Abstract

ATTWOOD, BRIAN CHRISTOPHER. Global phase diagram for monomer/dimer mixtures. (Under the direction of Carol K. Hall)

The objective of this thesis is to calculate the global phase diagram predicted by the Generalized Flory Dimer equation of state for mixtures of square-well monomers and dimers. Towards that goal, we first extend the Generalized Flory Dimer (GFD) theory for hard sphere monomer/dimer mixtures to square-well monomer/dimer mixtures. Theoretical predictions for the compressibility factor as a function of volume fraction are compared to discontinuous molecular dynamic simulation results on monomer/dimer mixtures at well depth ratios 0.5 - 1.5 and dimer mole fractions 0.111 - 0.667 and on monomers/8-mer mixtures at well depth ratios 0.5 - 1.5. Agreement is found generally to be good and consistent with the agreement obtained when the GFD theory is applied to other square-well systems.

Next we calculate the GFD predicted global phase diagram for square-well monomer/dimer mixtures using a brute force method. The locus of critical points in the $P - T$ plane is calculated for a grid of points in the $\Lambda - \zeta$ plane, where ζ is a measure of the difference between the monomer and dimer well depths and Λ is a measure of the strength of the attraction between monomers and dimers. Initially, the locus of critical points was calculated for 360 points in a square grid between the values of -0.9 and 0.9 for both ζ and Λ . Additional points were calculated as necessary to gain resolution in areas where more detail was needed.

The most significant features of the resulting global phase diagram are the absences of type IV and type VI behaviors. The absence of type VI behavior is not surprising because the existence

of closed loop liquid-liquid immiscibility predicted by equations of state for molecules of spherical potentials is a matter of debate. The absence of type IV behavior is somewhat more unexpected because such behavior is found in most previous work on systems of spherical molecules. Although we performed extra calculations in the area in the $\zeta - \Lambda$ plane where type IV behavior should be exhibited, it is possible that our search was not intense enough to find the small region where type IV behavior might exist. The phase diagram is shifted towards the negative ζ and Λ directions when compared to the van der Waals global phase diagram for equal diameter spherical molecules. The shift in the ζ direction can be attributed to the size difference between monomers and dimers. The shift in the Λ direction implies that monomer/dimer systems have a greater tendency towards liquid-liquid immiscibility in our system than in monomer/monomer systems.

GLOBAL PHASE DIAGRAM FOR MONOMER/DIMER MIXTURES

by

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Biography

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1 Introduction

Prediction of phase equilibria for multicomponent systems containing chain like molecules is important in a number of areas in industry, including oil refining, pharmaceutical purification, and the processing of many types of polymers, such as rubbers, plastics, and lubricants. Foreknowledge of the phase behavior of a solution containing chainlike molecules during processing allows us to induce or avoid phase separation as needed and hence is critical to successful design and operation of that process. One way to approach this problem that has become popular in recent years is to construct a global phase diagram that predicts the phase behavior expected for a particular equation of state. A global phase diagram gives a map of the types of phase behavior associated with a particular equation of state in intermolecular interaction parameter space. Using the knowledge embodied in a global phase diagram, a process engineer could tune a process, for example, with regards to the solvent strength, to select one type of phase behavior over another less-desirable phase behavior.

Applying phase equilibria conditions to a particular equation of state for the purpose of calculating phase coexistence is a technique that is well established. Usually such calculations are carried out for specific values of the molecular interaction parameters in order to predict the phase equilibrium of a particular system. A different approach was taken in the late sixties by van Konynenburg and Scott [1, 2] who chose to examine the phase behavior predicted for a binary mixture by the van der Waals equation of state over the entire range of interaction parameters. Their approach involved simultaneously solving the two equations, $(\partial^2 G / \partial x_i^2)_{P,T} = 0$ and $(\partial^3 G / \partial x_i^3)_{P,T} = 0$, that define a mixture critical point, where G is the Gibb's free energy of mixing, x_i is the mole fraction of component i , P is the pressure, and T is the temperature and hence calculating the locus of critical points as a function of composition, pressure, and temperature. The type of phase behavior could

then be classified into one of six types based on the projection of the locus of critical points onto the P - T plane.

For their analysis of mixtures of equal sized components, Scott and van Konynenburg [1, 2] used two dimensionless parameters, ζ and Λ , which were a function of the attractive interaction parameters a_{11} , a_{22} , and a_{12} between molecules of components 1 and 2, where $\zeta = (a_{22} - a_{11}) / (a_{22} + a_{11})$ and $\Lambda = (a_{11} - 2a_{12} + a_{22}) / (a_{22} + a_{11})$. For equal sized molecules, ζ is related to the differences in critical temperatures or pressures of the pure components and Λ to the molar heat of mixing at $T = 0$. By determining the locus of critical points for a range of these parameters, they were able to construct a global phase diagram which divides the $\zeta - \Lambda$ parameter space into regions of similar phase behavior. Their global phase diagram for the van der Waals equation of state accounts for five of the six types of phase behavior known to exist in nature. The only type of phase behavior not found by Scott and van Konynenburg was type VI, which is distinguished from the other types by a region of closed loop immiscibility. This was an important result because it showed that although the van der Waals equation of state is simplistic and quantitatively inaccurate for most fluids, it is able to predict much of the phase behavior exhibited in nature.

Since that landmark paper, a number of other groups have made similar explorations of the phase behavior for other equations of state. Furman *et al.* calculated the global phase behavior for a regular solution model of a three-component mixture that is nearly equivalent mathematically to a van der Waals model for binary mixtures with b independent of concentration (implying the molecules are of equal size) and a a quadratic function of composition [3]. They found significant agreement between the phase diagram they calculated and the one calculated by van Konynenburg and Scott for equal diameter molecules. Later Furman and Griffiths [4] revisited the global phase di-

agram for the van der Waals model and discovered a heretofore unidentified “shield region”, a small region containing several new classes of phase behavior that had not been pointed out previously by van Konynenburg and Scott.

Mazur and Boshkov [5–7] investigated the global phase behavior of binary Lennard-Jones fluid mixtures using a polynomial form for the equation of state that was proposed earlier and regressed to simulation data by Ree [8]. This was the first analysis of the phase behavior of a relatively modern equation of state that included a systematic look at the entire interaction parameter space. Mazur and Boshkov’s papers revealed that the global phase behavior predicted for Lennard-Jones fluids was qualitatively similar to that of the van der Waals equation of state, except that Type VI phase behavior was also predicted. This result was controversial because closed loop immiscibility was thought to occur only in systems with strong directional bonding, e.g. hydrogen bonding. More recently, Yelash *et al.* [9, 10] presented evidence that strong directional forces may not be necessary for the appearance of closed loop immiscibility and that large deviations in the cross-interaction parameters from the averages of the pure substances interaction parameters are sufficient. Dieters and Pegg calculated the global phase diagram for the Redlich-Kwong equation of state [11] in 1989 and found that for equal sized molecules, the global phase diagram predicted by the Redlich-Kwong equation of state is similar to that found for the van der Waals fluid or the Lennard-Jones fluid. In this case however, no instances of Type VI behavior were found. As the difference in molecular size was increased, the topology of the global phase diagram changed considerably, with new sub-classes of phase behavior being predicted. Kraska and Dieters [12] analyzed the Carnahan-Starling-Redlich-Kwong equation of state a few years later in 1992. For equal sized molecules the results were again similar to those for the van der Waals equation of state. For molecules of different sizes, some unusual new phase behavior was found involving four-phase states and high density instabilities.

