Chemical Potentials of Polymer Blends from Monte Carlo Simulations: Consequences on SANS-Determined χ Parameters

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ABSTRACT: Monte Carlo simulations on symmetric polymer blends were conducted to examine critically the applicability of Flory theory to polymer blends and the random phase approximation that is used to analyze scattering data from these blends. The novelty of the approach presented here is that the chemical potentials of chains are evaluated using the chain increment method. Surprisingly, we find that the chemical potentials at constant pressure can be modeled by the Flory–Huggins free energy form with a *composition-independent* χ parameter. The numerical values of χ, however, cannot be anticipated *a priori*, and we therefore surmise that the good fit obtained to Flory theory is simply due to the cancellation of errors. The corresponding results for blends whose molar volumes are independent of composition, however, can only be modeled with a composition-dependent χ, in agreement with previous lattice simulations of Binder. These results suggest that, contrary to accepted concepts, the incorporation of equation-of-state effects has important consequences in determining the thermodynamic properties of polymer blends. We have also attempted to model these simulation data by incorporating the effects of fluctuations but show that currently available theories predict improper trends. As a consequence of these results we show that the unusual composition dependence for χ parameters determined from scattering experiments (χ_{SANS}) can be attributed, at least in part, to small excess volume changes on mixing which are not incorporated in the incompressible random phase approximation (i-RPA). The simple treatment presented here, which incorporates volume changes on mixing, then allows for the prediction of the "upturn" or "downturn" of χ_{SANS} as a function of composition that is observed experimentally. Subsequently, we show that even extremely small volume changes on mixing, such as 0.05%, are sufficient to explain experimental trends for χ_{SANS}. Finally, we make contact with past theories and show that the results presented here are qualitatively similar to previous work of Freed and co-workers and Schweizer and Curro, both of which emphasize the importance of packing effects in this context, although differences still exist.

1. Introduction

Binary polymer blends have been the focus of intense study in the past few years because they represent systems with controllable physical properties.[1-4] Although these materials are of practical importance, the primary understanding of their phase equilibria has been obtained through the mean-field Flory–Huggins lattice model,[5,6] which includes several uncontrolled approximations. This model, which is derived for chains placed on a fully filled quasi-lattice in the mean-field approximation, yields the following expression for the Gibbs energy of mixing two polymers:

$$\frac{\Delta G_{\mathrm{mix}}}{k_{\mathrm{B}}T} = \frac{\phi_1}{n_1}\ln\phi_1 + \frac{\phi_2}{n_2}\ln\phi_2 + \chi\phi_1\phi_2 \qquad (1)$$

Here ΔG_{mix} is the Gibbs energy of mixing per mole of lattice sites, k_{B} is Boltzmann's constant, T is the absolute temperature, ϕ_1 and ϕ_2 are the volume fractions of the two components in the blend ($\phi_1 + \phi_2 = 1$), and n_1 and n_2 are the chain lengths of the two polymeric species in the blend. The Flory interchange energy parameter,[5,6] χ, is assumed to be purely enthalpic in origin in the original theory and, consequently, it should be independent of the chain lengths of the two polymers and composition.

In an attempt to verify the predictions of this mean-field theory, small-angle neutron scattering (SANS) experiments[7] and computer simulations[8,9] have been performed on symmetric polymer blends (*i.e.*, where $n_1 = n_2 = n$), and these investigations have shown that the Flory χ parameter must scale as $(1/n)$ at a critical point, apparently validating the mean-field predictions.[10] In addition, these results also apparently verify the applicability of the incompressible random phase approximation (i-RPA)[11-16] in the analysis of SANS data for these near-critical blends.

In spite of the success in predicting the correct chain length dependence of the χ parameter at the critical point, measurements on several miscible off-critical polymer blends have shown that the SANS-determined χ parameter (χ_{SANS}) is composition and chain length dependent, apparently in contradiction to one of the primary assumptions of the Flory–Huggins theory.[5,6] Such results have been obtained experimentally on PS/PVME blends,[17,18] isotopic blends,[19] and blends of ethylene–butene copolymers.[20] In contrast, measurements on isotopic polystyrene blends,[21,22] polystyrene–poly(α-methylstyrene) mixtures,[23] and some blends of ethylene–butene copolymers apparently indicate that χ_{SANS} is essentially independent of composition.[24] Several different arguments have been proposed to explain this unexpected composition dependence of χ_{SANS} for polymer blends:

1. Muthukumar[19,25] has suggested that the mean-field Flory–Huggins theory is inadequate to model these systems and shows that the addition of concentration fluctuations yields a concentration-dependent χ. Similar results have also been reported by Olvera de la Cruz *et al.*[26] The implication of these two groups is that the composition dependence of χ_{SANS} reflects a general inadequacy of the mean-field Flory theory even for incompressible systems. These workers, therefore, indirectly imply that the i-RPA is a reasonable means to extract thermodynamic properties from scattering data. It should be noted, however, that both of these models predict that a plot of χ *vs* volume fraction always shows a "downturn" (*i.e.*, χ assumes a maximum value at $\phi = 0.5$ in the case of symmetric blends)

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although most experimental results available to date show the opposite trend.[24]

2. Han, Sanchez, and co-workers,[17,27] assume the validity of the Flory theory in the context of a system whose molar volume is independent of composition. They then suggest that the incorporation of volume changes on mixing, which is appropriate when one deals with experimental systems at constant pressure,[28,29] gives rise to the composition-dependent χ parameters. These workers, who incorporate equation-of-state (EOS) effects in the free energy of mixing,[30] argue that the composition dependence of χ_{SANS} is simply a manifestation of the failings of the incompressible Flory theory when applied to experimental situations. No comment is made on the validity of the i-RPA, which consequently is assumed to not introduce any artifacts when used to analyze scattering data.

3. Freed and Dudowicz[31-33] assume that the Flory model is adequate in determining the thermodynamics of incompressible polymer blends with a composition-independent χ as long as one considers chains which have monomers of identical size. They then note that the incorporation of the effects of holes (or "free volume") in the thermodynamics of mixing naturally introduces a composition dependence to the χ parameter as noted by Han and Sanchez.[17] Further, they argue that "free-volume" effects give rise to additional composition dependences for χ_{SANS} due to the failure of i-RPA. Following this idea, Tang and Freed[34,35] have developed a compressible form of the RPA (c-RPA), which properly accounts for the effects of free volume on the scattering obtained from a typical blend. This analysis shows that the three partial structure factors in a binary blend (which have identical, absolute numerical values in the original i-RPA) now assume different values and thus, in principle, lead to a composition-dependent χ_{SANS}. This theory therefore suggests that the composition dependence of χ_{SANS} is a direct manifestation of having ignored the compressibility of the blend, both at the level of the Flory–Huggins theory and in the i-RPA.[24,36]

4. Schweizer and Curro[2-4,37] suggest that χ_{SANS} has a composition dependence since χ is a nonlocal parameter which can be expressed exactly as a difference of direct correlation functions. These authors therefore attribute departures from the Flory assumption of a χ defined through nearest neighbor interactions[5,6] as being the source for the unusual composition dependence of χ_{SANS}. Recently,[38,39] these workers have analyzed simple symmetric polymer blends using molecular closures in their PRISM model and illustrate that the χ which describes the free energy of mixing two polymers should have a parabolic dependence on volume fraction even for systems whose molar volumes are independent of composition. In addition, other effects such as the differences in monomer size, bond length, and stiffness also cause additional deviations from Flory theory. These workers therefore suggest that a primary cause for the composition dependence of χ_{SANS} is deviations from Flory theory. Second, i-RPA is also shown to be inherently inaccurate in modeling SANS data since the assumption of incompressibility, which allows for the separation of concentration and density fluctuations, is incorrect when one deals with real, liquid-like systems.[16] Although these workers show the limitations of i-RPA when applied to real systems, they nevertheless argue that volume changes on mixing do not play a significant role in determining the composition dependence of χ_{SANS}.

5. Binder and co-workers[40-45] have performed an exhaustive series of Monte Carlo calculations for blends on a lattice under the assumption that their molar volumes are independent of composition. It was found that the free energy of mixing could only be described by a χ parameter which was approximately parabolic in composition. Further, the results of these simulations demonstrate that the variation of χ with volume fraction shows an "upturn" at the wings, in agreement with most experimental data available on miscible polymer blends.[24] These simulations therefore suggest that deviations from Flory theory are responsible for the unusual composition dependence observed experimentally for χ_{SANS}.

The results of these past investigations are that the SANS-determined χ parameter can have a composition dependence due to the following two different issues which have been ignored when the i-RPA is employed in conjunction with the mean-field Flory theory to model scattering data: (a) the validity of Flory theory for "realistic" polymer blends, and the consequences of volume changes on mixing (or free-volume effects) and concentration fluctuations on the applicability of Flory theory; (b) the validity of the i-RPA when analyzing scattering data from real polymer blends. At this time, therefore, the molecular basis for the composition dependence of χ_{SANS} even for the simple cases examined experimentally is not clearly understood. Here, we present results from Monte Carlo simulations that attempt to assess the relative importance of these effects on χ_{SANS} for the simplest case of symmetric polymer blends. The novelty of our approach is that we evaluate the chemical potentials of polymer chains in a blend under experimental conditions from the simulations,[46-49] thus allowing us to examine directly the validity of the Flory theory and the importance of fluctuations in this context. We have performed two series of simulations, and in the first series we consider a variety of blend compositions at the same temperature and pressure conditions. The second series of simulations, which are then conducted under conditions where the molar volume is independent of composition, allow us to assess the importance of EOS effects in determining the thermodynamics of polymer blends. These simulations also permit for the critical examination of the applicability of the i-RPA in modeling SANS data.

