Prediction of the Properties of Model Polymer Solutions and Blends

D. Ghonasgi and Walter G. Chapman
Dept. of Chemical Engineering, Rice University, Houston, TX 77251

In this work we present an extension of the statistical associating fluid theory (SAFT) developed for associating fluids by applying this extension to polymer solutions and blends. The polymer molecule is modeled as a flexible chain made of bonded spherical segments. These segments interact with the Lennard-Jones potential. The extension of SAFT is compared with molecular simulation results for polymer solutions and blends. Since the same force model is used in the simulation and theory, this comparison is a strong test of the assumptions made in deriving the theory. Results are presented for pure polymers of up to 50 segments long, polymer solutions of a polymer 20 segments long dissolved in its own monomer, and blends of polymers of 25 segments each. The theory produces results that are in better agreement with simulation results than the Flory-Huggins theory for the systems studied.

Introduction

Polymer solutions and polymer blends exhibit very complex phase behavior (Shean-Jer et al., 1992). The complexity in their phase behavior can be attributed to free-volume and energetic contributions of the constituent components. When these systems contain components that can associate, the situation is further complicated. Understanding the phase behavior of polymer systems is important for polymer processing and separations. For example, phase behavior is important in the use of supercritical fluids (SCFs) as antisolvents in polymer solutions (McHugh and Krukonis, 1986).

Most of the thermodynamic modeling for these systems have been done using the Flory-Huggins (FH) lattice theory (Flory, 1941; Huggins, 1941). The original theory was developed independently by Flory and Huggins for athermal systems. To apply the theoretical results to real polymers, that is, systems which are not athermal, the Flory-Huggins theory was modified by adding a semi-empirical part to the Gibbs free energy of mixing (Flory, 1954). This term contains a parameter called the Flory "Chi parameter" (χ). The χ parameter is determined by the energies which characterize interactions between pairs of polymer segments, solvent segments, and polymer-solvent segments. This parameter is assumed to be independent of the composition of the mixture. Experimental data for polymer solutions have shown that χ is a function of composition, molecular weight, and temperature (Schweizer and Curro, 1989).

In light of recent advances in statistical mechanics based equations of state for polyatomic molecules, it is of interest to study how variations in pressure, density, and composition affect the properties of polymer solutions and polymer blends. The fact that these equations of state are based in statistical mechanics means that the equation of state has a theoretically sound form and physical parameters. After these physical parameters are fit to available experimental data, the form of the equation of state allows the prediction of properties outside the range of available data. For example, an engineer can ask how the phase behavior of a mixture changes when the number of carbons in a solvent molecule is increased or decreased or when a hydrogen bonding group is added to one of the components.

To test the approximations made in developing such an equation of state, comparisons are made with molecular simulation results. Molecular simulation is a "brute force" method (that in one case solves Newton's equations of motion for a large number of molecules) to determine the thermodynamic properties of a fluid (Allen and Tildesley, 1987; Haile, 1992; and Gubbins, 1993). The only approximation in the molecular simulation is the force of interaction between molecules. By

---

Correspondence concerning this article should be addressed to W. G. Chapman.

comparing an equation of state with molecular simulation using the same force model, there are no adjustable parameters and the approximations that have been made in developing the equation of state can be rigorously tested. In this work, we attempt to validate one such equation of state for polymer blends and polymer solutions.

Recently, equations of state based on statistical mechanics have been derived to explain the behavior of chain molecules, molecules made of bonded spherical segments. Dickman and Hall (1986) have used the original mean field ideas of Flory and Huggins and applied them to off-lattice chains. They developed the Generalized Flory (GF) and the Generalized Flory Dimer (GFD) equation of state (Honnell and Hall, 1989). These equations have been tested against molecular simulation results (Dickman and Hall, 1988) for flexible chains of hard-sphere segments (hard chain molecules). Honnell and Hall (1991) have tested the theories for binary mixtures of hard chain molecules with the same segmental diameter but with different chain lengths. They also compare the performance of the GFD equation of state with the Flory-Huggins theory. Based on their comparisons Honnell and Hall (1991) concluded that, for mixing at constant pressure, the free energy and entropy of mixing from GFD are close to FH predictions at high pressure, while for mixing at constant volume the results from GFD reduce to the original FH theory. Yethiraj and Hall (1991) have also investigated the behavior of square-well chains in which the segments interact via a square-well intermolecular potential.

At the same time as GF and GFD equations were developed another statistical mechanics based approach based on Wertheim's (Wertheim, 1984a,b, 1986a,b) first-order perturbation theory for associating fluids was developed. Associating fluids are defined as fluids which have strong short range, highly directional interactions, for example, hydrogen bonding fluids. Wertheim (1987) extended his theory to nonassociating chain fluids and developed the first- and second-order thermodynamic perturbation theories (TPT1 and TPT2) for a polydisperse mixture of chains of varying lengths with mean length $\overline{m}$. At about the same time and independently, Chapman et al. (1988) extended Wertheim's theory to mixtures of associating fluids and based on this extension developed a theory which describes the thermodynamic properties for chains of fixed length m. The equation derived by Chapman et al. (1988) gives identical results when compared to TPT1 for a polydisperse mixture of nonassociating chains with mean length $\overline{m} = m$. The work by Chapman et al. (1988) led to an equation of state for associating chain molecules called the Statistical Associating Fluid Theory (SAFT) (Chapman et al., 1990; Huang and Radosz, 1990). SAFT has been used to correlate and predict experimental results for complex systems like solutions of alternating poly (ethylene-propylene) in supercritical and subcritical olefins (Shean-Jer et al., 1992), and solutions of Nylon-6 in trifluoroethanol and carbon dioxide (Suresh et al., 1994). Although the theory has been used to correlate experimental results, it has not been tested against molecular simulation results for mixtures of chain molecules. Such a test involves no adjustable parameters and is therefore a stronger test of the theory. In this work we test an extension of SAFT (Chapman, 1990) with recent computer simulation results of Kumar (1992a,b; 1994). Kumar obtained thermodynamic properties for chain molecules which are made up of segments that interact with the Lennard-Jones (LJ) potential. Adjacent segments in the chain interact via the spring potential. Kumar obtained the chemical potential for the chain molecules using the chain increment method that he developed (Kumar et al., 1991). This is the first comparison of this extension of SAFT with simulation data for polymer solutions and polymer blends which interact with the LJ potential.

We discuss details of the theory in the next section, followed by results and discussions. Finally, we present conclusions of this work and provide some ideas for future work.