One of the important results of this last study was that it showed that calculations based on a more “sophisticated,” non-cubic equation of state yielded results that were, in the case of equal sized molecules, surprising similar to those found for cubic equations of state.

In this study, we consider the global phase diagram associated with the Generalized Flory Dimer equation of state for a binary mixture. The Generalized Flory Dimer theory evolved from work done in this laboratory to develop equations of state that predict the behavior of fluids containing chainlike molecules. Our approach has been to start with extremely simple models and then to systematically add more realistic features with the goal of thoroughly understanding the impact of each new feature on the fluid behavior. The generalized Flory theories were first introduced in 1986 by Dickman and Hall [13] who extended the probabilistic assumptions of the Flory lattice model to hard chains moving in continuous space. These theories were based on estimating the probability of inserting a chain molecule into a chain fluid and substituting this into the osmotic equation of state to find the compressibility factor of the chain fluid. The insertion probability estimate was built up in terms of the probability of inserting a monomer into a monomer fluid, which could be derived from an equation of state for that monomer fluid. Honnell and Hall [14] later refined the estimate for chain insertion to include terms related to the insertion of a monomer into a monomer fluid and a dimer into a dimer fluid culminating in the Generalized Flory-dimer (GFD) theory. Yethiraj and Hall [15, 16] extended the generalized Flory theory to square-well chains in 1991, adding a little more realism to what had previously been an equation of state for athermal chains. Our efforts over the past five years have been devoted to extending GFD to more realistic and/or complex fluids including: hard chain mixtures [17], alternating, block, and random heteronuclear square-well chain fluids [18–20], hard-chain networks [21] and gels [22]. One thing that Hall and coworkers did not do was derive a GFD expression for square well monomer/dimer mixtures.

In this paper, we first derive the Generalized Flory Dimer theory for binary mixtures of square well monomers and dimers by extending the GFD theory for hard monomer/dimer mixtures to include attractions. This is accomplished in a manner similar to that used to extend GFD for pure hard chain fluids to pure square well chain fluids. The associated global phase diagram is found by calculating the locus of critical points at discrete points in interaction parameter space and then classifying the phase behavior at those points based on the resulting critical point locus topography. The calculation proceeds in a manner similar to that used by Van Konynenburg and Scott for the van der Waals equation of state, with the exception that numerical procedures are required to solve the governing equations. The locus of critical points for monomer/dimer mixtures of equal segment diameter was calculated at more than 100 discrete points in ζ - Λ space, with ζ and Λ each ranging from -0.9 to 0.9. For this range of ζ and Λ , the value of $\epsilon_{11}/\epsilon_{22}$ ranged from 0.0526 to 19.0 and the value of $\epsilon_{12}/(\epsilon_{11}\epsilon_{22})^{(1/2)}$ ranged from 0.1 to 4.36.

Highlights of our results are the following. The Generalized Flory Dimer theory was found to produce good agreement with simulation for mixtures of monomers and dimers of equal segment diameter at varying temperatures, interaction strengths, and compositions. The agreement between simulation and theory improved when the dimer component in the mixtures was replaced with an 8-mer. This result was to be expected based on an analysis by Kumar and coworkers [23] of the errors associated with the assumptions made in the derivation of the Generalized Flory dimer theories. The resulting global phase diagram was found to represent four of the six types of phase behavior found by Scott and van Konynenburg. Type IV and VI phase behaviors were absent from our phase diagram. Additional calculations in the areas where Type IV behavior was presumed to exist were not productive, leading us to believe that either we did not look hard enough, or that these types of phase behavior were not predicted by the GFD theory. Much like the Scott and van Konynenburg

results for molecules of unequal diameter, the vertical line of symmetry in our $\zeta - \Lambda$ plot was found to be shifted towards negative values of ζ . The horizontal boundary between regions that display liquid-liquid immiscibility, i.e. II and III, and those that do not, i.e. I and V, was shifted slightly in the negative Λ direction.

The remainder of this paper is organized as follows. In Section 2 the Generalized Flory Dimer theory for hard chains and square-well chains is reviewed and the Generalized Flory Dimer theory for square-well chain/monomer mixtures is derived. Theoretical predictions for the compressibility factor are compared to simulation results. In Section 3 the method used to calculate the global phase diagram is described. In Section 4, the global phase diagram resulting from the GFD prediction for square-well monomer/dimer mixtures is presented. Section 5 concludes the paper with a brief summary.

2 GFD equation of state for mixtures of square well chains and monomers

In this section, we derive the Generalized Flory-Dimer (GFD) equation of state for mixtures of square-well monomers and chains and compare the theory with simulation results. The starting point for the Generalized Flory-Dimer theory is the osmotic equation of state

$$\frac{P(\eta, n)}{kT} = \frac{\eta}{v_n} [1 - \ln p_n(\eta)] + \frac{1}{v_n} \int_0^n \ln p_n(\eta') d\eta', \quad (1)$$

which relates the n -mer pressure, P , to the n -mer insertion factor, p_n , the volume of one molecule, $v_n = (\pi/6)n\sigma^3$, and the volume fraction, $\eta \equiv Nv_n/V$, where σ is the segment diameter. The insertion factor is defined as

$$p_n(\eta) = \left\langle \exp \left(-\frac{U}{kT} \right) \right\rangle, \quad (2)$$

where U is the potential energy change upon inserting a test chain of length n into the fluid and the brackets indicate an average taken over all configurations of the test chain and the chains in the fluid. For hard chains, the insertion factor takes on values of 0 and 1, leading to the interpretation of this parameter as the chain insertion probability. The insertion factor is also related to the chemical potential [23] by

$$\frac{-\mu_n^*(\eta)}{kT} = \ln p_n(\eta) \quad (3)$$

where $\mu_n^*(\eta)$ is the corrected residual chemical potential, defined as the difference between the residual chemical potential and the residual chemical potential at zero density. (The residual chemical potential is the difference between the real and ideal chemical potentials at a given set of conditions.)

The compressibility factor, Z , can be expressed in terms of the chain insertion factor as

$$Z \equiv \frac{P(\eta, n)v_n}{\eta kT} = [1 - \ln p_n(\eta)] + \frac{1}{\eta} \int_0^n \ln p_n(\eta') d\eta'. \quad (4)$$

Because equation (4) is thermodynamically exact, the only challenge in deriving a good equation of state for a chain fluid is to accurately estimate the insertion factors. The Generalized Flory-Dimer theory uses simple geometric arguments to estimate the chain insertion factors based on the insertion factors for monomers and dimers in monomer and dimer fluids; the latter are available because accurate equations of state have been developed for monomer and dimer fluids. The GFD approach has been applied to pure fluids of athermal and square-well chains and to mixtures of athermal chains. Below, we briefly review the GFD approach for pure hard chain fluids and pure square-well fluids, since this will be relevant to our derivation of the GFD theory for square-well chain/monomer mixtures.