2. Theory

We begin by reconsidering the thermodynamic definition of the zero wave vector limit of the partial structure factor for component 1 in a binary polymer blend, $S_{11}(0)$,

$$\frac{1}{S_{11}(0)} = \frac{N_T}{k_B T}\left[\frac{\partial(\mu_1/n_1)}{\partial N_1}\right]_{T,V,\mu_2} \tag{2}$$

which follows from standard fluctuation theory and is directly relevant in interpreting SANS data.[33,50] Here n_1 ($\equiv n_2$ for all cases we shall consider here) is the chain length of component 1, μ_1 is the chemical potential of component 1, N_1 is the number of molecules of type 1, N_T ($=N_1n_1 + N_2n_2$) is the total number of segments in the fluid, k_B is Boltzmann's constant, and T is the temperature. To calculate the partial structure factor of a binary polymer blend, we have performed free-space simulations on symmetric polymer blends, and the results of these investigations are discussed below. It suffices, at this juncture, to note that the specific volumes of both pure homopolymers are set to be identical under the simulation conditions, and it is stressed that the rest of the analysis presented here is only valid for situations where this condition holds. On simplifying eq 2 we obtain

$$S_{11}(0) = \phi_1\phi_2(\rho\bar{V}_2)^2\left[\frac{\partial(\beta\mu_1^{seg})}{\partial \ln \phi_1}\right]_{T,P}^{-1} + \rho k_B T\kappa_T\phi_1^2 \tag{3}$$

where μ_1^{seg} is the chemical potential per segment of component 1, ϕ_1 is its volume fraction ($\equiv N_1 n_1/N_T = 1 - \phi_2$), ρ is the density, $\bar{V}_2$ is the partial molar volume of component 2 in the blend, κ_T is the isothermal compressibility of the medium, and $\beta = 1/k_BT$. We now simplify this expression under the assumption that the isothermal compressibility of the medium is small, where the second term can now be ignored,

$$S_{11}(0) \approx \phi_2(\rho\bar{V}_2)^2\left[\frac{\partial(\beta\mu_1^{\mathrm{seg}})}{\partial\phi_1}\right]_{T,P}^{-1} \tag{4}$$

The process of going from eq 3 to eq 4 is analogous to the experimental procedure where the scattering arising from the density fluctuations in the pure components is subtracted out from the blend scattering. It should be stressed, however, that the consequences of the finite compressibility of the blend are still present in eq 4, and an examination of this equation suggests that although $\rho\bar{V}_2$ is equal to unity in a blend with no "free volume" (or with linear volume changes on mixing), it is expected to assume different values in *normally encountered experimental situations* where mixtures normally display excess volumes on mixing. The term involving the partial molar volume, then, should show any departure of blend behavior from the incompressibility assumed in the derivation of the i-RPA used in analyzing SANS data. Similarly, the last term in the equation, which incorporates the segmental chemical potentials, directly reflects the validity of the Flory–Huggins theory or one of its modifications in this context. The static structure factor, therefore, reflects the applicability of the Flory theory and the i-RPA and suggests that departures from either of these could lead to composition-dependent values of χ_{SANS}. These conclusions are consistent with past work on scattering from metal alloys[16] where it has been shown that excess volume changes on mixing and concentration fluctuations separately contribute to the observed excess scattering. The interested reader is referred to this paper for more details.

We now relate the partial structure factors to the total structure factor of the blend, which is the quantity of relevance when the χ parameter is obtained from a neutron scattering experiment. Two methods can be utilized to make this connection:

1. *Method of Scattering Contrasts*: This technique is based directly on standard scattering theory[51] and utilizes the fact that the partial structure factors and the scattering lengths of the two different species in the system are necessary to define the scattered intensity,

$$S(0) \propto \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_i\sum_j b_i b_j S_{ij}(0) \tag{5}$$

Here the b_i's are the scattering lengths, $S(0)$ is the total blend structure factor, and $\mathrm{d}\sigma/\mathrm{d}\Omega$ is the scattered intensity per unit solid angle. We now use eq 4 and simplify to obtain

$$S(0) \propto \frac{\phi_1\phi_2}{\left[\frac{\partial(\beta\mu_1^{\mathrm{seg}})}{\partial \ln\phi_1}\right]_{T,P}}[\rho\bar{V}_1\bar{V}_2]^2\left[\frac{b_1}{\bar{V}_1} - \frac{b_2}{\bar{V}_2}\right]^2 \tag{6}$$

where the Gibbs–Duhem equation has been used[52] and the last term represents the "contrast factor". It should be realized in this context that the partial molar volumes of the two components in the blend, which normalize the scattering length of the species, generally are dependent on the composition (except in the case where the mixture is incompressible). When contrasted to classical approaches,[1] this result suggests that one manifestation of excess volumes on mixing is that the contrast factor becomes composition dependent. While this equation clearly illustrates the effects of volume changes on mixing in analyzing neutron scattering data, we will not use this form to obtain χ_{SANS} from our simulations since we do not want to make *ad-hoc* assumptions regarding the numerical values of the scattering lengths.

2. *Post Facto Imposition of Incompressibility*: Although real polymer blends are not incompressible, the i-RPA makes this a central assumption in deriving the structure factor for the polymer blend. To reconcile this discrepancy we choose a method proposed originally by Schweizer and Curro[2–4] and used subsequently by Ohta and Kawasaki,[53] where the incompressibility criterion that is implicitly assumed in i-RPA is imposed *post facto* on the system. One then obtains an expression for the total structure factor of the blend, $S(0)$.

$$\frac{4}{S(0)} = \frac{1}{S_{11}(0)} + \frac{1}{S_{22}(0)} - \frac{2}{S_{12}(0)} \tag{7}$$

On using eq 4 and the appropriate definitions for the other partial structure factors we get

$$\frac{1}{S(0)} = \frac{1}{4\phi_1\phi_2}\left[\frac{\partial(\beta\mu_1^{\mathrm{seg}})}{\partial\ln\phi_1}\right]_{T,P}\frac{1}{\rho^2}\left[\frac{1}{\bar{V}_1} + \frac{1}{\bar{V}_2}\right]^2 = \frac{1}{n\phi_1\phi_2} - 2\chi_{\mathrm{SANS}} \tag{8}$$

where the final equality has been obtained by invoking the i-RPA.[11] We shall utilize this form to obtain the composition dependence of the SANS-determined χ parameter from our simulations. It should be realized that, although we have chosen to use this form to avoid using arbitrary values for the scattering lengths of the two blend components, a more reliable technique to analyze experimental data would be through the use of scattering contrasts as discussed above.

3. Model and Simulation Procedure

The novelty of the approach presented here is that we evaluate the chemical potentials of polymer chains in a blend from computer simulations. We can therefore directly consider the validity of the Flory–Huggins theory for describing the free energy of mixing two polymers[46] and consequently examine the applicability of i-RPA in analyzing neutron scattering data. We consider blends with a range of composition and in one series of simulations we constrain all of them to be at the same temperature and pressure as would be realized in a typical experimental situation. In parallel, we shall consider simulations for the same blends, but under the constraint that all the blends in the series are at the same temperature and molar volume (as in the lattice simulations of Binder and co-workers[45]). These two series of simulations allow for a critical analysis of the effects of equation-of-state (EOS) contributions to the free energy of mixing of simple polymer blends and also allow us to make contact with the past simulations of Binder and co-workers.[45]

3.1. Model. We have performed free-space simulations on a series of binary polymer blends each characterized by a different value of the volume fraction of component 1, ϕ_1 ($\equiv 1 - \phi_2$), where the temperature and pressure were set to the same value at all compositions. Standard Metropolis Monte Carlo simulations in the isothermal–isobaric ensemble were therefore performed in each case.[54,55] Most simulations were performed on a system which contained 800 total monomers. Periodic boundary conditions were utilized in all three spatial directions. Polymer chains were modeled as a collection of bead–springs, and the springs connecting any two monomers were associated with a potential energy, U_b, which is described as[46]

$$U_b(r) = {}^1/_2\kappa(r-\sigma)^2 \qquad 0.5 \le (r/\sigma) \le 1.5 \tag{9}$$

Here κ is the spring constant, r is the instantaneous bond length, and σ is the set value of the bond length. U_b is infinity elsewhere.[56] The numerical values of κ, as well as σ, the equilibrium bond length, are listed below. Both blend components were chains of length 25 (*i.e*, $n_1 = n_2 = n = 25$) repeat units, and all nonbonded beads interacted with a standard Lennard-Jones potential,

$$\begin{aligned} U(r_{ij}) &= 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad \text{for } r_{ij} < r_c \\ &= 0 \qquad \text{for } r_{ij} \ge r_c \end{aligned} \tag{10}$$

where r_{ij} is the distance between the beads and ϵ is the well depth associated with this potential. r_c is the distance at which the potential was truncated, and we have used two different values of r_c corresponding to 2.5σ or 4.0σ. All thermodynamic quantities of interest were computed under these conditions and corrected for long-range effects arising from interactions with monomers (or beads) present beyond the cutoff distance, r_c.[57] We shall show below that the results obtained at both cutoff distances yielded identical results for thermodynamic properties, and we have in general, therefore, used the shorter cutoff for convenience.[46]