Theory

SAFT was developed based on Wertheim's theory for associating fluids (Wertheim, 1984a,b, 1986a,b). Several articles explain the theory, its extensions, and its testing using molecular simulations (Joslin et al., 1987; Jackson et al., 1988; Chapman et al., 1988; Nezbeda et al., 1989; Nezbeda and Inglesias-Silva, 1990; Chapman, 1990; Johnson and Gubbins, 1992; Ghonasgi et al., 1993; Ghonasgi and Chapman, 1993a,b). Joslin et al. (1987) presented a generalization of Wertheim's theory for fluids associating at a single site to multicomponent liquid mixtures. They studied a model binary fluid mixture with the association potential modeled as site-site columbic interactions. Jackson et al. (1988) studied the effect of molecular association on the phase coexistence properties of hard-sphere fluids with one- and two-directional association sites. In order to study phase equilibria using Wertheim's theory, Jackson et al. (1988) added a simple van der Waals mean field term to represent the dispersion forces. Chapman et al. (1988) extended the theory to mixtures of molecules with multiple bonding sites. An equation of state for associating hard-sphere chains was obtained based on this extension. Chapman (1990) extended the theory which was originally developed for associating hard-core molecules to associating LJ spheres with one and two association sites. Chapman (1990) also developed an equation of state for chains in which the segments interact with the LJ potential. Johnson and Gubbins (1992) presented results for phase equilibria from simulations for associating LJ pure fluids and LJ mixtures. They also performed simulations for diatomic LJ fluids. Johnson and Gubbins compared the extension of the theory to LJ spheres with their simulation results. Ghonasgi and Chapman (1993a) tested the theory for spherical molecules with four association sites. This fluid could be considered as a model of water. Ghonasgi and Chapman (1993b) later tested the theory for associating chain molecules. In this work, we are testing the equations developed by Chapman (1990) for mixtures of chain molecules in which the segments interact with the LJ potential. Simulation results for such a system have only recently appeared in the literature (Kumar, 1991, 1992a,b, 1994).

In this section, we explain the assumptions made in deriving the theory and the development of the chain equation of state for polyatomic LJ fluids. Wertheim (1984a,b, 1986a,b) developed a theory to explain the behavior of associating fluids. The molecules of the associating fluid are assumed to interact by the following pair potential:

$$\phi(12) = \phi_R(12) + \sum_A \sum_B \phi_{AB}[\,|\mathbf{r}_2 + \mathbf{d}_B(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_A(\Omega_1)|\,] \quad (1)$$

A and B represent sites in the molecules where association occurs. $\phi_R(12)$ is the pair potential in the reference fluid. The notation (12) is used to denote the positions and orientations of molecules 1 and 2. r_i is the position of the molecular center, $\boldsymbol{d}_A$ is the vector joining the center of the molecule to association site A on the molecule, and Ω_i represents the orientation. ϕ_{AB} is the association interaction and is assumed to be attractive ($\phi_{AB} \leq 0$).

As with any theory, SAFT is based on several assumptions; these assumptions are:

(1) Only one bond can form at any association site (Wertheim, 1986a).

(2) Only single bonds form between molecules.

(3) The properties of the fluid are independent of the angles between association sites on the molecule (Ghonasgi and Chapman, 1993b).

(4) When solved by thermodynamic perturbation theory, the theory includes the effect of chain like and tree like associated clusters but not of ring clusters.

The theory was extended to mixtures of spherical and polyatomic associating molecules by Chapman et al. (1988). We present the equations for this extension. Based on the assumptions given above and the pair potential given by Eq. 1, the Helmholtz free energy for a mixture of associating molecules residual to an ideal gas at the same temperature and density is given by:

$$\frac{A^{\text{mix}}}{NkT} = \frac{A_R^{\text{mix}}}{NkT} + \frac{A_{\text{assoc}}^{\text{mix}}}{NkT} \tag{2}$$

A_R^{mix} is the residual Helmholtz free energy of the nonassociating reference fluid, N is the total number of molecules in the system, T is the temperature, and k is Boltzmann's constant. $A_{\text{assoc}}^{\text{mix}}$ is the change in the residual Helmholtz free energy due to association and is given by:

$$\frac{A_{\text{assoc}}^{\text{mix}}}{NkT} = \sum_i X^{(i)} \left[\sum_A \left(\ln X_A^{(i)} - \frac{X_A^{(i)}}{2} \right) + \frac{1}{2} M^{(i)} \right] \tag{3}$$

where $X^{(i)}$ is the mole fraction of component i, $X_A^{(i)}$ is the fraction of component i not bonded at site A, the second sum is over all bonding sites on a molecule of component i, and $M^{(i)}$ is the number of bonding sites on a molecule of component i. The X_As are obtained from the following equation:

$$X_A^{(i)} = \left[1 + \sum_j \sum_B \rho X^{(j)} X_B^{(j)} \Delta_{AB}^{(ij)} \right]^{-1} \tag{4}$$

where $\rho = N/V$ is the total number density of the mixture, the sums are over all components j and all sites B on a molecule of component j, and $\Delta_{AB}^{(ij)}$ is defined by:

$$\Delta_{AB}^{(ij)} = \int g_R^{(ij)}(12) f_{AB}^{(ij)}(12)\, d(12) \tag{5}$$

$f_{AB}^{(ij)}(12) = \exp[-\phi_{AB}^{(ij)}(12)/kT] - 1$ is the Mayer f-function for the association interaction. $g_R^{(ij)}(12)$ is the nonassociating reference fluid pair correlation function. The notation $\int d(12)$ denotes an unweighted average over all possible orientations of molecules 1 and 2 and an integral over all possible separations of molecules 1 and 2.

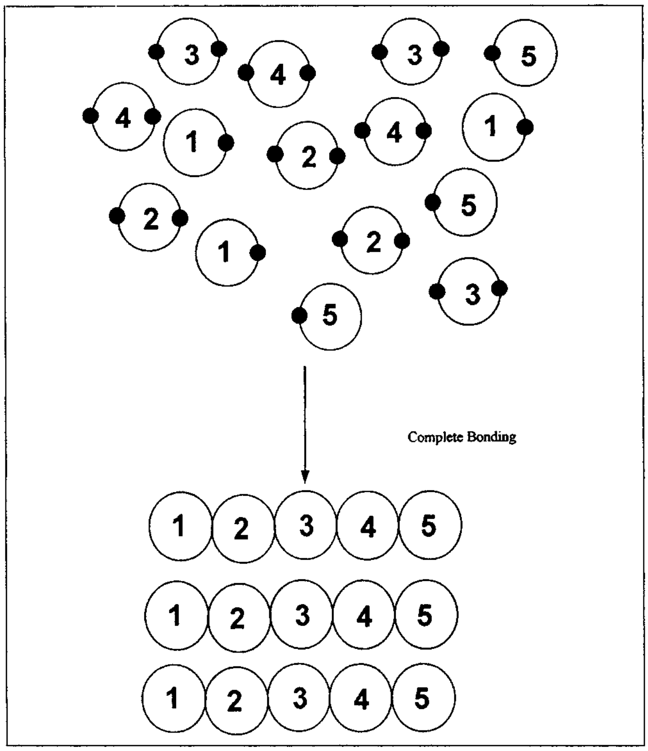

Figure 1. Formation of chain molecules.

Comparisons between the theory and molecular simulation results have shown excellent agreement for associating hard-sphere (Joslin et al., 1987; Jackson et al., 1988; Ghonasgi and Chapman, 1993a,b) and Lennard-Jones (Chapman, 1990; Johnson and Gubbins, 1993; Ghonasgi and Chapman, 1993a,b) systems. These include results for associating polyatomic molecules with "chemical" strength association (Ghonasgi et al., 1993; Ghonasgi and Chapman, 1993b).