2.1 Review of Generalized Flory-Dimer theory for hard chain fluids

For pure fluids, the GFD estimate for the probability of inserting a hard chain into a hard chain fluid is given by

$$p_n^{hs}(\eta) = p_1^{hs}(\eta) \left[\frac{p_2^{hs}(\eta)}{p_1^{hs}(\eta)} \right]^{(v_e(n) - v_e(1))/(v_e(2) - v_e(1))}, \quad (5)$$

$$= p_1^{hs}(\eta)^{-Y_n} p_2^{hs}(\eta)^{Y_n} + 1, \quad (6)$$

where p_1^{hs} and p_2^{hs} are the probability of inserting a hard monomer and a hard dimer, respectively, into a hard n -mer fluid, $v_e(n)$ is the volume excluded by an n -mer to a monomer, and

$$Y_n = \frac{v_e(\eta) - v_e(2)}{v_e(2) - v_e(1)}. \quad (7)$$

Eq. (5) may be understood by imagining that the test chain is inserted into the chain fluid one segment at a time. The exact expression for the test chain insertion probability is given by

$$p_n(\eta) = \left(\begin{array}{c} \text{Probability} \\ \text{of} \\ \text{inserting} \\ \text{bead 1} \end{array} \right) \left(\begin{array}{c} \text{Conditional} \\ \text{probability} \\ \text{of} \\ \text{inserting} \\ \text{bead 2} \\ \text{given bead 1} \end{array} \right) \left(\begin{array}{c} \text{Conditional} \\ \text{probability} \\ \text{of inserting} \\ \text{bead 3} \\ \text{given beads} \\ \text{1 and 2} \end{array} \right) \cdots \left(\begin{array}{c} \text{Conditional} \\ \text{probability} \\ \text{of inserting} \\ \text{bead n} \\ \text{given beads} \\ \text{1, ..., n-1} \end{array} \right). \quad (8)$$

The first term on the right hand side of Eq. (8) is the probability of inserting the first bead of the test chain, p_1^{hs} , and using mean field arguments may be approximated by the probability of inserting a monomer into a monomer fluid. The second term on the right hand side of Eq. (8) is the conditional probability of inserting the second bead of the test chain next to the already-inserted first bead, i.e. the probability of finding a hole in the chain fluid large enough to accommodate the extra excluded volume, $v_e(2) - v_e(1)$, required. This term may be approximated by p_2^{hs}/p_1^{hs} where p_2^{hs} is the probability of inserting a dimer into a chain fluid which is itself approximated by the probability of inserting a dimer into a dimer fluid. The third term is the conditional probability of inserting the third bead next to the second, i.e. the probability of finding a hole in the chain fluid large enough to accommodate the extra excluded volume, $v_e(3) - v_e(2)$, required. This term may be approximated

by $[p_2^{hs}/p_1^{hs}]^{(v_e(3)-v_e(2))/(v_e(2)-v_e(1))}$, the conditional probability of inserting the second bead next to the first bead, raised to a power that corrects for the difference between the size of the hole required to place the third bead next to the second and that required to place the second bead next to the first. This type of reasoning is used repeatedly as beads are added to the chain, resulting in the chain insertion probability estimate given in Eq. (5).

Inserting Eq. (6) into the osmotic equation of state yields an expression for the compressibility factor of a hard n -mer fluid

$$Z_n^{hs}(\eta) = (Y_n + 1)Z_2^{hs}(\eta) - Y_n Z_1^{hs}(\eta), \quad (9)$$

where $Z_2^{hs}(\eta)$ and $Z_1^{hs}(\eta)$ are the compressibility factors of hard dimer and monomer fluids. The monomer and dimer compressibility factors can be obtained from appropriate equations of state, such as the Carnahan-Starling [24] and Tildesley-Street [25] equations of state, respectively. The excluded volume of an n -mer, $v_e(n)$ can be approximated as a linear function of chain length [13]

$$v_e(n) \approx v_e(3) + (n - 3)[v_e(3) - v_e(2)], \quad (10)$$

for $2 \leq n \leq 8$ and

$$v_e(n) \approx v_e(1)[10.094 + 0.6374(n - 15)], \quad (11)$$

for $n > 8$. [26]

2.2 Review of Generalized Flory-Dimer theory for square-well chain fluids

The Generalized Flory-Dimer approach can also be applied to square-well chain fluids [15]. By using geometric and mean field arguments similar to those used in the development of a GFD equation of state for hard chain fluids, the insertion factor for a square-well chain in a square-well fluid, $p_n^{sw}(\eta)$ is given by

$$p_n^{sw}(\eta) = p_1^{sw}(\eta) \left[\frac{p_2^{sw}(\eta)}{p_1^{sw}(\eta)} \right]^{(v_e(n) - v_e(1))/(v_e(2) - v_e(1))}, \quad (12)$$

$$= p_1^{sw}(\eta)^{-Y_n} p_2^{sw}(\eta)^{Y_n + 1}, \quad (13)$$

where p_1^{sw} is the insertion factor for a square-well monomer in a square-well monomer fluid, p_2^{sw} is the insertion factor for a square-well dimer in a square-well dimer fluid, and Y_n is the excluded volume ratio defined in Eq. (7). Note that this has the same functional form as the GFD expression for the insertion factor for a hard chain in a hard chain fluid (Eq. 5) except that the hard monomer and hard dimer insertion factors are replaced by square-well monomer and dimer insertion factors. When the above estimate for the square-well chain insertion factor is used in the osmotic equation of state, the resulting expression,

$$Z_n^{sw}(\eta) = (Y_n + 1)Z_2^{sw}(\eta) - Y_n Z_1^{sw}(\eta), \quad (14)$$

is the Generalized Flory-Dimer equation of state for square-well chain fluids, where $Z_2^{sw}(n)$ and $Z_1^{sw}(n)$ are the compressibility factors for square-well dimer and monomer fluids, respectively. The square-well monomer and dimer compressibility factors can be obtained by a number of methods, such as perturbation theory [27, 28], coordination number models [29], or by using the RISM theory

with the mean-spherical approximation closure [15, 30].

2.3 Generalized Flory-Dimer theory for square-well chain/monomer mixtures

The Generalized Flory-Dimer theory for binary mixtures is obtained by substituting suitable expressions for the insertion factors of each component in the so-called “alternate” form of the osmotic equation of state. The alternate form of the osmotic equation of state represents the process of inserting both species in the mixture simultaneously in proportion to their mole fractions, and is given by

$$\begin{aligned} \frac{P(\eta_a, \eta_b)}{kT} = & \frac{x_a \eta}{\bar{v}} [1 - \ln p_a(\eta_a, \eta_b)] + \frac{x_a}{\bar{v}} \int_0^\eta \ln p_a(\eta'_a, \eta'_b) d\eta' \\ & + \frac{x_b \eta}{\bar{v}} [1 - \ln p_b(\eta_a, \eta_b)] + \frac{x_b}{\bar{v}} \int_0^\eta \ln p_b(\eta'_a, \eta'_b) d\eta', \end{aligned} \quad (15)$$

where x_a and x_b are the mole fractions of species a and species b in the fluid, the volume fraction of the mixture is $\eta = (\pi/6)\rho \sum_i x_i n_i \sigma_i^3$, and $\bar{v} = x_a v_a + x_b v_b$ is the mole fraction average of the volumes of species a and b . The integration is performed at constant mole fraction of each species in the mixture so that

$$\eta'_a = x_a \frac{v_a}{\bar{v}} \eta'; \quad \eta'_b = x_b \frac{v_b}{\bar{v}} \eta' \quad (16)$$

Before we derive the Generalized Flory-Dimer theory for chain/monomer mixtures, it is useful to introduce the following notation for the mixture insertion probabilities. The probability of inserting a molecule of species i and length n_i into a mixture at total volume fraction η and composition x_a containing species a and b chains of lengths n_a and n_b , respectively, is denoted as $p(\eta, x_a)_{i n_i}^{(n_a, n_b)}$. In general, species i will be one of the mixture components, a or b , but its length may not be the

same as the length of the chains of component a or b in the mixture. The chain insertion factor will be written in terms of the more commonly used variables, total volume fraction and mole fraction, thus differing from the notation used in Eq. (16).