Segments of both chains were assumed to have the same value of σ, the bead diameter, and energy of interaction between like segments (i.e., $\epsilon_{11} = \epsilon_{22}$, where $\epsilon_{\alpha\alpha}$ is the Lennard-Jones well depth parameter characterizing interactions between two monomers of type α [=1 or 2]). However, the energetic interaction between unlike monomers was different and we have considered two different cases:

$$\text{(i) } \epsilon_{12}/\epsilon_{11} = 1.2; \qquad \text{(ii) } \epsilon_{12}/\epsilon_{11} = 0.9 \tag{11}$$

where ϵ_{12} is the Lennard-Jones parameter associated with interactions between dissimilar monomers. The first case was called *attractive* and corresponded to a situation where unlike interactions were favored, while the second case (termed *repulsive*) corresponded to unfavorable cross interactions. Further, for these calculations we have chosen $(\kappa\sigma^2/\epsilon_{11}) = 400$ for all springs in the system, independent of the component.

Chains were equilibrated through standard reptation and crankshaft moves, and these moves were accepted through standard Metropolis sampling.[46] In addition to these standard moves, which have been used in canonical ensemble simulations,[58] a volume change move was also implemented so as to fix the simulation pressure. This move involved a uniform expansion or contraction of the simulation cell at random in the range of 0–2% of its original value. Since we deal with bead–spring chains, this step therefore involves the expansion or contraction of the springs connecting the beads. The probability of acceptance of this volume change step was

$$P_{\text{acc}} = \min\left(1, \exp\left[-\beta\Delta U + N_T \log\left(\frac{V+\Delta V}{V}\right) - \beta P^*\Delta V\right]\right) \tag{12}$$

where P_{acc} is the acceptance probability of the volume change step, ΔV represents the volume change that is implemented on the system, N_T is the total number of beads in the system, and P^* ($\equiv P\sigma^3/\epsilon_{11}$) is the imposed pressure, which is set to 0 in this case. β is the thermodynamic temperature ($\equiv 1/(k_BT)$).

The initial state of the system was generated at random ensuring chain connectivity and that no two beads were closer than *ca.* 0.8σ. After equilibration, a typical simulation involved 2.5×10^7 attempted reptations and 2.5×10^7 attempted crankshaft moves, while 1.25×10^4 attempted volume changes were also performed. On average, *ca.* 50% of the volume change moves, 2% of the attempted reptations, and 20% of the crankshaft moves were accepted under the conditions studied. Each of these simulations has been repeated 5–8 times with different starting guesses to ensure reproducibility, as well as to get a good measure of the uncertainties associated with the computer properties.

Simulations were conducted at two different temperatures, T^* ($\equiv k_BT/\epsilon_{11}$) = 2 and 2.5, respectively, and a pressure $P^*(P\sigma^3/\epsilon_{11})$ of 0 which corresponds closely to atmospheric pressure, the experimental condition of interest. Molar volumes (and hence partial molar volumes) then resulted naturally from this formalism. In parallel, we have also conducted a series of canonical ensemble simulations, so that a variety of blend compositions were examined at $T^* = 2$ and the same molar volume, V^* ($\equiv V\sigma^3 = 1.42$). These free-space simulations, which closely parallel the earlier lattice computations of Binder and co-workers,[45] were conducted in a fashion similar to the constant-pressure calculations except that the volume change step was not implemented.

3.2. Calculation of Chain Chemical Potentials. We have previously shown that the incremental chemical potential associated with a chain of length x when it is in a homopolymer matrix containing N chains of the same chemical structure but of length n, $\mu_r(x)$, can be obtained from simulations in the canonical ensemble as[46–49]

$$\beta\mu_r(x) = \beta\mu^r{}_{\text{chain}}(x) - \beta\mu^r{}_{\text{chain}}(x-1) = -\ln\langle\exp[-\beta U(\mathbf{r}_x)]\rangle_{x-1,N,n,T,V} \tag{13}$$

where $\langle\ldots\rangle$ denotes an ensemble average under conditions where the quantities $x-1, N, n, T$, and V are held constant. Here $\mu^r{}_{\text{chain}}(x)$ is the residual chemical potential of a whole chain of length x [$\equiv \mu_{\text{chain}}(x) - \mu^{\text{ID}}{}_{\text{chain}}(x)$, where $\mu_{\text{chain}}(x)$ and $\mu^{\text{ID}}{}_{\text{chain}}(x)$ are the chemical potentials of the chain in the system and in the ideal gas state, respectively] when it is in a homopolymer matrix of chains of length n. Equation 13 suggests that one method for the calculation of the incremental chemical potential associated with a chain of length x is to consider a system comprised of N chains of length n and one chain of length $x-1$ which is of identical monomer structure as the other chains in the system. One considers a frozen snapshot of this system, inserts an identical bead onto one of the ends of the chain of length $x-1$, and evaluates $U(\mathbf{r}_x)$, the test bead energy. The incremental chemical potential associated with a chain of length x, $\mu_r(x)$, is then computed by averaging the appropriate Boltzmann factor over many different realizations of the simulated system. The chemical potential of the chains of length n in the system can then be obtained through the relationship

$$\mu^r{}_{\text{chain}}(n) = \mu_r(n) + \mu_r(n-1) + \ldots + \mu_r(1) \tag{14}$$

where the $\mu_r(x)$ are, in general, a function of x. It should be recognized that, although we obtain the incremental chemical potentials associated with a chain of length x when it is present in infinite dilution in a matrix of chains of length n (*i.e.*, we obtain a mixture property), eq 14 shows that the sequential sum of these incremental chemical potentials actually yields a quantity that is appropriate for the homopolymer chains of length n in the system. This fact has been illustrated in ref 46, and we refer the interested reader to these papers for more details.

The extension of this method to the calculation of the chemical potentials of the two components of a binary polymer blend is straightforward, and there are only two points to be noted. First, the medium into which the insertion is performed would correspond to N_1 chains of length n_1 and N_2 chains of length n_2. Further, there would be a chain of length $x - 1$ of type α (α = 1 or 2) in the medium. The incremental chemical potential of a chain of length x and type α would therefore be obtained by inserting another bead of the same type onto the chain of length $x - 1$ and computing the interaction energy experienced by this test bead, $U^\alpha(\mathbf{r}_x)$. The incremental chemical potential is then obtained from the relationship

$$\beta\mu_r^\alpha(x) = \beta\mu^{r,\alpha}{}_{\text{chain}}(x) - \beta\mu^{r,\alpha}{}_{\text{chain}}(x-1) = -\ln\langle\exp[-\beta U^\alpha(\mathbf{r}_x)]\rangle_{x-1,N_1,n_1,N_2,n_2,T,V} \quad (15)$$

where it is emphasized that the quantities $x - 1$, N_1, n_1, N_2, n_2, T, and V are all maintained constant during the course of the simulations. Here $\mu^{r,\alpha}{}_{\text{chain}}(x)$ is the residual chemical potential of a whole chain of length x of type α [$\equiv\mu^\alpha{}_{\text{chain}}(x) - \mu^{\text{ID},\alpha}{}_{\text{chain}}(x)$, where $\mu^\alpha{}_{\text{chain}}(x)$ and $\mu^{\text{ID},\alpha}{}_{\text{chain}}(x)$ are the chemical potentials of the chain of length x and type α in the system and in the ideal gas state, respectively], and it is emphasized that $\mu_r^\alpha(x)$, the incremental chemical potential, is, in general, a function of x. The chemical potential of a chain of length n_α is then obtained by summing all the incremental chemical potentials associated with chains of length smaller than n_α,

$$\mu^{r,\alpha}{}_{\text{chain}}(n_\alpha) = \mu^\alpha{}_r(n_\alpha) + \mu^\alpha{}_r(n_\alpha-1) + ... + \mu^\alpha{}_r(1) \quad (16)$$

for each component (α = 1 or 2). A special case of the chain increment method which will be used extensively in this work due to its computational expediency is to consider a system with N_1 chains of length n_1 of type 1 and N_2 chains of length n_2 of type 2. One equilibrates this system and considers a frozen snapshot. Any chain of type α (=1 or 2) in the simulated system is selected at random and a monomer of type α added to one of the ends of this chain. Following eq 15, the bead insertion procedure then directly yields $\mu^\alpha{}_r(n_\alpha+1)$ with great accuracy due to the large number of chains of type α in the simulation cell.