Chain Equation of State

By considering the limit that the association bond is of covalent strength, the theory can predict the equation of state of chain-like molecules. Consider a fluid made up of five spherical components 1, 2, . . . , 5. Let us say that there are 3 molecules of each component in the fluid. Molecules 1 and 5 have one association site; molecules 2, 3, and 4 have two association sites, as shown in Figure 1. We restrict the bonding between molecules such that molecule 1 can bond to 2, molecule 2 can bond to 1 and 3, and so on. The extension of Wertheim's theory to mixtures is applied to this system and the condition of total bonding is imposed on the system by setting the fraction of spheres not bonded at the appropriate sites to zero. This will result in the formation of 3 chain molecules which are 5 segments long, as shown in Figure 1. The same argument is applied to a more general system of a mixture of N chains having r components; each component i has N_i chain molecules with m_i segments. Here, we consider the case of mixtures of homonuclear chains. On applying the total bonding condition to the equation for pressure corresponding to Eq. 2 we obtain:

$$Z = 1 + (Z_o - 1)\sum_i X^{(i)} m_i + \sum_i X^{(i)} \times (1 - m_i)\rho \left[\frac{\partial \ln y_R^{ii}(l_i)}{\partial \rho} \right]_{T, X^{(j)}} \tag{6}$$

where Z_o is the compressibility factor of the spherical segments before they form chains. Integrating Eq. 6, we obtain the following expression for the residual Helmholtz free energy of the fluid of chain like molecules. This is now residual to an ideal gas mixture of chains.

$$\frac{A^{\text{mix}}}{NkT}=\frac{A_R^{\text{mix}}}{NkT}+\frac{A_{\text{chain}}^{\text{mix}}}{NkT} \tag{7}$$

and $A_{\text{chain}}^{\text{mix}}$ is the change in the residual Helmholtz free energy due to chain formation and is given by:

$$\frac{A_{\text{chain}}^{\text{mix}}}{NkT}=\sum_i X^{(i)}[(1-m_i)\ \ln\ (y_R^{ii}(l_i))] \tag{8}$$

$y_R^{ii}(l_i)$ is the cavity correlation function for the reference fluid mixture (spherical segments prior to bonding); it is related to the pair correlation function of the reference fluid by $y_R^{ii}(l_i) = g_R^{ii}(l_i)\ \exp\ (\phi_{R_{ii}}(l_i)/kT)$. l_i is the bond length for the chains of component i. Equation 8 is a general form of the change in residual free energy due to chain formation for mixtures. Equation 8 reduces to TPT1 for a polydisperse mixture of chains of equal segment size, bond length, and energy of interaction. In fact, Eq. 8 predicts for this case that the change in residual Helmholtz free energy due to chain formation is dependent only on the average chain length in the mixture. In this case, Eq. 8 becomes:

$$\frac{A_{\text{chain}}^{\text{mix}}}{NkT}=(1-m_{\text{avg}})\ \ln\ (y_R(l)) \tag{9}$$

where m_{avg} is the mole fraction averaged degree of polymerization.

If the segments in the chain molecule are not rigidly bonded, the bonding potential can be included in the chain equation of state (Eq. 8) to obtain:

$$\frac{A_{\text{chain}}^{\text{mix}}}{NkT}=\sum_i X^{(i)}(1-m_i)\ \ln \times \left\{\frac{\displaystyle\int_{l_{i,\min}}^{l_{i,\max}}\left\langle\exp\left[-\frac{\phi_{i,\text{bond}}(r,\ \omega_1,\ \omega_2)}{kT}\right]\right\rangle_{\omega_1,\omega_2} y_R^{ii}(r)dr}{\displaystyle\int_{l_{i,\min}}^{l_{i,\max}}\left\langle\exp\left[-\frac{\phi_{i,\text{bond}}(r,\ \omega_1,\ \omega_2)}{kT}\right]\right\rangle_{\omega_1,\omega_2} dr}\right\} \tag{10}$$

$\phi_{i,\text{bond}}(r,\ \omega_1,\ \omega_2)$ is the potential of interaction between the adjacent segments in the i chain molecule, ω_1 and ω_2 represent the orientations of the segments, and the $\langle\ \rangle$ represents an average over all orientations of the two segments. We have assumed in Eq. 10 that the bonding potential becomes infinite for $r<l_{i,\min}$ and $r>l_{i,\max}$, where $l_{i,\min}$ and $l_{i,\max}$ are the minimum and maximum possible bond lengths for the molecule of component i.

The residual chemical potential due to chain formation for component i is obtained by differentiating the Helmholtz free energy (see Eq. 8) with respect to N_i at constant temperature and composition of the other components. The resulting expression for the chain part of the residual chemical potential is given by:

$$\frac{\mu_i^{\text{chain}}}{kT}=(1-m_i)\ \ln\ (y_R^{ii}(l_i)) + \sum_j \rho_j(1-m_j)\left[\frac{\partial\ \ln\ y_R^{jj}(l_j)}{\partial\rho_i}\right]_{T,\rho_{k\neq i}} \tag{11}$$

$\rho_i = X^{(i)}\rho$ is the number density of component i. The contribution to the residual chemical potential from the reference fluid is given by:

$$\frac{\mu_i^R}{kT}=\frac{m_i\mu_{o_i}^R}{kT} \tag{12}$$

where $\mu_{o_i}^R$ is the residual chemical potential of the spherical segments at the same temperature and a density of $\sum_i \rho_i m_i$.

The chemical potential of component i that we report is the residual chemical potential (including the reference and chain term together) per segment of component i given by:

$$\frac{\mu_i}{m_i kT}=\frac{\mu_{o_i}^R}{kT}+\frac{(1-m_i)\ \ln\ (y_R^{ii}(l_i))}{m_i} + \frac{\displaystyle\sum_j \rho_j(1-m_j)\left[\frac{\partial\ \ln\ y_R^{jj}(l_j)}{\partial\rho_i}\right]_{T,\rho_{k\neq i}}}{m_i} \tag{13}$$

Kumar (1992b) has calculated the chemical potential of a polymer using the chain increment method (Kumar et al., 1991) in Metropolis Monte Carlo simulation (Allen and Tildesley, 1987). In the chain increment method, Kumar calculates the incremental chemical potential between a homopolymer chain of length ν and one of length $\nu+1$, $\mu_r(\nu+1)$, while each is in identical solvents:

$$\mu_r(\nu+1)=\mu^r(\nu+1)-\mu^r(\nu) \tag{14}$$

$\mu^r(\nu)$ is the residual chemical potential of a chain of length ν. Kumar et al. (1991) observed that $\mu_r(\nu)$ for melt chains are essentially independent of chain length for $\nu \geq 3$. In his articles for polymer solutions (Kumar, 1992b) and polymer blends (Kumar, 1994) Kumar reports the quantity $\mu_r(\nu)$ and assumes that the total residual chemical potential of a chain of length ν is given by:

$$\mu^r(\nu)\approx \nu\mu_r \tag{15}$$

The quantity μ_r is the incremental residual chemical potential which is assumed to be independent of the chain length by Kumar (1992b, 1994). Kumar reported results for binary mixtures of a polymer dissolved in its own monomer (1992b) and symmetric polymer blends $(m_1 = m_2)$ (1994). Assuming that Eq. 15 is valid, we can directly compare the incremental residual chemical potential with the residual chemical potential per segment given by Eq. 13. This comparison is presented in the figures discussed below. We can also use the theory to predict the incremental residual chemical potential as it is calculated in the chain increment method. In the chain increment method a single chain is grown one segment at a time. Since the density of molecules is held fixed, the segment density changes each time a segment is added. If the number of molecules in the simulation cell is large, this change in segment density should be negligible. Assuming the concentration of segments is held constant, the theory predicts $\mu_r(\nu)$ is independent of ν for $\nu \geq 2$. In this case, $\mu_r(\nu)$ is given by:

$$\frac{\mu_r(\nu)}{kT} = \frac{\mu^R_{o_i}}{kT} - \ln\ (y^{ii}_R(l_i)) - \rho_i \left[\frac{\partial \ln y^{ii}_R(l_i)}{\partial \rho_i} \right]_{T,\rho_{k \neq i}} \tag{16}$$