To apply the GFD theory to binary mixtures, it is necessary to estimate the insertion factors of each component in the fluid mixture. Consider a mixture of chains of component a and monomers of component b . The insertion factor for chains of component a takes the form

$$p(\eta, x_a)_{a_{n_a}}^{(n_a,1)} \approx \left(p(\eta, x_a)_{a_1}^{(n_a,1)} \right)^{-(Y_{n_a}^a)_{mix}} \times \left(p(\eta, x_a)_{a_2}^{(n_a,1)} \right)^{[(Y_{n_a}^a)_{mix}+1]}, \quad (17)$$

where $p(\eta, x_a)_{a_1}^{(n_a,1)}$ is the factor for inserting a monomer of species a into the chain/monomer mixture, $p(\eta, x_a)_{a_2}^{(n_a,1)}$ is the factor for inserting a dimer of species a into the chain/monomer mixture, and $(Y_{n_a}^a)_{mix}$ is the volume excluded in the mixture by a molecule of species a and length n_a . Expressions for $(Y_{n_a}^a)_{mix}$ are presented in Appendix A. Using arguments similar to those made in the GFD pure hard chain theory, the factor for inserting a monomer of species a into the chain/monomer mixture is taken to equal the factor for inserting a monomer of species a into the hypothetical monomer mixture created by breaking all of the chain bonds

$$p(\eta, x_a)_{a_1}^{(n_a,1)} \approx p(\eta, y_a)_{a_1}^{(1,1)}, \quad (18)$$

where y_a is the mole fraction of species a monomers in the hypothetical binary monomer mixture. Similarly the factor for inserting a dimer of species a into the chain/monomer mixture is taken to equal the factor for inserting a dimer of species a into the hypothetical dimer/monomer mixture

creating by breaking every other bond along the chain

$$p(\eta, x_a)_{a_2}^{(n_a,1)} \approx p(\eta, y_a)_{a_2}^{(2,1)}, \quad (19)$$

where y_a is now the mole fraction of species a dimers in the hypothetical dimer/monomer mixture.

The factor for inserting a monomer of species b into the chain/monomer mixture is taken to be equal to the factor for inserting a monomer of species b into the hypothetical dimer/monomer mixture formed by breaking every other chain bond

$$p(\eta, x_a)_{b_1}^{(n_a,1)} \approx p(\eta, y_a)_{b_1}^{(2,1)}, \quad (20)$$

where y_a is again defined to be the mole fraction of species a dimers in the hypothetical dimer/monomer mixture.

The species a monomer (Eq. 18) and dimer (Eq. 19) insertion probabilities are substituted into Eq. (17) and then the species a chain (Eq. 17) and species b monomer (Eq. 20) insertion probabilities are substituted into the binary osmotic equation of state (Eq. 16) to obtain the GFD equation of state for chain/monomer mixtures

$$\begin{aligned}
Z^{GFD}(\eta, x_a)^{n_a,1} &\equiv \frac{P(\eta, x_a)\bar{v}}{\eta kT} \\
&= x_a \{1 - [(Y_{n_a}^a)_{mix} + 1] \ln p_{a_2}^{(2,1)} + (Y_{n_a}^a)_{mix} \ln p_{a_1}^{(1,1)}\} \\
&\quad + \frac{x_a}{\eta} [(Y_{n_a}^a)_{mix} + 1] \times \int_0^\eta \ln p_{a_2}^{(2,1)} d\eta' \\
&\quad - \frac{x_a}{\eta} (Y_{n_a}^a)_{mix} \times \int_0^\eta \ln p_{a_1}^{(1,1)} d\eta' + x_b [1 - \ln p_{b_1}^{(2,1)}] \\
&\quad + \frac{x_b}{\eta} \int_0^\eta \ln p_{b_1}^{(2,1)} d\eta'.
\end{aligned} \tag{21}$$

Eq. (21) can be written in a more compact form if we define a term, $\gamma(\eta, y_a)_{i_{n_i}}^{(n_a,1)}$, similar to that in the single component osmotic equation of state

$$\gamma(\eta, y_a)_{i_{n_i}}^{(n_a,1)} = 1 - \ln p(\eta, y_a)_{i_{n_i}}^{(n_a,1)} + \frac{1}{\eta} \int_0^\eta \ln p(\eta', y_a)_{i_{n_i}}^{(n_a,1)} d\eta', \tag{22}$$

where the subscripts and superscripts on γ are analogous to the subscripts and superscripts on the mixture insertion probabilities, and the inserted species i is either a species a chain of length n_a or a species b monomer. Using the γ notation, the equation of state can then be written as

$$Z^{GFD} = x_a [((Y_{n_a}^a)_{mix} + 1) \gamma(\eta, y_a)_{a_2}^{(2,1)} - ((Y_{n_a}^a)_{mix}) \gamma(\eta, y_a)_{a_1}^{(1,1)}] + x_b \gamma(\eta, y_a)_{b_1}^{(2,1)}. \tag{23}$$

The γ 's can be written in the form

$$\gamma(\eta, y_a)_{i_{n_i}}^{(n_a,1)} = \gamma^{hs}(\eta, y_a)_{i_{n_i}}^{(n_a,1)} + \gamma^{sw}(\eta, y_a)_{i_{n_i}}^{(n_a,1)}, \tag{24}$$

where γ^{hs} is the hard sphere, or repulsive, contribution to the compressibility factor and γ^{sw} is the

square-well, or attractive, contribution to the compressibility factor. Eq. (23) can then be written as

$$Z^{GFD} = \quad (25)$$

$$\begin{aligned} & x_a [((Y_{n_a}^a)_{mix} + 1) \{ \gamma^{hs}(\eta, y_a)_{a_2}^{(2,1)} + \gamma^{sw}(\eta, y_a)_{a_2}^{(2,1)} \} - ((Y_{n_a}^a)_{mix}) \{ \gamma^{hs}(\eta, y_a)_{a_1}^{(1,1)} \\ & + \gamma^{sw}(\eta, y_a)_{a_1}^{(1,1)} \}] + x_b [(\gamma^{hs}(\eta, y_a)_{b_1}^{(2,1)} + \gamma^{sw}(\eta, y_a)_{b_1}^{(2,1)})]. \end{aligned}$$

Calculation of the hard sphere contribution to the compressibility factor is done using scaled particle theory (SPT). The derivation of γ^{hs} for that equation of state was given by Wichert *et al.* [17] The general result is

$$\begin{aligned} \gamma(\eta, y_a)_i^{(n_a, n_b)} = \quad (26) \\ & -[1 + W(y_a)_i^{(n_a, n_b)} + Y(y_a)_i^{(n_a, n_b)} + 3Z(y_a)_i^{(n_a, n_b)}] \frac{\ln(1 - \eta)}{\eta} \\ & + \left\{ -[Y(y_a)_i^{(n_a, n_b)} + 3Z(y_a)_i^{(n_a, n_b)} + W(y_a)_i^{(n_a, n_b)}] \right. \\ & + \eta[-X(y_a)_i^{(n_a, n_b)}/2 + (5/2)Y(y_a)_i^{(n_a, n_b)} + (15/2)Z(y_a)_i^{(n_a, n_b)} \\ & + 3W(y_a)_i^{(n_a, n_b)}] - \eta^2[X(y_a)_i^{(n_a, n_b)}/2 + (5/2)Y(y_a)_i^{(n_a, n_b)} \\ & \left. + (11/2)Z(y_a)_i^{(n_a, n_b)} + 3W(y_a)_i^{(n_a, n_b)}] + \eta^3 W(y_a)_i^{(n_a, n_b)} \right\} (1 - \eta)^{-3}, \end{aligned}$$

where the coefficients W , X , Y , and Z are determined from SPT and are listed in Table 1. The shape parameter ratios and shape parameters required to calculate W , X , Y , and Z can be found in Tables 2 and 3, respectively.