While we have shown how to calculate the incremental chemical potentials for a chain of length x of component α in the canonical ensemble, we are also interested in the corresponding quantities for simulations performed at constant pressure. The extension of the Widom test particle method for the chemical potentials of small molecules[59] to the isothermal–isobaric ensemble has been performed earlier by Frenkel[60] and Shing and co-workers.[61] The extension of the chain increment method, which is based directly on the Widom method in the canonical ensemble, to this ensemble can be performed in a similar fashion. We present the result here and defer the derivation to Appendix I,

$$-\beta\mu^\alpha{}_r(x) = \ln\left[\frac{\langle V\exp(-\beta U^\alpha(\mathbf{r}_x))\rangle_{x-1,N_1,n_1,N_2,n_2,T,P}}{N_1n_1 + N_2n_2 + x - 1}\right] \quad (17)$$

Here V is the system volume, which is a fluctuating quantity, and it should be recognized that the ensemble averages are performed under conditions of constant T, P, and number of molecules of type α (=1 and 2). The chemical potential of the whole chain of length n_α is then obtained following eq 16.

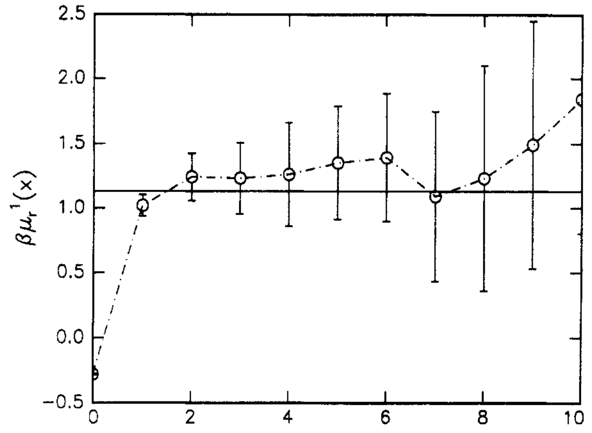

Figure 1. Comparison of the incremental chemical potentials computed from the Rosenbluth method (O) and the special implementation of the chain increment method (—) for an attractive blend comprised of 50% of each component at T^* = 2 and P^* = 0.

In past work[46] we have shown for homopolymer systems at meltlike densities that the incremental chemical potential becomes independent of chain length for chains longer than *ca.* 5. To check the validity of this approximation in the context of polymer blends, we have, separately, computed the incremental chemical potentials of chain molecules of length 25 in blends by using the Rosenbluth method proposed earlier by Frenkel and coworkers[62–64] and dePablo *et al.*[65] which allows for the calculation of the chemical potentials of chains of length n_α, and all smaller lengths, in one simulation. Consequently, incremental chemical potentials for all chains shorter than n_α can be obtained in one simulation, and in Figure 1 we show a sample result obtained from an attractive blend comprised of 50% of chains of type 1 and chains of type 2 at T^* = 2 and P^* = 0 using the Rosenbluth method. The incremental chemical potential associated with a chain of length 25, which was obtained by using the special implementation of the chain increment method (*i.e.*, by adding a bead of type α as a test bead to any chain of type α and length 25 in the system), is also plotted in this figure as a line that is independent of chain length. Two points are to be noted in this figure. First, it is clear that the incremental chemical potentials become independent of chain length for all chains longer than *ca.* 3 and that this value is equal to the quantity obtained from the special implementation of the chain increment method within simulation uncertainty. This allows us to make a simplifying assumption that

$$\mu^{r,\alpha}{}_{\text{chain}}(n_\alpha) \approx n_\alpha\mu^\alpha{}_r \quad (18)$$

where $\mu^\alpha{}_r$, which represents the chain length independent incremental chemical potential of chains of type α, is the *residual segmental* chemical potential. This approximation, which ignores any chain end effects since it assumes that the incremental chemical potentials are independent of chain length, is clearly not a good approximation for short chains ($n \leq 5$) as shown in Figure 1. However, it will become an asymptotically better estimate of chain chemical potentials with increasing length. The second point to be noted is that the Rosenbluth method, which in principle is capable of yielding the chemical potentials of all chains shorter than n_α in the system in a single simulation, experiences serious finite size effects associated with inserting a long chain length polymer into a frozen snapshot of the system. These sampling errors, which have been documented elsewhere,[66] prevent us from using the Rosenbluth method for calculating the chemical potentials of long chains, although this method is still of value for very short chains ($n \leq 5$) where the incremental chemical potentials are chain length dependent. We shall therefore only calculate the chain length independent incremental chemical potential, $\mu^\alpha{}_r$, from the chain increment method in its special implementation as discussed above and approximate the chain chemical potentials following eq 18.

To relate the residual chemical potential of a chain of type 1, $\mu^{r,1}_{\text{chain}}(n_1)$, to its absolute value, $\mu^1_{\text{chain}}(n_1)$, we utilize the relationship

$$\mu^1_{\text{chain}}(n_1) = n_1\mu_1^{\text{seg}} \approx \ln \phi_1 + n_1\mu^1_{\text{r}} \tag{19}$$

where the first term on the right-hand side ($=\ln \phi_1$) represents the ideal gas contribution. μ_1^{seg} is the segmental chemical potential and is the quantity that is required to calculate the structure factor of these blends. In summary, the route to evaluating the static structure factors of the blends will be as follows:

1. Obtain the molar volume, and hence the partial molar volumes of the different components in the blends by performing simulations at different compositions while maintaining all the simulations at the same value of temperature (T^*) and pressure (P^*).

2. Calculate the incremental chemical potentials associated with chains of length 25 for both components in the blend using the special implementation of the chain increment method. We then use the approximation listed in eq 18 to obtain the chemical potentials of whole chains.

Equation 4 is then utilized to evaluate $S_{11}(0)$, and χ_{SANS} is obtained from eq 8. We shall utilize these procedures in relating our simulations to experiments and explaining the composition dependence of the SANS-determined χ parameters.

4. Results and Discussion

4.1. Results for Blends at Constant Pressure. We begin by considering the attractive system, and in Figure 2A the chain length independent values of the incremental chemical potential for component 1, $\mu^1_{\text{r}} - \mu^1_{\text{r}}(\phi_1 = 1)$, are plotted as a function of ϕ_1 at $T^* = 2$ and $P^* = 0$. It should be noted that the incremental chemical potential of the pure polymer, $\mu^1_{\text{r}}(\phi_1{=}1)$, is always subtracted out so that the data represent the chemical potential change associated with mixing the two polymers. The data corresponding to $\phi_1 = 0$ were obtained through the use of the Rosenbluth method and inserting a single chain of type 1 into a medium containing all chains of type 2. All the other chemical potentials shown in Figure 2A were obtained through the special implementation of the chain increment method.

Two important facts emerge from this figure. First, it is clear that the results obtained from the two cutoff distances ($r_{\text{c}} = 2.5\sigma$ and 4.0σ) are in quantitative agreement. This allows us to consider data from the smaller cutoff distance as being reliable estimates of system properties, so long as they are corrected appropriately for long-range effects.[57] Second, we point to the fact that Flory theory[5,6] predicts that the incremental chemical potential for a component in a symmetric blend would assume the functional form

$$\beta\mu^1_{\text{r}}(\phi_1) - \beta\mu^1_{\text{r}}(\phi_1{=}1) = \chi\phi_2^{\,2} \tag{20}$$

where χ represents a composition-independent interaction parameter. In Figure 2A we show that the attractive system at $T^* = 2$ and $P^* = 0$ apparently obeys this parabolic relationship within simulation uncertainty where a χ value of -0.75 has been utilized in fitting the functional form to the simulation data. This result,[45] which is in good agreement with earlier findings of Honnell and Hall on tangent hard sphere chain mixtures,[67] suggests that the Flory form for the Gibbs energy of mixing with a composition-independent χ adequately describes the simulation results at constant pressure for these symmetric polymer blends. Similar results are also found for the attractive and repulsive systems at $T^* = 2.5$ (see Figure 3), although the results from the repulsive system are associated with large uncertainties due to imminent phase separation of this blend.[68] The first surprising conclusion from these simulations is that the mean-field Flory functional form is adequate to model the chemical potentials of the components of symmetric blends with a composition-independent χ parameter.