Consider the special case of a binary system of a polymer at infinite dilution dissolved in its own monomer. Let us denote the polymer component by the subscript 2 and the monomer by the subscript 1. At infinite dilution $\rho_1 \to \rho$ and $\rho_2 \to 1/V$ where V is the volume of the mixture, Eqs. 11 and 12 when added together give the following expression for the residual chemical potential of the polymer at infinite dilution dissolved in its own monomer.

$$\mu_2^\infty = m_2 \mu_1 + [(1 - m_2) kT \ln\ (y(l))] \tag{17}$$

note that $m_1 = 1$ and $\mu^R_{o_1} = \mu_1$ in this case. $y(l)$ is the cavity correlation function for the monomer at a separation of l. Equation 17 is exact for dispheres. The chemical potential at infinite dilution is related to the Henry's law constant by:

$$\frac{\mu_i^\infty}{kT} = \ln \left(\frac{K_i}{\rho kT} \right) \tag{18}$$

where K_i is the Henry's law constant. Thus, based on $y(l)$ for the monomer, we can calculate the Henry's law constant for a polymer dissolved in its own monomer. Equation 17 has been shown to be in excellent agreement with molecular simulation results for polymers made of up to 15 LJ segments (Ghonasgi et al., 1993).

At any other composition, the thermodynamic properties of the polymer solution or blend are related to the cavity correlation function of the mixture of segments prior to bonding to form chains. In this work, we are primarily interested in linear chain molecules with a fixed segment bond length. Segments of different molecules interact with the LJ potential function. The LJ interaction potential is given by:

$$\phi_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{19}$$

where ϵ is the LJ energy parameter and σ is the LJ size parameter. The bond length between the spherical segments making up the chain is equal to the LJ distance parameter (σ). For this special case, $y_R^{ii}(\sigma_i) = g_R^{ii}(\sigma_i)$, where g_R^{ii} is the reference pair correlation function for the i-i interaction.

The reference system is a mixture of spheres with composition of the spherical segments of chain i given by:

$$\phi_i = \frac{m_i X^{(i)}}{\sum_i m_i X^{(i)}} \tag{20}$$

ϕ_i is the segment fraction of chain i, and it is equal to the volume fraction if all the chains in the mixture have segments of the same diameter. To obtain the pair correlation function for mixtures of LJ spheres we use the Mean Density Approximation (MDA) (Mansoori and Leland, 1972) which has been shown by Hoheisel and Lucas (1984) to be superior to the van der Waals 1 fluid theory (vdW1) (Leland et al., 1968). The MDA relates the pair correlation function for components in a mixture of LJ spheres to the pair correlation function for a pure LJ fluid. The MDA equation for the pair correlation function of component i interacting with component j g_R^{ij} is given by:

$$g_R^{ij} = g_o(r^*, T^*_{ij}, \rho^*_x) \tag{21}$$

where $g_o(r^*, T^*_{ij}, \rho^*_x)$ is the pair correlation function for a pure LJ fluid with $r^* = r/\sigma_{ij}$, $T^*_{ij} = kT/\epsilon_{ij}$, $\rho^*_x = \rho \sigma_x^3 \sum_i X^{(i)} m_i$, and σ_x^3 is given by:

$$\sigma_x^3 = \sum_i \sum_j \phi_i \phi_j \sigma_{ij}^3 \tag{22}$$

Here ϵ_{ii} and σ_{ii} are the LJ energy and size parameters for pure component i. We have used $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$; ϵ_{ij} will be specified. We use Weeks Chandler Anderson (WCA) theory (Weeks et al., 1971) or molecular simulation to calculate the pair correlation function for the pure LJ fluid. g_o in Eq. 21 is approximately equal to the pair correlation function for the WCA reference fluid. The pair potential defining the WCA reference fluid is:

$$\phi_{\mathrm{WCA}} = \begin{cases} \phi_{\mathrm{LJ}}(r) + \epsilon & r < 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma \end{cases}. \tag{23}$$

This approximation for the LJ pure fluid pair correlation function assumes that the structure of the LJ fluid is determined by the repulsive part of the potential. This approximation is not valid at low densities. The WCA reference fluid pair correlation function $g_{\mathrm{WCA}}(r)$ can be estimated from:

$$g_{\mathrm{WCA}}(r) \approx y_d(r) \exp\ (-\phi_{\mathrm{WCA}}(r)/kT) \tag{24}$$

$y_d(r)$ is the cavity correlation function for a hard-sphere fluid with hard-sphere diameter d chosen by equating the compressibility of the WCA reference system to that of the hard-sphere system. An algorithm given by Verlet and Weiss (1972) was used to calculate this diameter. The cavity correlation function for the hard-sphere fluid was calculated using the Percus-Yevick (PY) approximation solution given by Wertheim (1963). The derivatives of the pair correlation function with respect to density can be obtained analytically from Eqs. 23 and 24.

The residual Helmholtz free energy of the reference LJ mixture is calculated from vdW1 (Leland et al., 1968). In vdW1, we approximate the residual Helmholtz free energy of a mixture with the residual Helmholtz free energy of a pure fluid with parameters σ_x^3 given by Eq. 22 and ϵ_x calculated from:

$$\sigma_x^3 \epsilon_x = \sum_i \sum_j \phi_i \phi_j \sigma_{ij}^3 \epsilon_{ij} \tag{25}$$

The properties of the pure LJ fluid were calculated from the

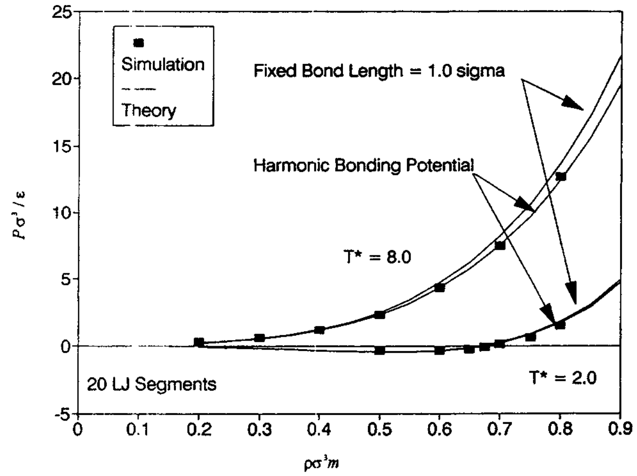

Figure 2. Reduced pressure ($P\sigma^3/\epsilon$) vs. reduced segment density ($\rho\sigma^3 m$) for pure chain molecules (20 LJ segments) at reduced temperature ($T^* = kT/\epsilon$) of 2.0 and 8.0.