The square well contribution to the compressibility factor of the mixture, $\gamma^{sw}(\eta, y_a)_{i_{n_i}}^{(n_a, 1)}$, is derived from a local composition theory. Local composition theory predicts the coordination

numbers of the various species in the mixture, which in turn can be used to calculate insertion factors for the two species. We chose to use the form of local composition theory introduced by Lee and Chao [29] and to apply the high density correction of Vimalchand *et al.*[31]. The empirical parameters appearing in this equation are fit to our own simulation data.

The coordination number z_{ij} represents the number of molecules of component j located inside the energy well of a square-well molecule of component i . It is related to the radial distribution function, $g_{ij}(r)$, by

$$z_{ij} = \frac{4\pi N_j}{V} \int_{\sigma_i}^{\lambda_i \sigma_i} g_{ij}(r) r^2 dr, \quad (27)$$

where λ_i is the ratio of the outside diameter of the SW potential to the hard-core diameter of component i and is set equal to 1.5. The model of Lee and Chao defined z_{ij} to be

$$z_{ij} = \frac{V_{s,ij} Z_i \rho_j \Omega_{ij}}{1 + \rho \sigma_{ij}^3 [\Omega - 1]}, \quad (28)$$

where,

$$\Omega_{ij} = \exp(\alpha \epsilon_{ij} / kT),$$

$$\Omega = \sum_i \sum_j x_i x_j \Omega_{ij},$$

$$\alpha = 1 - \frac{\rho^*}{\sqrt{2}},$$

$$\rho^* = \rho_1 \sigma_1^3 + \rho_2 \sigma_2^3, \quad \rho_i = x_i \rho$$

and $V_{s,ij} (\equiv \frac{4}{3}\pi(\lambda^3 - 1)\sigma_{ij})$ is the volume of the coordination shell. The inter-species hard-core diameter, σ_{12} , is defined as $\frac{1}{2}(\sigma_{11} + \sigma_{22})$, while the inter-species well-depth, ϵ_{12} , normally defined

to be $(\epsilon_{11}\epsilon_{22})^{1/2}$, is allowed to vary. The parameter Z_t differs from that of Lee and Chao due to the application of the high density correction of Vimalchand *et al* and is defined as

$$Z_t = A + B\rho^* - C(\rho^*)^4, \quad (29)$$

where the coefficients A , B , and C depend on the types of components in the mixture and can be found in Table 4. Because Vimalchand *et al.* did not apply the high density correction to the model of Lee and Chao, the coefficients in Table 4 were regressed from a least squares fit of our own simulation data of square-well monomers and dimers.

Once the z_{ij} 's have been calculated, the internal energy of the square-well fluid, U , is determined by

$$U = - \sum_i \sum_j \frac{N_i}{2} z_{ij} \epsilon_{ij}. \quad (30)$$

The Helmholtz energy, A , is obtained by integrating the equation

$$\left[\frac{\partial(A/T)}{\partial(1/T)} \right]_{N,V} = U \quad (31)$$

to get an expression for the Helmholtz energy,

$$A = T \int_0^{1/T} U d(1/T'). \quad (32)$$

Because the Helmholtz energy as calculated above is dependent on the overlap of the square wells, the Helmholtz free energy at ideal gas conditions and at zero density will both be equal to zero. For this reason, the chemical potential so calculated will be equal to the corrected residual

potential and can be set equal to the insertion factor.

To calculate the chemical potential of species i from the Helmholtz energy, we differentiate with respect to N_i , the number of molecules of species i . However, for our purposes the chemical potential can be expressed more conveniently in terms of a partial derivative with respect to x_i

$$\begin{aligned}
\ln p(\eta, y_a)_{i_{n_i}} &= \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} \\
&= A - x_i \left(\frac{\partial A}{\partial x_i} \right)_{T, V, x_{j \neq i}} \\
&= T \int_0^{1/T} \left[U - x_i \left(\frac{\partial U}{\partial x_i} \right)_{T, V, x_{j \neq i}} \right] d(1/T)'.
\end{aligned} \tag{33}$$

The resulting expressions for $\ln p(\eta, y_a)_{i_{n_i}}$ can then be substituted in Eq. (22) to calculate $\gamma^{sw}(\eta, y_a)_{i_{n_i}}^{(n_a, 1)}$ for $i_{n_i} = a_1, a_2, b_1$ which, along with the expressions for $\gamma^{hs}(\eta, y_a)_{i_{n_i}}^{(n_a, 1)}$ for $i_{n_i} = a_1, a_2, b_1$ derived previously, can be used to calculate the compressibility factor of the square-well chain/monomer mixture by Eq. (23).

2.4 Comparison of GFD theory to molecular dynamic simulation

In this section we compare the Generalized Flory Dimer equation of state derived in Section 2.3 with discontinuous molecular dynamics simulations of monomer-dimer and monomer-chain mixtures. Figure 1 compares the GFD theory predictions and discontinuous molecular dynamics simulation values for the compressibility factor as a function of the volume fraction for mixtures of square-well monomers (species 1) and dimers (species 2) of equal segment diameter $\sigma_{11} = \sigma_{22}$, equal volume fraction in the mixture $x_1 v_1 = x_2 v_2$, temperature $T^* \equiv kT/\epsilon = 2.0$, and well depth parameter ratios $(\epsilon_{11}/\epsilon_{22})$ ranging from 0.5 to 1.5. Agreement between theory and simulation is quite good,

although the GFD theory tends to slightly overpredict the compressibility over the entire range of volume fraction.

Figure 2 compares the GFD theory predictions and simulation values for the compressibility factor of mixtures of square-well monomers and dimers of equal segment diameter at $T^* = 2$, $(\epsilon_{11}/\epsilon_{22}) = 1.5$, and $x_2 = 0.111, 0.333$, and 0.667 . For $x_2 = 0.111$, the agreement is quite good except at the highest volume fraction. As the mole fraction of dimer increases, the agreement between theory and simulation became worse for the mixtures in the mid-range of total volume fraction, suggesting that some improvement in accounting for the effect of the presence of dimer species on the compressibility factor may be needed.

Figure 3 compares the GFD theory for the compressibility factor to discontinuous molecular dynamics simulation data for mixtures of square-well monomers (species 1) and 8-mers (species 2) of equal segment diameter $\sigma_{11} = \sigma_{22}$, equal volume fraction $x_1 v_1 = x_2 v_2$, $T^* = 2.0$, and well depth parameter ratios $(\epsilon_{22}/\epsilon_{22})$ ranging from 0.667 to 2.0 . Agreement between the theory and simulation is good for all well depth parameter ratios in this case. It is not surprising that the agreement between theory and simulation increases as the length of the “chain” component increases based on the findings of Kumar, *et al* [23] concerning the accuracy of the various predictions made in the Generalized Flory Dimer theory. They found that although the estimate for the probability of inserting the first bead is not very accurate, this tended to be offset by errors in estimating the probability of inserting the third through n th segments. Thus, it might be expected that the Generalized Flory Dimer theory would make more accurate predictions for mixtures of monomers and chains than for monomers and dimers.