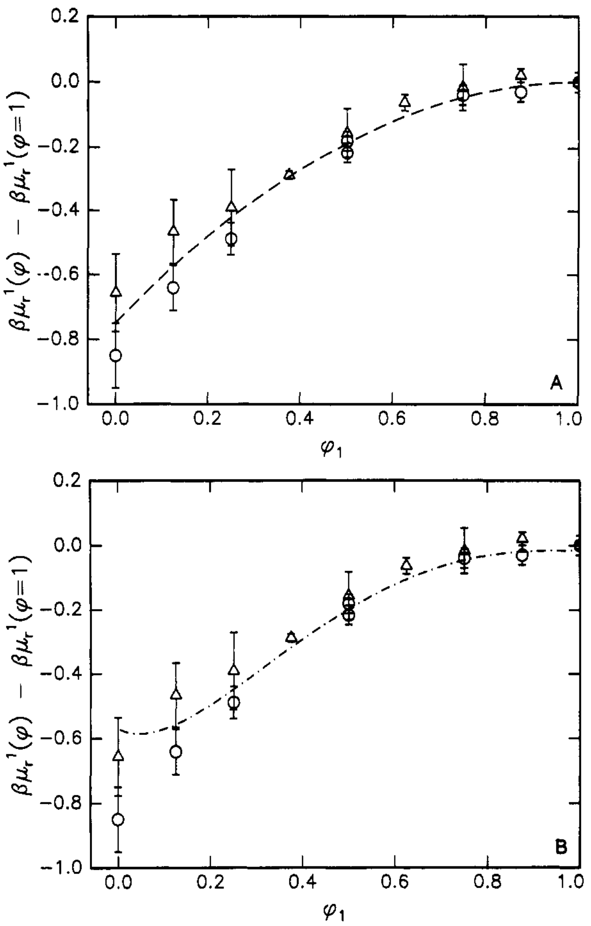

Figure 2. (A) Chain length independent value of the incremental chemical potential, μ^1_{r}, at a volume fraction ϕ_1 minus its pure component contribution plotted as a function of composition, ϕ_1, for the attractive blend at $T^* = 2$ and $P^* = 0$. Results were obtained from the special implementation of the chain increment method for all compositions except $\phi_1 = 0$, which was obtained from the Rosenbluth scheme. Results correspond to two cutoff distances, r_{c}, corresponding to (○) 2.5σ and (△) 4.0σ. The dashed line corresponds to a fit to Flory theory with a χ value of -0.75. (B) Symbols have the same meaning as in (A), while the line corresponds to the best fit to the fluctuation theory of Muthukumar[69] with $\chi = -0.25$.

Past work by Muthukumar[25] and Olvera de la Cruz *et al.*[26] have suggested that concentration fluctuations, at the length scale of a monomer, should affect the thermodynamics of mixing and could therefore give rise to deviations from Flory theory. We have attempted to use the Muthukumar theory as utilized in ref 19 (*i.e.*, with w, the parameter describing three-body interactions, set to zero) to fit the data in Figures 2A and 3 but find that this theory cannot even qualitatively reproduce the simulation results.[25] Recently, Muthukumar[69] has shown the earlier theory to be somewhat incorrect and presented a corrected form. Concentration fluctuations in incompressible symmetric polymer blends, in this corrected model, therefore

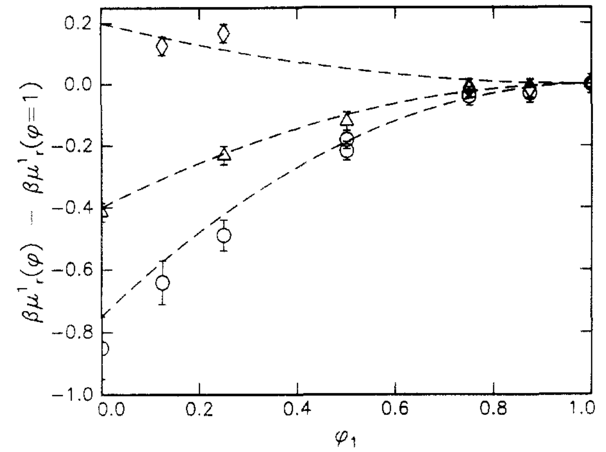

Figure 3. Incremental chemical potentials for the component 1 in a symmetric binary polymer blend at constant pressure (P^* = 0) as a function of composition. (○) and (△) represent results for the attractive blend at T^* of 2 and 2.5, respectively, while (◇) are results for the repulsive blend at T^* = 2.5. The lines represent best fits to Flory theory with a composition-independent χ.

contribute the following term to the free energy of mixing: 26

$$\frac{\Delta G_{\text{fluc}}}{k_B T} = -\frac{1}{12\pi}[36(\chi_s - \chi)\phi_1\phi_2]^{3/2} \qquad (21)$$

where ΔG_{fluc} is the fluctuation contribution to the free energy of mixing and χ_s is the value of the Flory parameter at the spinodal [$=1/(2N\phi_1\phi_2)$]. The contribution of fluctuations to the chemical potentials can then be computed through standard means, and the contribution of fluctuations to the total residual segmental chemical potential computed from this model is[52]

$$\beta\mu^1{}_r(\phi) = -\frac{9}{2^{1/2}\pi N^{3/2}}[(1 - 2\chi N\phi_1\phi_2)^{1/2} - 3\chi N(1 - 2\chi N\phi_1\phi_2)^{1/2}\phi_1(1 - 2\phi_1)] \qquad (22)$$

We find the best possible fit of this result to the simulation data for the attractive system at T^* = 2 and P^* = 0 by assuming a χ value of −0.25, and the results of this analysis are shown in Figure 2B. Qualitatively similar results were obtained from the theory of Olvera de la Cruz *et al.*[26] It can be seen that satisfactory agreement of this fluctuation result is found with the simulation data except for ϕ_1 values less than 0.125, where the chemical potentials computed from the fluctuation model show a minimum as a function of composition. This minimum in a plot of the residual segmental chemical potentials as a function of composition is a consistent feature of incompressible fluctuation models, and we find for χ values less than *ca.* −3 that this minimum corresponds to a spinodal for a binary blend of composition $\phi_1 \approx 0.1$. This is clearly an unphysical result, which could be a manifestation of the short chain lengths utilized as well as the strong attractive potentials which could cause deviations from the Gaussian assumption made in the derivation of these free energies. At this stage therefore we suggest that the effects of fluctuations on the free energies of the polymer blends considered here are not properly reproduced by this model. Further, this result also signals that the use of these fluctuation models to describe the deviation of blend behavior from Flory–Huggins theory and consequently to explain the composition dependence of χ_{SANS} could lead to incorrect findings.

Based on this finding, therefore, we conclude that the mean-field Flory treatment is able to better capture the trends for the composition dependence of μ_r observed in the simulations at constant pressure. In spite of this conclusion we stress that fluctuations will definitely affect the thermodynamics of mixing two polymers. Current treatments of fluctuations, which ignore compressibility effects, however, are shown to be inappropriate in the context of the simulated models, and we therefore emphasize the need for better models incorporating these effects.

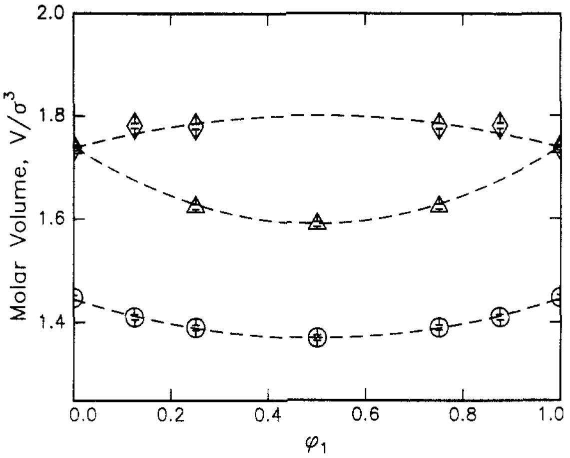

Figure 4. Molar volume as a function of composition with the same symbols as in Figure 3. The lines represent best fit parabolas.

We now return to analyzing the simulation data with the mean-field Flory model and find that χ assumes values of *ca.* −0.75 ± 0.1 and −0.4 ± 0.1 for the attractive blend at the two different temperatures, T^*, of 2 and 2.5, respectively, while the repulsive blend yields a χ value of 0.2 ± 0.1 at T^* = 2.5. It should be realized that, although the numerical values of χ cannot be anticipated *a priori* for systems in free space, the values for the repulsive and attractive systems at T^* = 2.5 are in good internal agreement. Since χ is defined as

$$\chi = \frac{z}{k_B T}\left[\epsilon_{12} - \frac{\epsilon_{11} + \epsilon_{22}}{2}\right] \qquad (23)$$

we can see that the χ values obtained for the attractive blends at the two different temperatures cannot be reproduced with a constant value of z, the coordination number. While this may point to a general inadequacy of the Flory lattice model,[5,6] we note that z must change with temperature since the density of the system, at constant pressure, decreases with increasing temperature.

To understand this effect in more detail, we begin by examining the molar volumes of the pure components, and in Figure 4 we see that the V^* for the homopolymer changes from a value of 1.42 at T^* = 2 to V^* = 1.73 at T^* = 2.5. It should be noted that realistic polymer liquids will not show such large volume changes with temperature, and we attributed this to the relatively higher compressibility and lower densities associated with the simple bead–spring model utilized here.[70] We now make a simplifying assumption that the lattice coordination number, z, depends directly on density

$$z \propto [\sigma^3/V] \qquad (24)$$

from which it follows that the χ at two different temperatures should be connected by the expression

$$\frac{\chi_2}{\chi_1} = \frac{T_1}{T_2}\left[\frac{V_1}{V_2}\right] \qquad (25)$$

On using the molar volumes of the pure polymers at the two different temperatures, and a χ value of −0.4 ± 0.1 at T^* = 2.5, we estimate that χ must assume a value of −0.6 ± 0.1 at T^* = 2 for the attractive system. This result is still not in agreement with the simulations, and we conclude

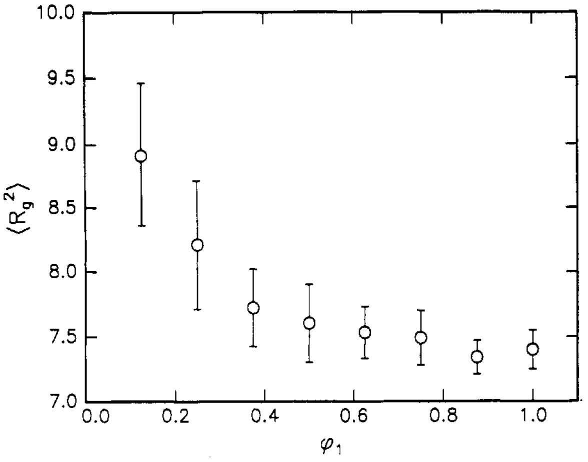

Figure 5. Mean-squared radius-of-gyration for chains of type 1 in an attractive blend at $T^* = 2$ and $P^* = 0$ as a function of composition, ϕ_1.

that the χ parameter used to fit the simulation data even for these simple systems should only be considered as a fitting parameter with no addition physical significance. As a consequence we surmise that the remarkably good fit obtained to the simulation data by employing the Flory form of the free energy of mixing may be a consequence of fortuitous cancellation of errors.