Nicolas equation of state (Nicolas et al., 1979). When carrying out the differentiation in Eqs. 6 and 11 one has to take into account the density and composition dependence of g_{ij} implied in Eqs. 20 through 25.

Results and Discussions

Before applying the theory for mixtures, the theory should be validated for pure fluids of LJ chain molecules. In Figure 2, we plot the pressure vs. the reduced segment density, $\rho^* = \rho\sigma_x^3 \sum X^{(i)} m_i$, at two reduced temperatures for a pure fluid in which the molecules are made up of 20 LJ segments. The points are Monte Carlo simulation data of Kumar (1992a) and the curves are our predictions. The simulation results are obtained for a fluid in which the molecules are modeled as beads with springs, and a harmonic bonding potential is used for adjacent segments in the chain. At low temperature, the effect of the harmonic potential on the pressure of the fluid is small as seen in Figure 2. Henceforth, we exclude the harmonic potential from the theory. In Figure 3, the pressure is plotted vs. the reduced segment density for a chain made up of 50 LJ segments. The agreement between simulation results and the theory is good in both the figures.

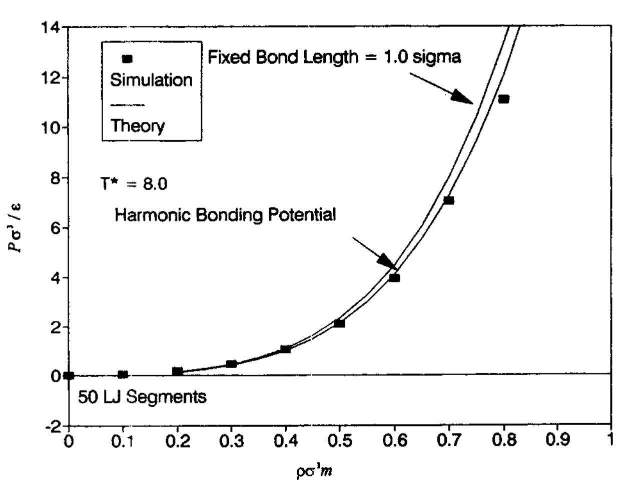

Figure 3. Reduced pressure ($P\sigma^3/\epsilon$) vs. reduced segment density for pure chain of 50 LJ segments at a reduced temperature of 8.0.

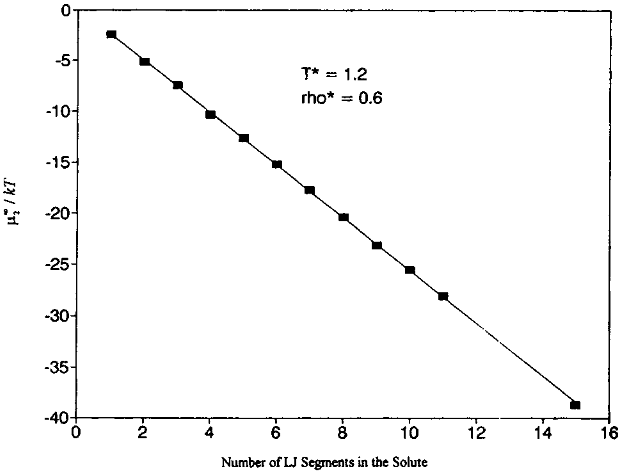

Figure 4. Residual chemical potential of a polymer at infinite dilution in its own monomer vs. the number of segments in the polymer chain.

Reduced temperature of 1.2 and reduced solvent density of ($\rho\sigma^3$) 0.6, from simulation (points) and theory (curves).

Equation 17 can be used to calculate the chemical potential of a polymer in a solvent of its own monomers at infinite dilution. A comparison of simulation results (Kumar, 1992a) and theory for the infinite dilution chemical potential of polymers of various numbers of segments is shown in Figure 4. The agreement between theory and simulation results is excellent.

At finite concentrations we use Eq. 13 to calculate the residual chemical potential per segment. Figure 5 shows results

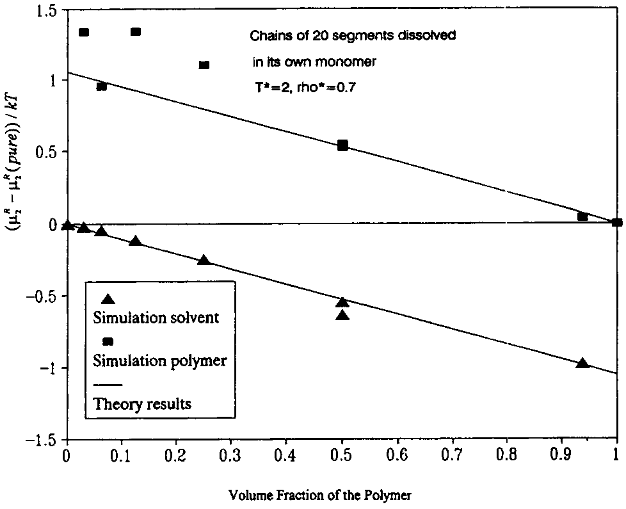

Figure 5. Residual chemical potential for a polymer chain (squares) of 20 LJ segments dissolved in its own monomer (triangles) vs. the volume fraction of the polymer.

Reduced temperature ($T^* = kT/\epsilon$) of 2.0 and a reduced segment denstiy ($\rho\sigma_x^3 \sum X^{(i)} m_i$) of 0.7.

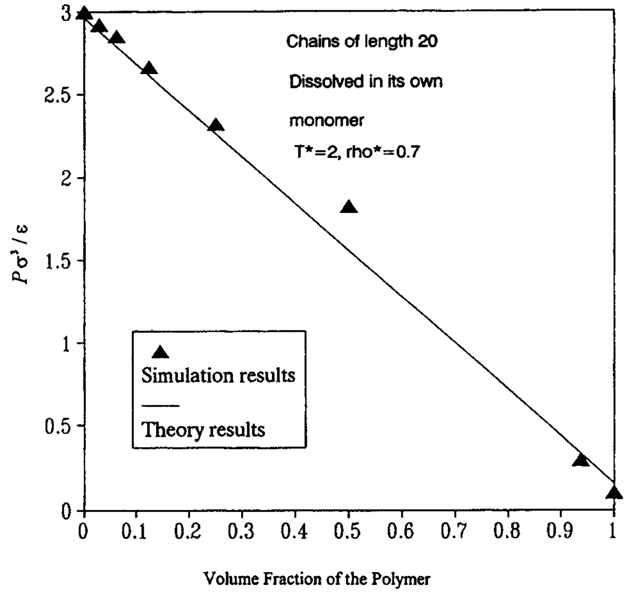

Figure 6. Reduced pressure ($P\sigma^3/\epsilon$) vs. the volume fraction of the polymer for chains of 20 LJ segments dissolved in its own monomer.