3 Calculation of Global Phase Diagram

In order to construct a global phase diagram it is necessary to determine the boundaries between regions of different types of phase behavior. Although, there are several of ways to do this [1, 11], the most straightforward way is to determine the type of phase behavior exhibited on a grid of points in interaction parameter space. The interaction parameters generally depend on the same-species interaction energies, ϵ_{ii} , and on the inter-species interaction energies, ϵ_{ij} . As is the case in most previous studies of global phase behavior for species of equal hard-core diameter, we will use the two parameters

$$\zeta = \frac{\epsilon_{22} - \epsilon_{11}}{\epsilon_{22} + \epsilon_{11}} \quad (34)$$

$$\Lambda = \frac{\epsilon_{11} - 2\epsilon_{12} + \epsilon_{22}}{\epsilon_{22} + \epsilon_{11}}. \quad (35)$$

to define the parameter space for our global phase diagram. The type of phase behavior exhibited at each point ζ, Λ was determined by first calculating the locus of critical points. The phase behavior could then be classified based on the projection of the locus of critical points onto the $P - T$ plane. Figure 4 shows characteristic projections of the locus of critical points onto the $P - T$ plane for Types I-VI phase behavior [11]. The thick solid lines represent the boiling point curves of the pure fluids, the thin solid lines, if present, represent the temperature as a function of pressure at three phase coexistence, and the dashed line is locus of critical points for the mixtures.

The loci of critical points can be calculated by solving the following equations for the critical temperature and pressure over a range of compositions from pure component one to pure component

two

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{P,T} = \left(\frac{\partial^3 G}{\partial x^3}\right)_{P,T} = 0, \quad (36)$$

where G is the Gibbs free energy of the mixture. However, it is not convenient to calculate the derivatives of the Gibbs free energy at constant pressure using an equation of state explicit in pressure. This hurdle can be overcome by using a Legendre transformation to change the thermodynamic equations defining a critical point Eq. (36) from functions of the Gibbs free energy to functions of the Helmholtz free energy, leading to the following critical point equations

$$A_{2V}A_{2x} - A_{Vx}^2 = 0 \quad (37)$$

$$A_{3V}A_{2x}^2 - 3A_{2Vx}A_{Vx}A_{2x} + 3A_{V2x}A_{Vx}^2 - A_{3x}A_{2V}A_{Vx} = 0 \quad (38)$$

where,

$$A_{mVnx} \equiv \left(\frac{\partial^{n+m} A}{\partial^m V \partial^n x}\right)_T. \quad (39)$$

The Helmholtz free energy can be expressed in terms of the mixture compressibility factor, packing fraction, and mole fraction as [32]

$$\frac{A}{RT} - \frac{A^\circ}{RT} = \int_0^\eta \frac{Z-1}{\eta'} d\eta' - \ln \frac{V}{V^\circ} + \sum_i x_i \ln x_i, \quad (40)$$

where A° and V° are reference state conditions that are independent of volume and composition. Thus, when the partial derivatives in Eqs.(37) and (38) are performed A° and V° will drop out of the resulting expressions.

The compressibility factor used in equation Eq. (40) was calculated using the Generalized

Flory Dimer equation of state for square-well chain/monomer mixtures derived in Section 2.3. Eqs. (37) and (38) were then solved numerically using Newton's method [33] for the critical temperature and volume at fixed values of ζ , Λ , and composition. Newton's method is actually a function minimization method that can be used to solve a system of equations by constructing a function equal to the sum of the squares of the left hand sides of those equations. Given an initial estimate of the solution to the system of equations, Newton's method uses information from the Jacobian matrix to determine the direction in variable space in which the function would be minimized. In addition to providing a direction in which to take the next estimate, the method also provides the size of the step that should be taken in that direction. Rather than adopting this step size, we chose to find the minimum of the function along the Newton direction, because this could potentially lead to quicker convergence. At each iteration step the derivatives in Eqs. (37) and (38) and the Jacobian matrix were calculated numerically. Given a sufficient number of iterations the method was said to have converged when the value of the function went below a given tolerance. Once the critical volume and temperature were calculated, the pressure was determined from the compressibility factor in Eq. (23).

Because of the existence of multiple solutions, an accurate initial estimate was needed to ensure that the iteration procedure converges to the desired root. This requirement was circumvented in the following manner. The calculations were typically started at a composition close to zero or one. This was done because the values of the critical pressure and temperature of a nearly pure fluid should be close to the values of the critical pressure and temperature of a pure fluid, the critical point of which can be easily calculated. Convergence towards the desired solution was typically rapid due the proximity of the initial guess. The composition could then be incremented further and the solution for the old composition used as the initial guess for the new composition.

The procedure described above worked well in many cases, except when the locus of critical points did not connect with either of the pure component critical lines, such as occurs for example in liquid-liquid equilibrium. In these cases, it was necessary to find an alternative means of generating an initial guess for the solution. To accomplish this, we calculated phase diagrams in the $T - x$ plane and from them was able to make accurate initial estimates for points on the sections of the locus of critical points mentioned above. For example, for a given set of Λ and ζ , the upper critical solution temperature (UCST) obtained from a phase diagram in the $T - x$ plane could be used as a starting point for finding the rest of the UCST branch of the locus of critical points in the $P - T$ plane.

Calculating phase diagrams in the $T - x$ plane involves finding coexistence points at a number of temperatures at a given pressure. At each temperature for a given pressure, the coexistence points were found by solving the standard equations that define equilibrium between two phases α and β , namely $T^\alpha = T^\beta$, $P^\alpha = P^\beta$, $\mu_i^\alpha(T^\alpha, P^\alpha, x_i^\alpha) = \mu_i^\beta(T^\beta, P^\beta, x_i^\beta)$, where μ_i^j is the chemical potential of component i in phase j . Since the first two conditions are trivial, the calculation primarily involves finding the composition of each phase to satisfy the third condition.

The calculations of the compositions of the phases in equilibrium began by finding the volume as a function of composition at the given temperature and pressure according to Eq. (23). This required an iterative solution because Eq. (23) is implicit in volume and one or three solutions for the volume at each value of composition could be found depending on the composition, temperature, and pressure. Our approach was to fix the composition and then search for solutions while incrementing the volume upward from nearly close-packed until we were satisfied that all the solutions had been found. Solutions that were determined to be mechanically unstable based on the slope of

the pressure versus volume curve at that point were thrown out. Once this was accomplished for a number of compositions ranging from one pure component to another, the Gibbs free energy was calculated at each value of the volume and composition according to

$$\frac{G}{RT} - \frac{G^\circ}{RT} = \int_0^\eta \frac{Z-1}{\eta'} d\eta' - \ln \frac{V}{V^\circ} + Z - 1 + \sum_i x_i \ln x_i, \quad (41)$$

where G° and V° are reference state variables that could be set to 0 and 1 respectively and subsequently neglected. At this point, only the most stable value of volume (the one resulting in the lowest Gibbs free energy) was chosen for each composition. Once the Gibbs free energy had been calculated as a function of composition and volume over the entire range of composition, the chemical potential at x_i was then calculated by

$$\mu_i = G - x_i \left(\frac{\partial G}{\partial x_i} \right)_{T,P}. \quad (42)$$

The derivative appearing above was calculated numerically from the values calculated by Eq. (41).

