K, with 443 K being one of the temperatures considered in the measurements of Londono et al.[6] The model parameters specified at 430 K were used for all the calculations reported here (i.e., $T = 443$ and 473 K). We did this for two reasons: (1) Over the temperature range from 430 to 473 K the root mean squared radius of gyration of the polyethylene chains, R_g, were determined—within the RIS model used for the intrachain correlation functions—to change by only approximately 2%. For the measurements[6] we compared the calculations to, the experimental error in R_g is larger than this variation. (2) As mentioned above, the hard core diameter of the united atom monomers, d, is temperature dependent in the BH approximation. At present, we do not know how well the BH approximation works for the temperature dependence of d when modeling polymeric systems. Therefore, to avoid introducing additional unknown errors through this temperature dependence, we ignored any temperature dependence of the model parameters. However, over the narrow range of temperatures considered, d should change only slightly.

Finally the reference system correlation functions needed to solve eqs 2.16 and 2.17 were calculated using PRISM integral equation theory[10,11] by exploiting the physical interpretation of the various components of the reference correlation function matrix, $\underline{\underline{\hat{h}}}^{\circ}(k)$.[16] Details of this part of the calculation can be found elsewhere.[16] It should be noted that these reference system correlation functions could also be obtained from computer simulations of hard sphere chains.

To facilitate making contact with the measurements of Londono et al., we determined the effective SANS interaction parameter, χ_s, using in the following expression relating the zero-angle scattering cross section, $(d\Sigma^{coh}/d\Omega)(k = 0)$, to the partial structure factors[33]

$$\frac{d\Sigma^{coh}}{d\Omega}(k = 0) = \sum_{m,m'} b_m b_{m'} \hat{S}_{mm'}(k = 0) \qquad (2.21)$$

where b_m is the total scattering length of segment of type m. $\hat{S}_{mm'}(k)$ is the partial structure factor between sites of species m and m′ and is given by

$$\hat{S}_{mm'}(k) = \hat{\rho}_m[1 + \hat{s}_m(k)]\delta_{mm'} + \hat{\rho}_m\hat{\rho}_{m'}[\hat{h}^{\circ}_{mm'}(k) + \delta\hat{h}_{mm'}(k)] \qquad (2.22)$$

where $\hat{s}_m(k)$ is the Fourier transform of the average two-point intrachain correlation function, $s_m(r)$. By equating the expression for $(d\Sigma^{coh}/d\Omega)(k)$ to the incompressible-RPA (iRPA) form for the structure factor

$$\frac{d\Sigma^{coh}}{d\Omega}(k = 0) = \left(\frac{b_H}{V_H} - \frac{b_D}{V_D}\right)^2 \hat{S}_{RPA}(k = 0) \qquad (2.23)$$

with

$$\frac{1}{\hat{S}_{RPA}(k=0)} = \frac{1}{\phi_H N_H V_H} + \frac{1}{\phi_D N_D V_D} - 2\frac{\chi_s}{V_o} \qquad (2.24)$$

χ_s, was calculated in a manner similar to that used in neutron scattering measurements. In eq 2.24 V_m is the volume of segment m ($V_m = (\pi/6)d^3$) which is 31.06 Å^3 long and V_o, the reference volume, was set equal to the segment volume. With this definition for χ_s, all corrections to mean field theory due to compositional fluctuations, compressibility, and local liquid packing are lumped into χ_s. For isotopic polyethylene mixtures, the non mean field contributions to χ_s appear to have only a small effect on the location of the binodals—the binodal curve is rather insensitive to the compositional dependence of χ_s.[34] Therefore, the calculation of the compositional dependence of χ_s from eqs 2.21 to 2.24, instead of the determination of the binodals, followed by a comparison to experiment should provide a very sensitive means to evaluate the accuracy of the various theories for polymer blends. In addition, with χ_s determined in the manner described above, we found that the RPA form for the coherent scattering intensity, $(d\Sigma^{coh}/d\Omega)(k)$, yields a reasonable fit to $(d\Sigma^{coh})/d\Omega)(k)$ determined from the OCT, over the range of k values considered in the experimental investigations of Londono et al. (0.005−0.04 Å^{-1}).[6] However, we did notice that the calculated $(d\Sigma^{coh}/d\Omega)(k)$ generally decays faster than the RPA form over the range 0.005 Å^{-1} $< k <$ 0.04 Å^{-1}. This faster decay of $(d\Sigma^{coh}/d\Omega)(k)$ could be attributed to using the Koyama semiflexible chain model—whose intrachain correlation functions have a stronger k dependence than the Gaussian chain correlation functions (i.e. Debye functions) in the RPA expression—to approximate the intrachain correlation functions in eq 2.15 with $|\alpha - \gamma| > 5$. We anticipate that if the RIS model were used for all the intrachain correlation functions, the decay of $(d\Sigma^{coh}/d\Omega)(k)$ would more closely resemble the RPA form for the coherent scattering intensity, since Yoon and Flory[35] have shown that the segment−segment distribution functions for polyethylene, calculated from the RIS model, follow nearly Gaussian behavior for chains with more than 50 segments.