Reduced temperature of 2.0 and a reduced segment density ($\rho\sigma_x^3\sum X^{(i)}m_i$) of 0.7.

for the chemical potential of a polymer in its own monomer from infinite dilution of the polymer to infinite dilution of monomer. The polymer is 20 segments long with $T^*=2$, and a mixture density of $\rho_x^*=0.7$. Figure 6 shows the results for pressure ($P\sigma^3/\epsilon$) vs. the volume fraction of the polymer. The simulation results are due to Kumar (1992b). Again the agreement between simulation and theory is excellent. As explained in the derivation of Eq. 9, the properties of this mixture are dependent on only the average chain length in the mixture. This is in agreement with Brønsted and Koefoed's (Rowlinson and Swinton, 1982) principle of congruence (Peters et al., 1992).

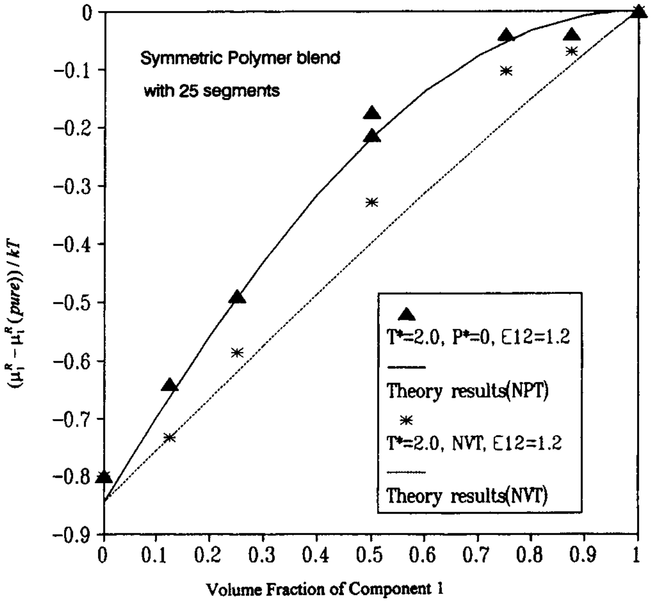

Figure 7. Residual chemical potential for component 1 of a symmetric polymer blend with chains of 25 LJ segments.

Reduced temperature ($T^*=kT/\epsilon$) of 2.0 at constant pressure (triangles) and constant volume (asterisks) for an attractive blend ($\epsilon_{12}=1.2$).

Next we consider results for polymer blends. Simulation results were obtained by Kumar (1994) for symmetric polymer blends with 25 segments. Segments of both components have the same bead diameter (σ), and energy of interaction between like segments ($\epsilon_{11}=\epsilon_{22}$). The energetic interaction between unlike chains are different and two cases were considered by Kumar (1994), an attractive blend ($\epsilon_{12}/\epsilon_{11}=1.2$) and a repulsive blend ($\epsilon_{12}/\epsilon_{11}=0.9$). Figure 7 shows the results for the attractive blend at $T^*=kT/\epsilon_{11}=2$. Kumar (1994) performed Monte Carlo simulations in the isothermal-isobaric (NPT) ensemble at $P^*=P\sigma^3/\epsilon_{11}=0$ and in the canonical ensemble (NVT) at a blend volume equal to the pure component molar volume at $T^*=2$ and $P^*=0$. When the theory is applied to the constant pressure case one needs to solve for the density iteratively for different compositions. Once the density is calculated the residual chemical potential per segment can be obtained from Eq. 13. For the constant volume case the density is fixed and thus the calculation of the chemical potential is straightfoward. One purpose of the study done by Kumar (1992b, 1994) was to learn how the Flory χ parameter depends on composition. The Flory-Huggins theory was derived for the constant volume case. For the symmetric polymer blend considered here Flory-Huggins theory predicts a parabolic relation between the residual chemical potential per segment and the volume fraction at constant volume (Kumar, 1992b, 1994). Figure 7 shows that a parabolic relation is obtained from the constant pressure simulations while the constant volume simulations do not follow the Flory-Huggins theory. We predict a parabolic relation at constant pressure in agreement with simulation but at constant volume we predict a curve which is nearly a straight line. The reason for the disagreement between the constant volume simulation results and our predictions is not clear. The disagreement might be due to our use of the mean density approximation for the reference fluid cavity correlation function, and errors in the simulation data. Figure 8 shows the results for constant pressure simulations at $T^*=2.5$ for the attractive and the repulsive blends. The agreement between the theory presented here and the simulation results is very good.

Flory theory (Huggins, 1941) predicts that at constant volume the difference between the residual chemical potential per segment for component 1 and residual chemical potential per segment of pure 1 in a symmetric binary polymer blend is related to the composition as:

$$\frac{\mu_1-\mu_1^{\text{pure}}}{m_1kT}=\chi^{\text{eff}}\phi_2^2 \qquad (26)$$

Thus, we can calculate an effective chi parameter (χ^{eff}) from simulation and theory which is a function of composition. The composition dependence predicted by theory is obtained by using Eq. 13 in Eq. 26. We have plotted the χ^{eff} obtained from Eq. 26 vs. the volume fraction of component 1 in Figure 9. As seen in the figure, χ^{eff} is relatively independent of composition for constant pressure conditions while it depends on composition for the constant volume conditions. The theory

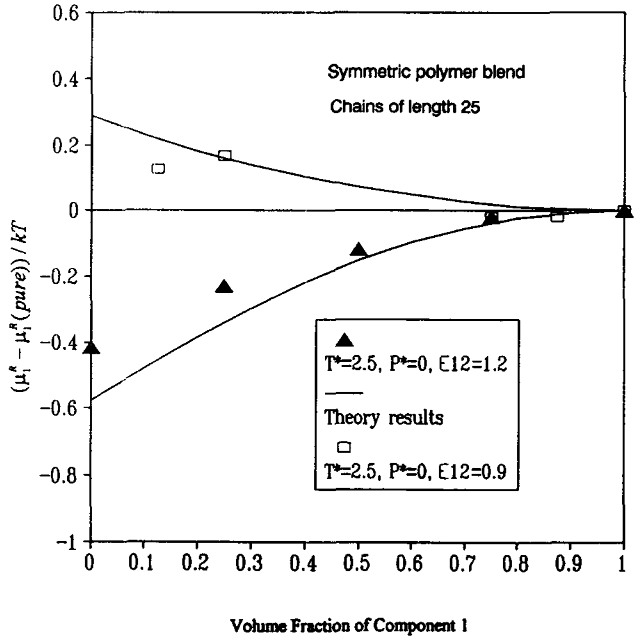

Figure 8. Residual chemical potential for component 1 of a symmetric polymer blend with chains of 25 LJ segments.

Reduced temperature ($T^* = kT/\epsilon$) of 2.5 at constant pressure for an attractive ($\epsilon_{12} = 1.2$) (triangles) and a repulsive blend ($\epsilon_{12} = 0.9$) (squares).