We now examine the volume changes on mixing and begin by considering the attractive mixture at $T^* = 2$ and 2.5 and $P^* = 0$ as a function of composition. As can be seen in Figure 4, the specific volumes of the attractive blend show a negative deviation from ideal mixing. Correspondingly, the repulsive blend displays a positive deviation from ideal mixing. As expected, the specific volume of the blends is also parabolic in composition[71]

$$V(\phi_1) = V_{\text{pure}} - C(T)\phi_1(1-\phi_1) \qquad (26)$$

where $C(T)$ is a temperature-dependent parameter. For the attractive blend we find that $C(T)$ assumes a value of 0.30 ± 0.01 and 0.60 ± 0.01 at the two temperatures, T^*, of 2 and 2.5, respectively. The point to be emphasized here is that although the Flory theory assumes a zero volume change on mixing, an assumption that is also built into the Sariban and Binder lattice simulations,[45] the blends actually show significant volume changes on mixing when they are considered at constant pressure. Note here that, similar to the results obtained for the pure polymers, the results obtained for the composition dependence of the blend molar volumes in these simulations are artificially enhanced as compared to realistic blends due to relatively simple bead–spring models used in this work. However, we expect real blends to show similar composition dependences, although at a much smaller scale.[72] We therefore stress that these volume changes on mixing, which are a manifestation of EOS effects, must be directly responsible for the difference in behavior of the χ parameters determined from our constant-pressure results and constant-volume calculations of Sariban and Binder.[45] This point will be explored in more detail in the next section.

Finally, we examine the variation of coil dimensions as a function of composition and consider the mean-squared radius of gyration of component 1 of the attractive blend at $T^* = 2$ and $P^* = 0$ in Figure 5. $\langle R_G^2 \rangle_\alpha$, which is the mean-squared radius of gyration of component α, is defined in this context as

$$\langle R_G^2 \rangle_\alpha = \frac{1}{n_\alpha - 1} \langle \sum_{i=1}^{n_\alpha} (\mathbf{r}_i - \mathbf{r}_{\text{CM}})^2 \rangle_\alpha \qquad (27)$$

where $\mathbf{r}_{\text{CM}}$ is the center of mass position of the chain. A very interesting trend emerges from this figure, and it can be seen that coil dimensions are essentially independent of composition for all cases where component 1 is the majority constituent in the blend. For cases where component 1 is the minority constituent, however, there is clear evidence of coil swelling, and one can see nearly a 10% increase in coil dimensions when $\phi_1 = 0.125$. These results are in good qualitative agreement with the earlier findings of Sariban and Binder,[45] who have observed a shrinking of coil dimensions for the minority component in a repulsive blend. A point that needs to be stressed here is that even in this extreme example where χ assumes a value of -0.75, it is clear that coil dimensions (*i.e.*, $\langle R_g^2 \rangle^{1/2}$) are only increased by 10% in the extremes of composition. This points to the fact that most "real" systems, which normally have weaker interactions, would not be expected to show significant variations in chain dimensions with composition, a result that is in good agreement with the predictions of Tang and Freed.[34] This result is also consistent with experimental findings on hydrocarbon blends which suggest that coil dimensions are constant, within experimental uncertainty, with changes in composition.[24]

To summarize, we have found for blends of different composition that the chemical potentials at constant temperature and pressure can be modeled by the Flory–Huggins form for the Gibbs energy of mixing with a composition-independent χ parameter. The variation of χ with temperature, however, cannot be predicted by using the original definition of this parameter, and we therefore speculate that the excellent fit obtained to the simulation data may be due to a cancellation of errors. Fluctuations might play a role in this context but it is clearly established that the currently existing theories, which lead to incorrect physics, cannot be used to assess their effects. Since the simulations were conducted at constant pressure, we find a change in system volume with composition, and this variation can be described by a simple parabolic dependence. Chain dimensions are also affected due to the presence of the second component, and we find, in agreement with expectations, that the dimensions of the minority blend component alone are modified. Finally, it should be realized that although these findings are relevant for the relatively simple symmetric blends considered here, these simple ideas are not expected to hold when more realistic blends, such as isotopic mixtures, which incorporate other factors such as differences in chain stiffnesses[73,74] and segment size and shape disparity[33] are considered.

4.2. Results for Blends at Constant Volume. The results at constant pressure which have been discussed above should be contrasted with the findings of Sariban and Binder,[45] who suggest that the χ parameter for lattice blends with a composition-independent molar volume should be approximately parabolic in composition. To reconcile the difference between these constant-volume lattice calculations and the off-lattice simulations at constant pressure presented above, we have separately conducted a series of simulations for the off-lattice symmetric blends at a variety of compositions but with a molar volume (*i.e.*, V^* $[=V/\sigma^3]$) that is independent of composition. We have chosen $V^* = 1.42$, since this corresponds to the molar volume for the pure polymer at

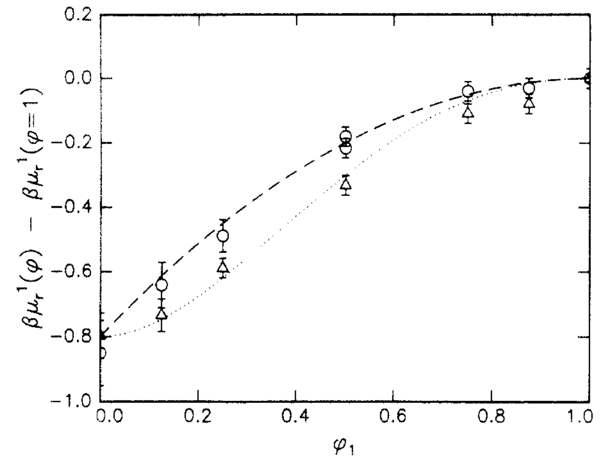

Figure 6. Chain length independent value of the incremental chemical potential, μ^1_r, at a volume fraction ϕ_1 minus its pure component contribution plotted as a function of composition, ϕ_1, for the attractive blend at $T^* = 2$. (○) are results for all blends with $P^* = 0$, while (△) are for blends whose molar volume, V^*, is set to 1.42, independent of composition. The constant-pressure data are fit to Flory theory (– – –), while the line through the constant-volume data (···) is a guide to the eye.

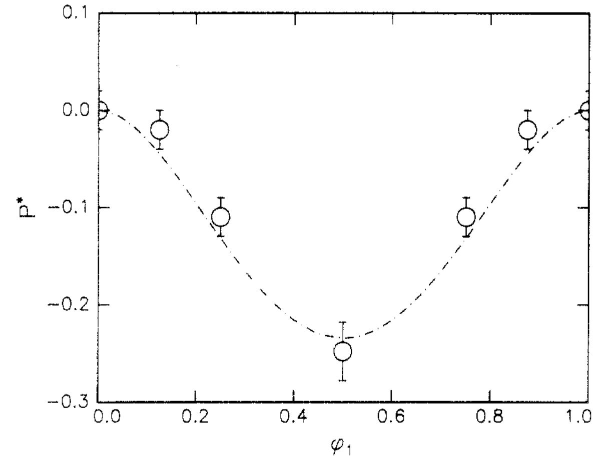

Figure 7. Variation of system pressure, P^*, for the constant-volume simulations at $T^* = 2$ and $V^* = 1.42$. The line is a guide to the eye.

$T^* = 2$ and $P^* = 0$ (see Figure 4). In Figure 6 it can be seen that the chemical potentials obtained at constant molar volume *cannot be modeled using the Flory form of free energy of mixing with a composition-independent* χ. While these simulations apparently are in qualitative agreement with the earlier findings of Sariban and Binder,[45] they surprisingly suggest that the assumptions inherent in the Flory theory make it more appropriate to model systems at constant pressure rather than at constant volume, although the initial derivation of the model was actually performed under constant-density conditions.