III. Results and Discussions

Previous work[16] established reasonable agreement with experiment for the compositional dependence of χ_s at a single temperature and molecular weight, although the theory was found to underestimate the upturn in χ_s at the compositional extremes. We now consider the molecular weight dependence of χ_s and further explore the compositional and temperature dependence of χ_s.

Figure 1 shows predictions of the theory for χ_s as a function of the volume fraction of the deuterated species, ϕ_D, for three different chain lengths, $N = 3290$, 5220, and 8749, and $T = 443$ and 473 K. In addition to exhibiting concave-up compositional dependence, χ_s was also found to display a chain length dependence. Both predictions have been observed in the neutron scattering measurements of Londono et al.[6] The curves appearing in Figure 1 correspond to fits to the expression

$$\chi_s = \beta(T,N) + \frac{\gamma(T,N)}{\phi_D(1 - \phi_D)} \qquad (3.1)$$

which was proposed by Krishnamoorti et al.[36] to fit experimental data on isotopic mixtures of ethylene-butene-1 copolymers. It can be seen from this figure that eq 3.1 provides a very good fit to the calculated χ_s over the entire range of composition. The coefficients, β and γ, in eq 3.1 corresponding to the conditions investigated are provided in Table 1. The trends observed for γ—γ is independent of temperature but varies with N—are in agreement with experiments; however, the predicted values obtained for γ from our theory are approximately an order of magnitude lower than that found in the measurements of Londono and co-workers.[6] Their experimental data suggest a weak

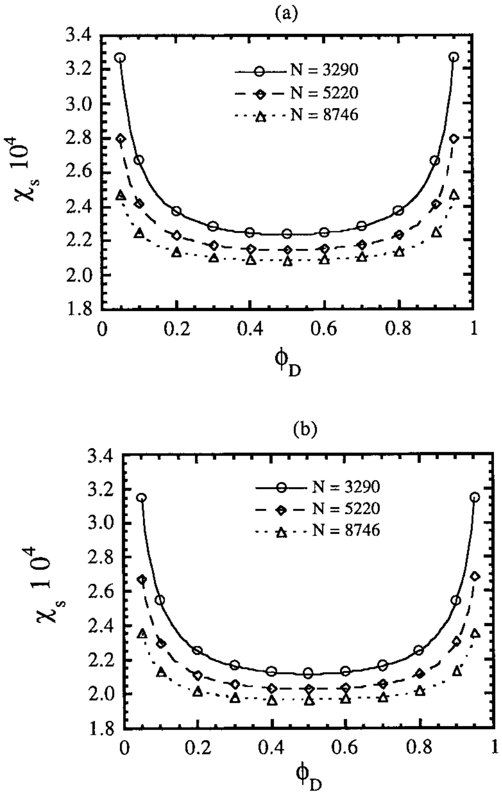

Figure 1. Calculated effective SANS interaction parameter, χ_s, as a function of the volume fraction of deuterated polyethylene, ϕ_D, in the isotopic mixture for $N = 3290$ (—○—), 5220 (– ◇ –), and 8749 (- -△- -). Results for (a) $T = 443$ K and (b) $T = 473$ K, where the curves correspond to fits to eq 3.1.