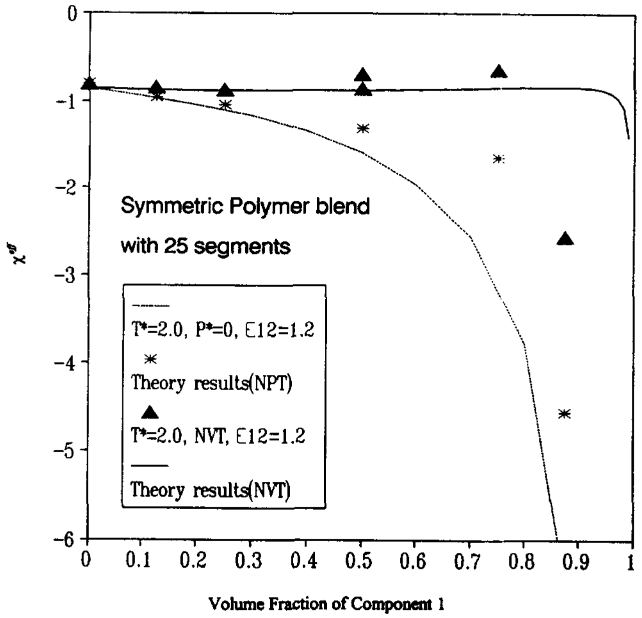

Figure 9. Effective "Chi" parameter of a symmetric polymer blend with chains of 25 LJ segments.

Reduced temperature ($T^* = kT/\epsilon$) of 2 at constant pressure (triangles) and constant volume (asterisks) for an attractive blend ($\epsilon_{12} = 1.2$).

predictions for χ^{eff}, though not in quantitative agreement with simulation results for constant volume conditions, show the correct qualitative trend.

Conclusions

Describing the complex phase behavior of polymer solutions and polymer blends is a difficult problem. Flory Huggins theory has been the primary theoretical tool for quite some time, though it was known to have deficiencies. With the advent of new off-lattice statistical mechanics based theories we expect to increase our ability to correlate and predict phase behavior for complex fluid mixtures. One of these advances was pioneered by Hall and coworkers. This approach uses the original mean field ideas of Flory and Huggins and applies them to off-lattice chains. Another approach is based on an extension of Wertheim's theory of associating fluids. This extension has resulted in an equation of state called SAFT.

In this article, we have used an extension of SAFT to explain the behavior of polymer solutions and polymer blends. Unlike SAFT which is based on the hard-sphere reference, in this extension we use LJ spheres as the reference. We expect that this extended form will be successful in correlating and predicting properties of real fluids since real fluids exhibit soft repulsion similar to the soft repulsions in the LJ fluid.

Based on our results from the extension of SAFT to the LJ reference we conclude that the theory gives results that are in good agreement with computer simulation results for simple models of pure chain fluids, polymer solutions at all concentrations, and polymer blends. Further study will consider more highly nonideal mixtures.

After our article had been accepted, we became aware of articles by Banaszak et al. (1994) and Johnson et al. (1994) that test the extension of Wertheim's theory for pure Lennard-Jones chains with fixed bond length.

Acknowledgment

The authors gratefully acknowledge discussions with Prof. Sanat Kumar and for providing his computer simulation data. The financial assistance of the Shell Oil Company Foundation is also gratefully acknowledged.

Notation

A^{mix} = Helmholtz free energy of a mixture residual to an ideal gas at the same temperature and density, J

$A^{\text{mix}}_{\text{assoc}}$ = change in the residual Helmholtz free energy due to association, J

$A^{\text{mix}}_{\text{chain}}$ = change in the residual Helmholtz free energy due to chain formation, J

A^{mix}_{R} = contribution of the reference interaction to the residual Helmholtz free energy, J

d_A = vector joining the center of a molecule to site A on the molecule

$f^{(ij)}_{AB}(12)$ = Mayer f-function for the association interaction of site A on a molecule of component i and site B on a molecule of component j, (12) represents all possible orientations and all possible separations of molecules i and j

$g^{(ij)}_{R}(12)$ = nonassociating reference fluid pair correlation function between molecules of component i and component j

$g^{ii}_{R}(l_i)$ = reference pair correlation function for molecules of component i at a separation of l_i

g^{ij}_{R} = pair correlation function between component i and component j of a LJ mixture

g_o = pair correlation function for a pure LJ fluid

k = Boltzmann's constant $\approx 1.381 \times 10^{-23}$ J/K/molecules

K_i = Henry's law constant for component i, J/Å^3

l_i = bond length of chain i, reduced by LJ size parameter σ

$l_{i,\text{min}}$, $l_{i,\text{max}}$ = minimum and maximum bond lengths of chain i, reduced by LJ size parameter σ

m_i = number of segments in chain i

$M^{(i)}$ = number of bonding sites on a molecule of component i

N = number of molecules in the mixture

r = separation between a pair of molecules, reduced by LJ size parameter σ

$\mathbf{r}$ = position vector of the center of mass of a molecule

r^* = separation between molecule i and molecule j reduced by LJ size parameter σ_{ij}

T = temperature, K

T_{ij}^* = reduced temperature, reduced by ϵ_{ij}/k

V = volume of the mixture, Å^3

$X_A^{(i)}$ = fraction of molecules of component i not bonded at site A

$X^{(i)}$ = mole fraction of component i

$y_R^{ii}(l_i)$ = cavity correlation function for segments of chain i at a distance l_i

Z = compressibility factor

Z_o = compressibility factor of segments before they form chains

Greek letters

$\Delta_{AB}^{(ij)}$ = strength of interaction between site A on molecule i and site B on molecule j, Å^3

ϵ = Lennard Jones energy parameter, J

ϵ_x = Lennard Jones energy parameter for the mixture, J

μ_2^{∞} = residual chemical potential of chain 2 at infinite dilution, J/molecules

μ_i^{chain} = chain contribution to the residual chemical potential for chain i, J/molecules

$\mu_{o_i}^R$ = residual chemical potential of the spherical segments, J/molecules

μ_i = total residual chemical potential for chain i, J/molecules

μ_i^R = residual chemical potential of the reference fluid, J/molecules

μ_r = incremental residual chemical potential for a polymer chain, J/molecules

$\mu^r(\nu)$ = total residual chemical potential for a chain of length ν, J/molecules

ρ = number density, number of molecules/Å^3

ρ_x^* = reduced number density for the mixture, reduced by σ_x^3

ρ_i = number density of component i, number of molecules of component i/Å^3

σ = Lennard Jones distance parameter, Å

σ_x = Lennard Jones distance parameter for the mixture, Å

ϕ = intermolecular interaction pair potential, J

ϕ_{AB} = association interaction potential between sites A and B, J

$\phi_{i,\text{bond}}$ = intramolecular potential between adjacent segments of chain i, J

ϕ_i = segment fraction of segments making up chain i

ϕ_R^{ii} = reference interaction potential between segments of type i, J

ϕ_{LJ} = Lennard Jones potential, J

ϕ_R = reference potential, J

χ = Flory interaction parameter

χ^{eff} = effective Flory interaction parameter

Ω, ω = orientation of molecules, radians

Literature Cited

Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987).

Banaszak, M., Y. C. Chien, R. O'Lenick, and M. Radoz, "Thermodynamic Perturbation Theory: Lennard Jones Chains," *J. Chem. Phys.*, **100**, 3803 (1994).

Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, "New Reference Equation of State for Associating Liquids, *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).

Chapman, W. G., G. Jackson, and K. E. Gubbins, "Phase Equilibria of Associating Fluids: Chain Molecules with Multiple Bonding Sites," *Molec. Phys.*, **65**, 1057 (1988).