To explore the difference between the constant-volume and constant-pressure systems, we consider the simulations where the molar volume of the blend is independent of composition (*i.e.*, $V^* = 1.42$). Since the molar volume is set to be independent of composition, it is clear that the pressure should vary with composition as is shown in Figure 7. We can therefore relate the chemical potentials obtained at $P^* = 0$, and in the constant-volume simulations ($V^* = 1.42$), and we use the identity[52]

$$\beta[\mu_1(P) - \mu_1(P^*{=}0)] = \beta\int_0^P \bar{V}_1 \, dP \qquad (28)$$

where P is the pressure corresponding to the constant-volume situation. We now consider the blend with equimolar composition and realize that the constant-volume simulation results in a P^* value of -0.24 ± 0.03. On approximating the partial molar volume to be independent of composition and equal to the molar volume, we find that the left-hand side should equal -0.17 ± 0.05. The actual difference in the incremental chemical potentials at $P^* = 0$ and the simulation with $V^* = 1.42$ is found to be -0.21 ± 0.05, in good agreement with this simple calculation. Similar results were found at the different compositions. While this result apparently explains the composition dependence of χ parameters found for simulations conducted at constant molar volumes and thus emphasizes the importance of equation-of-state effects, it however does not offer any insight as to the composition independence of the χ parameters evaluated at constant pressure.

To summarize, therefore, we find that the chemical potentials for the components of blends with constant molar volumes cannot be modeled with the Flory–Huggins form with a composition-independent χ.[5,6] This result, which is consistent with the lattice simulations of Sariban and Binder,[45] emphasizes the effects of free volume on the applicability of the incompressible Flory theory to "realistic" polymer blends and reiterates that equation-of-state effects have to be incorporated for the proper modeling of polymeric systems.

4.3. Composition Dependence of χ_{SANS}. As a consequence of these findings, we assert that the unusual composition dependence obtained for χ_{SANS} even in the case of simple blends must therefore stem, at least in part, from the failure of the "ideal volume change on mixing" assumption that is built into the i-RPA formalism. We now use the formula for the total structure factor of the blend, eq 8, in conjunction with the simulation result that the blend chemical potentials at constant pressure follow Flory theory with a composition-independent χ. This now yields the result

$$-\chi_{SANS} = \frac{1}{2n\phi_1\phi_2}\left[\frac{1}{4\rho^2}\left(\frac{1}{\bar{V}_1} + \frac{1}{\bar{V}_2}\right)^2 - 1\right] - \frac{\chi}{4\rho^2}\left[\frac{1}{\bar{V}_1} + \frac{1}{\bar{V}_2}\right]^2 \qquad (29)$$

where χ represents the parameter used to fit the chemical potential data obtained from the simulations at constant pressure. This equation suggests that the χ_{SANS} will diverge inversely with the product $\phi_1\phi_2$ as one approaches the wings of the composition, a result which is in excellent agreement with recent experimental data on hydrocarbon-like polymer blends where χ_{SANS} varies linearly with the quantity $1/(\phi_1\phi_2)$.[24] Further, this result suggests that the composition dependence should become less important as longer chain length blends are considered. To our knowledge this result has not been verified to date on blends, although it is consistent with neutron scattering determined χ parameters for block copolymer systems.[75] Finally, we note that this equation predicts that the χ_{SANS} will equal the χ parameter used to fit the composition dependence of chemical potentials when we consider a system with no excess volume changes on mixing (an "incompressible" system).

We now use this formalism to analyze the composition dependence of χ_{SANS} for the two different blends considered in this work. We find that the χ_{SANS} parameters do show strong composition dependences (Figure 8) and in a manner where both upward and downward trends are observed with changes in composition. The shape of the χ_{SANS} with composition is apparently correlated strongly with volume changes on mixing, and mixtures showing positive excess volumes have minima in the composition dependence, and vice versa.

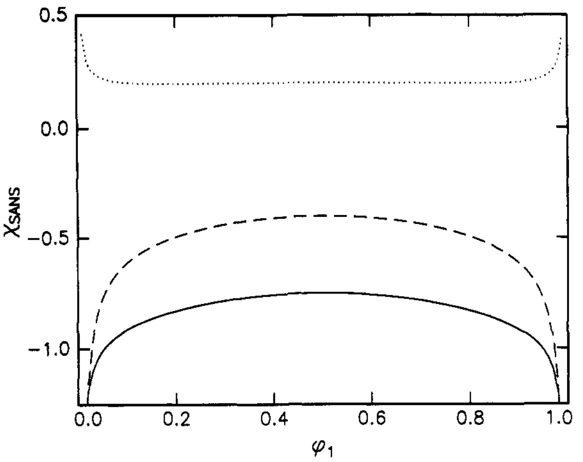

Figure 8. Predicted χ_{SANS} as a function of composition for the attractive system at $T^* = 2$ (—) and $T^* = 2.5$ (- - -). (···) are corresponding results for the repulsive system at $T^* = 2.5$.

These results, which are in good agreement with experimental data, are highly encouraging and suggest that the unusual composition dependence observed for χ_{SANS} must arise, at least in part, due to excess volume changes on mixing that are ignored in the i-RPA. This discrepancy arises even in the situation where the chemical potentials at constant pressure themselves, apparently, obey Flory-like composition dependences. It is gratifying to note that this extremely simple calculation allows us to capture both the "upturn" and "downturn" that is observed experimentally but could not be predicted by earlier works of Muthkumar[25] and Olvera de la Cruz *et al.*[26] A model that can reproduce both the upward and downward curvatures for χ_{SANS} is the PRISM integral equation theory of Schweizer and Curro[2-4] which suggests, independent of closure, that the χ parameter can be obtained from the relationship

$$2\chi n = \frac{\rho[G_{11} + G_{22} - 2G_{12}] + \frac{\rho^2}{n}[G_{11}G_{22} - G_{12}^2]}{n + \rho[\phi_1 G_{11} + \phi_2 G_{22}] + \phi(1-\phi)\frac{\rho^2}{n}[G_{11}G_{22} - G_{12}^2]} \qquad (30)$$

where ρ is the density, which is chosen to be independent of composition in these calculations, and $G_{\alpha\beta}$ is defined as

$$G_{\alpha\beta} = \int [g_{\alpha\beta}(\mathbf{r}) - 1]\, d\mathbf{r} \qquad (31)$$

where $g_{\alpha\beta}$ is the appropriate radial distribution function. These results were obtained for blends whose molar volumes are independent of composition, and we would like to illustrate that this could be a complicating factor. Kirkwood and Buff[76] have previously shown that the partial molar volumes of species 1 in a binary blend of simple liquids is expressible in terms of the G functions as

$$\bar{V}_1 = \frac{1 + \rho\phi_1[G_{22} - G_{12}]}{\rho + \rho^2\phi_1\phi_2[G_{11} + G_{22} - 2G_{12}]} \qquad (32)$$

This result clearly shows that the packing effects evoked by Schweizer and Curro for defining the composition dependence of χ, *i.e.*, the G functions, also result in composition-dependent partial molar volumes for the two blend components, a fact that has been ignored in the PRISM analysis. The necessary consequence of this argument is that the composition dependence of χ predicted by Schweizer and Curro[2-4] is appropriate to describe the constant-volume situation probed by Binder and co-workers[45] and also by us. The consequences of the inclusion of pressure effects on the PRISM predictions is unclear at this time, and we therefore cannot comment on the applicability of the PRISM findings in explaining the composition dependence of χ_{SANS} through eq 8.

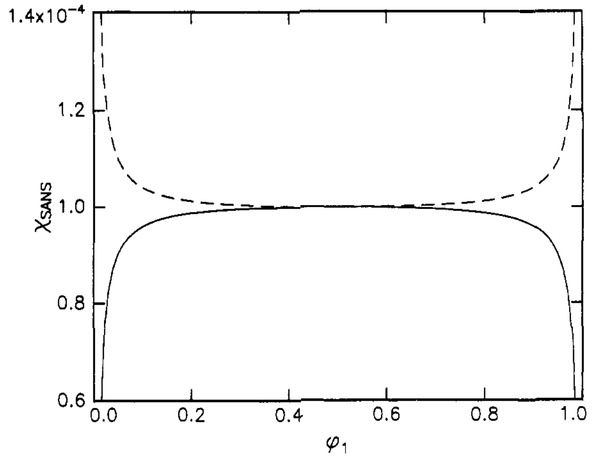

Figure 9. χ_{SANS} as a function of composition for a system containing "isotopic polymers" of length 1700 where (—) corresponds to an attractive blend and (- - -) corresponds to a repulsive blend.

To summarize our findings we suggest strongly that volume changes on mixing, which have been ignored in all previous formulations except those of Freed and co-workers,[33] must be incorporated into the i-RPA before thermodynamic quantities, such as χ_{SANS}, are extracted from scattering data. The lack of inclusion of these volume changes on mixing can give rise to an unphysical divergence of χ_{SANS} at the wings of the composition. Finally, it is stressed that, although the results presented here emphasize the importance of free-volume effects, they should by no means be seen as suggesting that deviations from Flory theory do not occur for realistic systems. Rather, we suggest that these deviations can only be monitored in a SANS experiment if the volume changes on mixing are properly accounted for when analyzing the scattering data.