The final step in the calculation involved finding values of the composition at which $\mu_i^\alpha = \mu_i^\beta$. The algorithm essentially boiled down to plotting a parametrized curve of μ_1 versus μ_2 with composition as the parameter; this is represented schematically in Figure 5. Point A in Figure 5 represents a point at which μ_1 and μ_2 have the same value at two different values of composition. Three phase coexistence would be represented in Figure 5 by having the solid line pass through point A three times. To find point A numerically, we first calculated the slope and intercept in the $\mu_1 - \mu_2$ plane for the line going from each value of composition to the successive value of composition, for example, from 1 to 2, 2 to 3, etc. in Figure 5. We then determined which line

segments intersected each other. For example the line segment connecting points 3 and 4 intersects the line segment connecting points 5 and 6. When such an intersection was found we interpolated along the μ_1 versus μ_2 line to arrive at the values of composition for the coexisting phases.

With this additional tool we calculated the locus of critical points for 360 points in $\zeta - \Lambda$ space, with grid values of each parameter ranging from -0.9 to 0.9, in steps of 0.1 units in each direction. As the loci were calculated the type of phase behavior exhibited was recorded and categorized according to Figure 4. After this initial grid search was completed approximately 100 additional calculations were performed along the boundary between Type V and I and between Types II and III. These calculations were done every 0.1 units in the Λ and ζ directions along the boundary at a point midway between the points in our initial grid that bracketed the boundary at that point. The effect was such that the resolution along the boundary was effectively doubled.

4 Global Phase Diagram for Monomer/Dimer Mixtures

Figure 6 shows the global phase diagram that we calculated based on the Generalized Flory Dimer equation of state for a mixture of square-well monomers and dimers. In the figure, the solid lines indicate the boundaries between different phase behavior types, while the dashed lines indicate boundaries between azeotropic and non-azeotropic behavior of a single type. Due to the finite number of calculations that were performed to locate the boundaries of the various regions, the boundaries in Figure 6 do not represent the exact boundary between any two regions. Because of the size of the grid used, the deviation between the actual boundary and that shown in Figure 6 should be no greater than 0.05 units in the Λ or ζ directions.

Figure 7 is a schematic of the global phase diagram predicted for the van der Waals equation of state as calculated by van Konynenburg and Scott [34]. Comparison of Figures 6 and 7 reveals the absence of Type IV and Type VI behaviors on Figure 7. The absence of Type IV behavior is surprising because it had been described in most of the papers cited earlier in our literature survey, albeit normally in a rather restricted region of the global phase diagram. In the case of the Carnahan-Starling-Redlich-Kwong equation of state, Kraska and Deiters [12] found that for molecules of different sizes, the region of Type IV behavior was nearly indistinguishable from the boundaries surrounding it. A possible explanation for its absence in our global phase diagram is that our search grid may not have been fine enough to find the Type IV. An additional 20 calculations were performed in the regions where Type IV phase behavior was expected ($\zeta = -0.75$ to -0.9 , $\Lambda = -0.1$ to 0.1 and $\zeta = 0.45$ to 0.6 , $\Lambda = -0.1$ to 0.1 , in steps of 0.05 units in both directions), but Type IV phase behavior was not observed. There are two possible explanations as to why no Type VI or other closed loop behavior was detected. The first is that our grid search may not have been fine enough to detect

Type IV behavior; support for this view came from the fact that closed loop behavior is typically represented by an area on the global phase diagram even smaller than that of Type VI behavior, and is normally located in the “shield” region. We performed an additional 25 calculations in this region ($\Lambda = 0.05$ to 0.25 , $\zeta = 0.55$ to 0.75 in steps of 0.05 in each direction). The second possible explanation is that the Generalized Flory Dimer theory simply does not predict Type VI, or closed loop liquid-liquid immiscibility, for this type of system. As mentioned in Section 1, there has been an ongoing debate as to whether or not closed loop liquid-liquid immiscibility exists in systems of spherical molecules or if it is a mathematical artifact of approximate equations of state.

Another difference between the GFD and van der Waals global phase diagram is that the GFD diagram is not symmetric around the $\zeta = 0$ axis. In light of the fact that van Konynenburg and Scott saw a similar shift for the case of unequal sized spheres, this result is not surprising. Since the molecules are not symmetrical they do not interact “symmetrically” and the global phase diagram is shifted accordingly. The final feature worth noting is that the boundary between regions with three phase coexistence and those without (the $\Lambda = 0$ axis in the van der Waals case) is shifted slightly in the negative Λ direction. This indicates that for monomer/dimer mixtures there is tendency towards liquid-liquid immiscibility when there are favorable energetic conditions for miscibility, indicating that entropic effects may play a role. Similar shifts were seen in the global phase diagrams predicted for other equations of state [11, 12], so this result has some precedence.

5 Summary

We have presented a derivation of the Generalized Flory Dimer theory for monomer/chain mixtures which accurately predicts compressibility factors compared to simulation data for mixtures at chain lengths 2 and 8 and varying compositions and ratios of $\epsilon_{22}/\epsilon_{11}$. The theory requires as input accurate equations of state for hard sphere monomer/dimer mixtures and for square-well monomer/dimer mixtures; these were obtained from scaled particle theory and the local composition model, respectively.

We have also presented the global phase diagram for mixtures of square-well monomer and dimers predicted by the Generalized Flory Dimer equation of state. The values of Λ and ζ covered in the global phase diagram each ranged from -1.0 to 1.0. The phase diagram was constructed from critical point loci calculations at over 360 grid points in the $\Lambda - \zeta$ plane, followed by many additional calculations performed during concentrated searches. While four of the six phase behavior types found in nature were represented in the global phase diagram, Types IV and VI were absent. While the absence of type VI behavior was not surprising due to the current debate over its physicality in systems of spherical potentials, the absence of Type IV behavior was unexpected. Due to the limited resolution of our grid search it is unclear whether these regions are indeed not present or are simply too small for us to find. Other features of note were the shifting of the major topographical features of the global phase diagram towards the negative ζ and Λ directions when compared to the van der Waals global phase diagram for equal diameter molecules. The former was expected based on the results of van Konynenburg and Scott. The latter implies that there is a factor working against the favorable interspecies interactions that leads to liquid-liquid immiscibility.

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Table 1: Values of the density-independent coefficients of Equations 27, determined using Boublík's equation of state[35] for mixtures. The coefficients are expressed in terms of the species i volume, b_i , the mole fraction average of the volume, $b = \sum_i y_i b_i$, the shape parameter ratios, ω and ψ , and their derivatives ω' and ψ' with respect to N_i , the number of species i molecules. The shape parameter ratios and their derivatives are defined in Table 2.