Table 1. β and γ from Eq 3.1 as a Function of Chain Length, *N*, for $T = 443$ and 473 K

	$T = 443$ K		$T = 473$ K	
N	$\beta \times 10^4$	$\gamma \times 10^4$	$\beta \times 10^4$	$\gamma \times 10^4$
3290	1.996	0.0606	1.875	0.0605
5290	1.998	0.0380	1.876	0.0381
8749	1.999	0.0226	1.877	0.0226

molecular weight dependence to β, although no clear trend was identified. From the present calculations, we found no N dependence to β over the range of chain lengths studied. The values of β are in fairly good agreement with the experiments, but wider ranges of temperatures need to be considered in the future to ascertain the functional form of temperature dependence of β. Finally, parts a and b of Figure 1 show that as ϕ_D approaches the extremes in concentration (i.e. 0 or 1), χ_s decreases with increasing temperature, also in agreement with numerous measurements on isotopic blends.[6,34]

The concave up compositional dependence to χ_s can be considered to be derived from concentration fluctuations in the system. From the theory of critical phenomena,[37] it is known that the addition of composition fluctuations will stabilize a system relative to the mean-field situation (i.e. move the system further away from the spinodal point). This implies that fluctuations will reduce the effective interaction parameter, χ_s, in the blend system. In addition, fluctuation effects are more pronounced for temperatures closer to the spinodal line—the correlation length for the composition fluctuations increases as the spinodal is approached and diverges at the spinodal.[38] For a binary mixture of structurally symmetric polymers, such as the isotopic polyethylene system studied here, as the composition is varied from $\phi_D = 0.5$ at constant temperature the system moves further away from the spinodal line. Therefore, the fluctuation effects will be diminished as the compositional extremes, $\phi_D = 0$ or 1, are approached and χ_s will increase in these limits. To quantify the role compressibility has on the compositional dependence of χ_s within the OCT used here, we will need to determine χ_s as a function of total monomer density. We plan to do this in the near future.

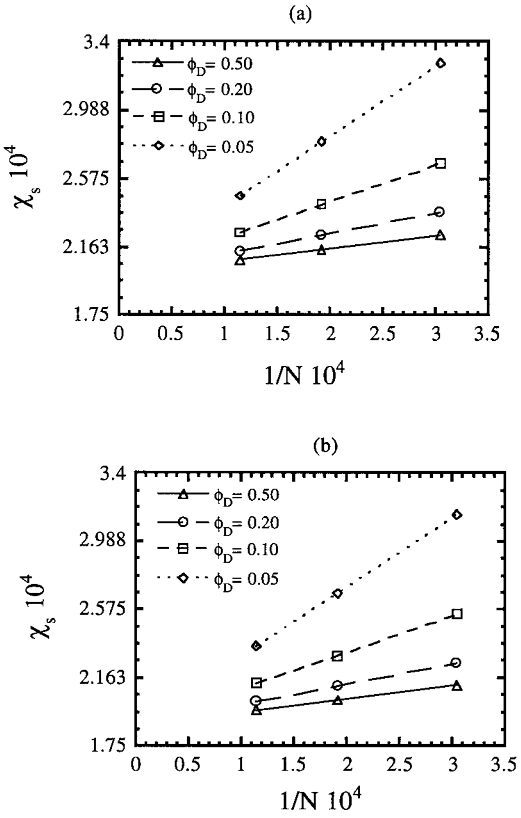

Figure 2. Calculated χ_s as a function of 1/N for four blend compositions: $\phi_D = 0.50$ (—△—), $\phi_D = 0.20$ (– ○ –), $\phi_D = 0.10$ (– □ –), and $\phi_D = 0.05$ (- -◇- -). Results are given for (a) $T = 443$ K and (b) $T = 473$ K.

Further examination of the chain length dependence for the calculated χ_s, obtained from a "best fit" of the calculated χ_s to the function form, $\chi_s = \chi_s(\infty) + D/N$, revealed χ_s to be proportional to $1/N$. Figure 2 gives a plot χ_s as a function of $1/N$. This predicted N dependence agrees with the reanalysis of the isotopic polyethylene blend data of Londono et al. performed by Crist.[39] We also found that in the long chain limit ($N \rightarrow \infty$), where compositional fluctuations are expected to be negligible based on the Ginzburg criterion,[38,40] χ_s does not approach the mean field value, χ_o, for either temperature considered. In this limit, χ_s was found to be approximately 4% lower than χ_o, suggesting that fluid compressibility and monomer packing renormalize the interactions even in the long chain limit. This result is in qualitative agreement with the lattice cluster theory (LCT) of Dudowicz and Freed.[7,8]