4.4. Extension to "Realistic" Systems. Finally, since we cannot simulate realistic blends of long chain length polymers, we make contact with experiment through the use of a few *ad-hoc* assumptions. First, we assume that the results obtained for the symmetric computer blends hold for realistic systems and assume that the variation of chemical potentials with composition at constant pressure can be modeled through the use of a composition-independent χ parameter. It should be recognized that the assumption of a symmetric blend is not even appropriate for isotopic polymer mixtures since isotopic substitution, which is known to modify the polarizability and size of a molecule,[77] ensures that the two isotopic monomers are not identical in size or intramolecular interactions. Nevertheless, we arbitrarily assume that chemical potentials for these isotopic blends at constant pressure can be modeled with a composition-independent χ value of 1.0×10^{-4}. We consider chains of length $n_1 = n_2 = 1700$. Volume changes on mixing are assumed to be parabolic with a maximum difference of 0.05% at a volume fraction of 0.5, a result that is in qualitative agreement with past experimental work.[78] Both positive and negative volumes on mixing are considered. It should be recognized that these state conditions represent typical numbers, and we utilize them to check if the experimentally observed composition dependences can be reproduced with the ideas presented here. We observe in Figure 9 that χ_{SANS} computed with these numbers shows composition dependences that are qualitatively similar to the experimental findings, in both shape and magnitude. However, these results are not in quantitative agreement with experimental findings.[19] Further, we find that χ_{SANS} shows convex and concave behavior depending on the sign of the excess volume changes on mixing.

We therefore assert that the volume changes on mixing account, at least partially, for the unusual composition dependence seen for SANS-determined χ parameters for simple isotopic polymer blends. It is stressed, again, that this result does not preclude any deviations from Flory theory, which would contribute an additional composition dependence to χ_{SANS}. To obtain these "real" deviations from Flory theory, therefore, it is necessary for SANS data to be analyzed in a fashion such that the volume changes on mixing are properly accounted for in the analysis.

5. Conclusions

In conclusion, we find that the Flory–Huggins description of the Gibbs energy of mixing is adequate to model the chemical potentials of the components of symmetric polymer blends even at off-critical compositions as long as one considers *all* compositions at constant pressure. Similar results do not hold for blends whose molar volumes are independent of composition, and we find, in agreement with the earlier lattice simulations of Binder,[45] that the χ parameters needed to fit these data have an approximately parabolic composition dependence. *These represent unexpected results which have not been reported earlier* and stress the importance of free-volume (or EOS) effects in describing the thermodynamics of polymer blends. We also note that the value of χ for the systems at constant pressure normally assume a renormalized value, as has been observed in the critical point simulations of Binder and co-workers,[45] and we conclude that the excellent agreement found for the constant-pressure chemical potentials with the Flory functional form must represent a fortuitous cancellation of errors. Further, we find that currently existing models incorporating the effects of fluctuations on the free energy of mixing do not adequately describe the chemical potential data, and we therefore stress the need for improved models in this context.

We show that the unusual composition dependence of χ_{SANS} is caused, at least in part, due to incorrect assumption of "no excess volume change on mixing" that is assumed by i-RPA. Contrary to most available theories, these volume changes on mixing allow us to predict both the "upturn" and "downturn" for the composition dependence of χ_{SANS} as measured experimentally on several blend systems. In addition, the curvature of a plot of χ_{SANS} with composition is directly related to the sign of the excess volumes on mixing. Finally, we consider "realistic" systems and show that even small excess volume changes on mixing (like *ca.* 0.05%) can describe the experimentally measured composition dependence of blend χ parameters, suggesting that a proper measure of *PVT* properties of polymer blends may be necessary before SANS data can be properly interpreted.

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Appendix. Derivation of Chemical Potential Formulas at Constant Pressure

We begin with the small-molecule situation and write the partition function for a pure system under isothermal–isobaric conditions,

$$\Xi = \exp\left(-\frac{G}{k_{\text{B}}T}\right) = \frac{1}{\Lambda^{3N}N!}\int \mathrm{d}V\, V^N \exp\left(-\frac{PV}{k_{\text{B}}T}\right) \times \int\int\ldots\int \exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N]\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\,\mathrm{d}\mathbf{r}_N \quad \text{(A.1)}$$

where G is the Gibbs energy of the system of interest and Λ is the deBroglie wavelength of the particles. We now follow a procedure similar to the Widom test particle method and use the identity[59]

$$\beta\mu = G(N+1) - G(N) \quad \text{(A.2)}$$

where $G(N)$ refers to the Gibbs energy of an N-particle system and μ is the chemical potential. Using eqs A.1 and A.2 for the case of $P^* = 0$, we can show that this yield the expression

$$\exp[-\beta\mu] = \frac{1}{\Lambda^3(N+1)} \times \frac{\int V^{N+1}\,\mathrm{d}V\int\int\ldots\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\,\mathrm{d}\mathbf{r}_N\,\mathrm{d}\mathbf{r}_{N+1}\exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,\mathbf{r}_{N+1})]}{\int V^N\,\mathrm{d}V\int\int\ldots\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\,\mathrm{d}\mathbf{r}_N\exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)]} \equiv \frac{1}{\Lambda^3}\frac{\langle V\exp[-\beta U_{N+1}]\rangle_{T,P,N}}{N+1} \quad \text{(A.3)}$$

where U_{N+1} is the energy of interaction experienced by the $(N + 1)$th particle placed in the medium containing N particles at T and P. This result is similar to the one derived by Wood.[55] Rewriting this equation yields

$$-\beta\mu = \ln\frac{\langle V\exp[-\beta U_{N+1}]\rangle}{N+1} + \ln\frac{1}{\Lambda^3} \equiv -\beta\mu_{\text{r}} - \beta\mu_{\text{ID}} \quad \text{(A.4)}$$

where μ_{ID} is the "ideal" gas contribution and μ_{r} is the residual chemical potential. Extensions of these ideas to binary mixtures is straightforward and the chemical potential of component α in a binary blend is obtained as

$$\exp[-\beta\mu_1] = \frac{1}{\Lambda^3(N_1+1)} \times \frac{\int V^{N_1+N_2+1}\,\mathrm{d}V\int\int\ldots\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\,\mathrm{d}\mathbf{r}_{N_1+N_2}\,\mathrm{d}\mathbf{r}_{N_1+1}\exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2\ldots\mathbf{r}_{N_1+N_2},\mathbf{r}_{N_1+1})]}{\int V^{N_1+N_2}\,\mathrm{d}V\int\int\ldots\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\ldots\,\mathrm{d}\mathbf{r}_{N_1+N_2}\exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2\ldots\mathbf{r}_{N_1+N_2})]} \equiv \frac{1}{\Lambda^3}\frac{N_1+N_2}{N_1+1}\frac{\langle V\exp[-\beta U_{N_1+1}]\rangle_{T,P,N}}{N_1+N_2} \quad \text{(A.5)}$$

where the first two terms are ideal gas contributions.

Extensions of these ideas to the chain increment method appropriate to a homopolymer system is straightforward. We now consider the incremental chemical potential between a chain of length x and one of length $x - 1$, when both chains are in a matrix of chains of length n under isothermal–isobaric conditions, *i.e.*, we examine the homopolymer situation under isothermal–isobaric conditions. By analogy we can therefore write under zero-pressure conditions that

$$\exp[-\beta\mu_{\mathrm{inc}}(x)] = \frac{1}{\Lambda^3(Nn+x)} \times \frac{\int V^{Nn+x}\,\mathrm{d}V \int\int \dots \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \dots \mathrm{d}\mathbf{r}_{Nn+x-1}\,\mathrm{d}\mathbf{r}_{Nn+x} \exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_{Nn+x-1}\mathbf{r}_{Nn+x})]}{\int V^{Nn+x-1}\,\mathrm{d}V \int\int \dots \int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2 \dots \mathrm{d}\mathbf{r}_{Nn+x-1} \exp[-\beta U(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_{Nn+x-1})]} = \exp[-\beta\mu_{\mathrm{ID}}]\frac{\langle V \exp[-\beta U(\mathbf{r}_{Nn+x})\,]\rangle}{Nn+x} \quad (\mathrm{A.6})$$

where the system is comprised of N chains of length n and one chain of length $x - 1$ and $\mu_{\mathrm{inc}}(x)$ is the incremental chemical potential associated with a chain of length x (this includes the ideal gas contribution). $U(\mathbf{r}_{Nn+x})$ is the energy experienced by the test bead added to the chain of length $x - 1$ in the system. When now extend these ideas to a binary mixture consisting of N_1 chains of type 1 of length n_1 and N_2 chains of length n_2 and write by analogy that the incremental chemical potential of a chain of length x_1 in this system is

$$\exp[-\beta\mu_{\mathrm{inc}}(x_\alpha)] = \frac{1}{\Lambda^3}\,\frac{N_1n_1 + x_1 - 1 + N_2n_2}{N_1n_1 + x_1}\,\frac{\langle V \exp[-\beta U(\mathbf{r}_{N_1n_1+x_1})]\rangle}{N_1n_1 + x_1 - 1 + N_2n_2} \quad (\mathrm{A.7})$$

where the last term is then the residual part of the incremental chemical potential that is utilized in this work and the first two terms correspond to the ideal gas contribution.

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