Chapman, W. G., "Prediction of the Thermodynamic Properties of Associating Lennard-Jones Fluids: Theory and Simulation," *J. Chem. Phys.*, **93**, 4299 (1990).

Dickman, R., and C. K. Hall, "Equation of State for Chain Molecules: Continuous-Space Analog of Flory Theory," *J. Chem. Phys.*, **85**, 4108 (1986).

Dickman, R., and C. K. Hall, "High Density Monte Carlo Simulations of Chain Molecules: Bulk Equation of State and Density Profiles Near Walls," *J. Chem. Phys.*, **89**, 3168 (1988).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **9**, 660 (1941).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY (1954).

Ghonasgi, D., M. Llano-Restrepo, and W. G. Chapman, "Henry's Law Constant for Diatomic and Polyatomic Lennard-Jones Molecules," *J. Chem. Phys.*, **98**, 5662 (1993).

Ghonasgi, D., and W. G. Chapman, "Theory and Simulation for Associating Fluids with Four Bonding Sites," *Molec. Phys.*, **79**, 291 (1993a).

Ghonasgi, D., and W. G. Chapman, "Theory and Simulation for Associating Chain Fluids," *Molec. Phys.*, **80**, 161 (1993).

Gubbins, K. E., "Applications of Molecular Simulation," *Fluid Phase Equil.*, **83**, 1 (1993).

Haile, J. M., *Molecular Dynamics Simulation: Elementary Methods*, Wiley, New York (1992).

Hoheisel, C., and K. Lucas, "Pair Correlation Functions in Binary Mixtures from Pure Fluid Data," *Molec. Phys.*, **53**, 51 (1984).

Honnell, K. G., and C. K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**, 1841 (1989).

Honnell, K. G., and C. K. Hall, "Theory and Simulation of Hard-Chain Mixtures: Equation of State, Mixing Properties, and Density Profiles Near Hard Walls," *J. Chem. Phys.*, **95**, 4481 (1991).

Huang, S. H., and M. Radosz, "Equation of State for Small, Large, Polydisperse, and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 2284 (1990).

Huggins, M. L., "Solutions of Long Chain Compounds," *J. Chem. Phys.*, **9**, 440 (1941).

Jackson, G., W. G. Chapman, and K. E. Gubbins, "Phase Equilibria of Associating Fluids: Spherical Molecules with Multiple Bonding Sites," *Molec. Phys.*, **65**, 1 (1988).

Johnson, J. K., and K. E. Gubbins, "Phase Equilibria for Associating Lennard-Jones Fluids from Theory and Simulation," *Molec. Phys.*, **77**, 1033 (1992).

Johnson, J. K., E. A. Müller, and K. E. Gubbins, "Equation of State for Lennard-Jones Chains," *J. Phys. Chem.*, submitted (1994).

Joslin, C. G., C. G. Gray, W. G. Chapman, and K. E. Gubbins, "Theory and Simulation of Associating Liquid Mixtures: II," *Molec. Phys.*, **62**, 843 (1987).

Kumar, S. K., I. Szleifer, and A. Z. Panagiotopoulos, "Determination of the Chemical Potentials of Polymeric Systems from Monte Carlo Simulations," *Phy. Rev. Lett.*, **66**, 2935 (1991).

Kumar, S. K., "Monte-Carlo Simulations of Polymeric Systems in Quenched and Annealed Media: Consequences on Computed Thermodynamic Properties," private communication (1992a).

Kumar, S. K., *Computer Simulations of Polymers*, E. A. Colbourn, ed., Longman, Harlow, UK (1992b).

Kumar, S. K., "Chemical Potentials of Polymer Blends from Monte-Carlo Simulations: Consequences of SANS-Determined Chi Parameter," *Macromol.*, **27**, 260 (1994).

Leland, T. W., J. S. Rowlinson, and G. A. Sather, "Statistical Thermodynamics of Mixtures of Molecules of Different Sizes," *Trans. Farad. Soc.*, **64**, 1447 (1968).

Mansoori, G. A., and T. W. Leland, "Statistical Thermodynamics of Mixtures: A New Version for the Theory of Conformal Solution," *J. Chem. Soc. Farad. Trans: II*, **8**, 320 (1972).

McHugh, M. A., and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston (1986).

Nezbeda, I., J. Kolafa, and Y. V., Kalyuzhnyi, "Primitive Model of Water: II. Theoretical Results for the Structure and Thermodynamic Properties," *Molec. Phys.*, **68**, 143 (1989).

Nezbeda, I., and G. A. Iglesias-Silva, "Primitive Model of Water III. Analytic Theoretical Results with Anomalies for the Thermodynamic Properties," *Molec. Phys.*, **69**, 767 (1990).

Nicolas, J. J., K. E. Gubbins, W. B. Streett, and D. J. Tildesley, "Equation of State for the Lennard-Jones Fluid," *Molec. Phys.*, **37**, 1429 (1979).

Peters, C. J., J. M. H. Sengers, and J. S. Gallagher, "Congruence—an Accurate Property Estimator for Mixtures of Long n-Alkanes?," AIChE Meeting, Miami Beach (1992).

Rowlinson, J. S., and F. L. Swinton, *Liquids and Liquid Mixtures*, 3rd ed., Butterworths, London (1982).

Schweizer, K. S., and J. G. Curro, "Integral Equation Theory of the Structure and Thermodynamics of Polymer Blends," *J. Chem. Phys.*, **91**, 5059 (1989).

Shean-Jer, C., I. G. Economou, and M. Radosz, "Density-Tuned Polyolefin Phase Equilibria: 2. Multicomponent Solutions of Alternating Poly(ethylene-propylene) in Subcritical and Supercritical Olefins. Experiment and SAFT Model," *Macromolecules*, **25**, 4987 (1992).

Suresh, S. J., R. M. Enick, and E. J. Beckman, "Phase Behavior of Nylon 6/Trifluoroethanol/Carbon Dioxide Mixtures," *Macromol.*, **27**, 348 (1994).

Weeks, J. D., D. Chandler, and H. C. Andersen, "Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids," *J. Chem. Phys.*, **54**, 5237 (1971).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics," *J. Stat. Phys.*, **35**, 19 (1984a).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. II. Perturbation Theory and Integral Equations," *J. Stat. Phys.*, **35**, 35 (1984b).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites," *J. Stat. Phys.*, **42**, 459 (1986a).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization," *J. Stat. Phys.*, **42**, 477 (1986b).

Wertheim, M. S., "Exact Solution of the Percus-Yevick Integral Equation for Hard Spheres," *Phys. Rev. Lett.*, **10**, 321 (1963).

Verlet, L., and Jean-Jacques Weis, "Equilibrium Theory of Simple Liquids," *Phys. Rev.*, **A5**, 939 (1972).

Yethiraj, A., and C. K. Hall, "Square-Well Chains: Bulk Equation of State Using Perturbation Theory and Monte Carlo Simulations of the Bulk Pressure and of the Density Profiles Near Walls," *J. Chem. Phys.*, **95**, 1999 (1991).

Manuscript received June 18, 1993, and revision received Aug. 16, 1993.