The predictions of the OCT for the composition and chain length dependence of χ_s can be contrasted with other investigations of model isotopic blends. PRISM calculations using molecular closures,[13] at meltlike densities have been performed on "energetically symmetric blends" (a simplified model for isotopic blends) and a concave up compositional dependence for χ_s was found. In addition, the compositional dependence was found to decrease with increasing chain length, although the quantitative dependence of χ_s with N at constant temperature was not determined in the PRISM study. Further, for chains consisting of 2500 segments at a temperature (characterized by $\chi_s N|_{\phi_D=0.5} = 1.9$) fairly close to the spinodal temperature, χ_s varied by approximately 5% over the entire composition range.[13] This is much smaller than the relative change of χ_s with composition observed in numerous measurements on polyolefin based isotopic blends.[2-6] The PRISM results can also be contrasted with the predictions of the OCT shown in parts a and b of Figure 1. OCT predicts a substantial increase in χ_s as the compositional extremes are approached for much lower values of $\chi_s N$ or much larger chain lengths—results in Figure 1(a) at $T = 443$ K correspond to $\chi_s N|_{\phi_D=0.5} = 1.827$ ($N = 8746$), $\chi_s N|_{\phi_D=0.5} = 1.123$ ($N = 5220$), and $\chi_s N|_{\phi_D=0.5} = 0.7367$ ($N = 3290$)—than considered in the PRISM calculations. The results of the OCT also show that compositional dependence of χ_s increases as the temperature is lowered and/or the molecular weight is decreased at constant T; therefore, it is expected that the compositional dependence of χ_s would increase noticeably if temperatures corresponding to $\chi_s N|_{\phi_D=0.5} = 1.9$ and chain lengths close to 2500 segments are considered. It should be noted that the PRISM calculations employed a different method to determine χ_s than that used in the present study—the collective structure factor for the mixture was used to extract χ_s from eq 2.24 in ref 13—and it is possible that this could lead to lower than expected values for χ_s. Finally, an attempt to model the compositional dependence of χ_s in isotopic polyethylene blends,[9] using the LCT with interaction energies ($\epsilon_{\alpha\gamma}$) appropriate for isotopic mixtures were unable to yield concave up compositional dependence to χ_s as was found in neutron scattering measurements[6] and was found here using the OCT. Although, χ_s was determined using the same formalism described in section II.C., the experimental total scattering lengths (i.e., b_m in eqs 2.21 and 2.23) for the normal and deuterated methylene groups were not employed in these LCT calculations. Instead, these authors assumed that there was "complete scattering contrast" between the two monomers (only monmers of one type scatter).[9] This could be the source of the concave down compositional dependence predicted in the LCT calculations.

IV. Conclusions

The effective SANS χ parameter, χ_s, for model isotopic polyethylene blends was calculated using our recently developed optimized cluster theory for polymer mixtures. The theory includes in an approximate fashion corrections to mean field theory arising from density and composition fluctuations, local monomer packing, and chain correlations. We found that the calculated compositional and chain length dependence of χ_s is in fairly good agreement with experiment; however, the magnitude of χ_s at the extremes in composition is approximately an order of magnitude lower than the experimental values. This discrepancy between the calculated and experimental values could be attributed to a number of simplifications employed here. First, to reduce the computational effort, we only considered symmetric chain length for the two blend species. The experiments of Londono et al. contained slightly asymmetric chain lengths for the deuterated and hydrogenated species. It has been established from within the LCT that polymer mixtures become more compressible as the amount of structural asymmetry increases, and this leads to an additional entropic contribution to χ_s.[7] The role that structural asymmetries have on the thermodynamic properties of polymer blends, within the present theoretical framework, will be the subject of future work. Also, we ignored the temperature dependence of the average size of the polymer in the calculation of the intrachain correlation function, $s(k)$. Monte Carlo[41] simulations of symmetric (A/B) binary blends, where the relative amount of B is low, have established that dimensions of the polymer chains decrease as the temperature is lowered, with this effect being more pronounced for the minority chains. Changes in the coil size are expected to alter χ_s, since the number of contacts with monomers on other chains is directly related to the chain structure. The influence of coil size on χ_s can be rationalized based on the Ginzburg criterion[38,40] for the break down of mean field theory. Assuming the chains remain approximately Gaussian, a chain comprising N segments will occupy a volume on the order of $R_g{}^3$, where $R_g \sim lN^{1/2}$ and l is the Kuhn length. This implies that each chain interacts with $N^{1/2}$ other chains. For the case where the radius of gyration increases due to swelling, a greater number of chains (over the unswelled situation) will reside within the effective volume occupied by a given chain. Composition fluctuations, arising from the removal order addition of monomer segments within this volume, will then be reduced. This reduces the fluctuation contribution to χ_s. From the theory of critical phenomena,[37] fluctuations are known to stabilize a system relative to the mean field case when fluctuations are added; therefore, χ_s should increase when the fluctuation effects are reduced.

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