$W(y_a)_i^{(n_a, n_b)}$	$= -\psi'_i$
$X(y_a)_i^{(n_a, n_b)}$	$= -\psi'_i - \omega'_i - (\omega + 1)(b_i/b)$
$Y(y_a)_i^{(n_a, n_b)}$	$= \psi'_i + 2\omega'_i - 3(\psi - \omega - 2)(b_i/b)$
$Z(y_a)_i^{(n_a, n_b)}$	$= (\psi - 1)(b_i/b) - \omega'_i$

Table 2: The shape parameter ratios, ω and ψ , and their derivatives, ω' and ψ' with respect to N_i , in terms of species shape parameters and mixture shape parameters. The mixture shape parameters b , s , and $\bar{r}$ are the mole fraction average ($\tau = \sum_i y_i \tau_i$) of the shape parameters for the individual species and c is the mole fraction average of the radius of curvature squared $c = \sum_i y_i \bar{r}_i^2$. The species shape parameters for monomers and dimers are defined in Table 3

ω	$= \bar{r}s/b$
ψ	$= (cs^2)/(9b^2)$
ω'_i	$= \partial(N\omega)/\partial N_i = (r_i s + \bar{r}s_i - (b_i/b)\bar{r}s)/b$
ψ'_i	$= \partial(N\psi)/\partial N_i = (r_i^2 s^2 + 2css_i - 2(b_i/b)cs^2)/(9b^2)$

Table 3: Species shape parameters for monomers and dimers determined from the segment radius, $r_i = \sigma_i/2$.

shape	b_i	s_i	$\bar{r}_i$
monomer	$4\pi r_i^3/3$	$4\pi r_i^2$	r_i
dimer	$8\pi r_i^3/3$	$8\pi r_i^2$	$(3/2)r_i$

Table 4: Coordination number model parameters, where $\sigma_r = \sigma_{22}/\sigma_{11}$.

interacting species	A	B	C
monomer/monomer	0.919	0.791	0.339
dimer/dimer	1.754	4.986	1.951
dim/mon ($\sigma_r \geq 1.0$)	$3.207-2.226\sigma_r$	$-1.347+4.166\sigma_r$	$-1.795+3.544\sigma_r$
dim/mon ($\sigma_r < 1.0$)	$3.010-2.028\sigma_r^{-1}$	$0.017-2.802\sigma_r^{-1}$	$-1.997+3.746\sigma_r^{-1}$

Figure 1: Comparison of GFD equation of state to molecular dynamics simulation results for mixtures of monomers and dimers at $\epsilon_{22}/\epsilon_{11} = 0.5, 1.0$ and 1.5 , equal segment diameters and equal volume fractions $x_1 v_1 = x_2 v_2$ of the two species.

Figure 2: Comparison of GFD equation of state to molecular dynamics simulation results for mixtures of monomers and dimers at $\epsilon_{22}/\epsilon_{11} = 1.5$ and $x_2 = 0.111, 0.333$, and 0.667 and equal segment diameters.

Figure 3: Comparison of GFD equation of state to molecular dynamics simulation results for mixtures of monomers and 8-mers at $\epsilon_{22}/\epsilon_{11} = 0.5, 1.0$, and 1.5 , equal segment diameters and equal volume fractions $x_1 v_1 = x_2 v_2$ of the two species.

Figure 4: Six classifications of phase behavior. The thicker solid lines are the boiling point of the pure liquids, the thinner solid lines represent three phase coexistence, and the dashed lines are the loci of critical points.

Figure 5: Schematic of a parametrized plot of μ_1 vs. μ_2 with composition as the parameter. Point A represents the value of μ_1 and μ_2 at coexistence.

Figure 6: The global phase diagram predicted by the Generalized Flory Dimer theory for a mixture of square-well monomer and dimers.

Figure 7: A schematic of the global phase diagram predicted by the van der Waals equation of state for a mixture of equal-sized molecules as calculated by van Konynenburg and Scott [1]

Appendices

Appendix A Mixture Excluded Volume

The Generalized Flory Dimer theory for mixture requires a measure of the average size of the hole required to insert chain molecules with segment diameter σ_α into a chain fluid mixture of chains of segment diameter σ_α and σ_β . We estimate this hole size to be the average of the volumes that the inserted chain excludes to each type of chain in the mixture.

The volume excluded by a monomer of diameter σ_α to a monomer of diameter σ_β is given exactly by $((v_e^\alpha(1)))_\beta = 4\pi/3((\sigma_\alpha + \sigma_\beta)/2)^3$. The expression for the volume excluded by a dimer of diameter σ_α to a monomer of diameter σ_β is given exactly by

$$((v_e^\alpha(1)))_\beta = \frac{\pi\sigma_\alpha^3}{6} \left[2 + 6 \left(\frac{\sigma_\beta}{\sigma_\alpha} \right) + 4.5 \left(\frac{\sigma_\beta}{\sigma_\alpha} \right)^2 + \left(\frac{\sigma_\beta}{\sigma_\alpha} \right)^3 \right].$$

The volume excluded by chains of three segments or more to monomers are calculated using equations fitted to excluded volume data generated by a program developed by Dodd and Theodorou [36]. The volume excluded by a trimer of segment diameter σ_α to a monomer of diameter σ_β is given by

$$((v_e^\alpha(1)))_\beta = \sigma_\alpha^3 \left[1.57 + 4.75 \left(\frac{\sigma_\beta}{\sigma_\alpha} \right) + 2.99 \left(\frac{\sigma_\beta}{\sigma_\alpha} \right)^2 + 0.52 \left(\frac{\sigma_\beta}{\sigma_\alpha} \right)^3 \right].$$

For chains of 4 segments or more, we estimate the volume excluded by a chain of segment diameter σ_α to a monomer of diameter σ_β using an expression that has the same linear relation as Eq. 10, plus an additional non-linear term

$$((v_e^\alpha(n_\alpha)))_\beta \approx (v_e^\alpha(3))_\beta + (n_\alpha - 3)[(v_e^\alpha(3))_\beta - (v_e^\alpha(2))_\beta] + (\kappa^\alpha)_\beta$$

The non-linear term, $(\kappa^\alpha)_\beta$, is empirically based and is given by

$$(\kappa^\alpha)_\beta = -\sigma_\alpha^3 \left[0.04915(n_\alpha - 3)^{1.09} \left(\frac{\sigma_\beta}{\sigma_\alpha} \right)^2 .71 \right].$$

Given the above equations for the excluded volume, the mixture excluded volume is defined as

$$(Y_{n_\alpha}^\alpha)_{mix} = \Phi_\alpha \left(\frac{v_e^\alpha(n_\alpha) - v_e^\alpha(2)}{v_e^\alpha(2) - v_e^\alpha(1)} \right)_\alpha + \Phi_\beta \left(\frac{v_e^\alpha(n_\alpha) - v_e^\alpha(2)}{v_e^\alpha(2) - v_e^\alpha(1)} \right)_\beta,$$

where $\Phi_i = \eta_i/\eta$ is the occupation fraction of each species. The first term on the right hand side of the equation above is the excluded volume ratio corresponding to the insertion of segments of diameter σ_α into a pure fluid of segments of diameter α . The second term is the excluded volume ratio corresponding to the insertion of segments of diameter σ_α into a pure fluid of segments of diameter β .

Appendix B Code Listing

In this appendix, we provide the source code for the programs that were used in preparing this thesis. In Section B.1, we list the code used to calculate the locus of critical points. In Section B.2, we list the code used to calculate the phase coexistence envelopes. It should be noted that several subroutines used in Section B.1 are also used in Section B.2, but are listed only in Section B.1. The code was compiled using the Compaq FORTRAN 77 compiler using the -fast and -r8 flags, which enable the use of faster math libraries and convert all REAL type variables to DOUBLE PRECISION variables, respectively. The code was run on our cluster of Alpha processor machines.

B.1 Code listing for calculating the locus of critical points

```
PROGRAM GFDcrit

C*****
C**
C** This program calculates the locus of critical points for monomer/dimer
C** mixtures obeying the Generalized Flory Dimer equation of state. This section
C** of code primarily accepts the input parameters and then increments through
C** the range of composition specified using the subroutine NEWT to solve the
C** pair of equations that define a critical point. Subroutine NEWT and several
C** of its subroutines are borrowed from the "Numerical Recipes" book. The input
C** parameters are defined below as they are read in. The initial guess is either
C** a pure component critical point or a guess resulting from interpreting a phase
C** diagram in the T-x plane. Once NEWT returns with a solution XCALC is called
C** to calculate the pressure.
C**
C*****

REAL RRAT, RNL
REAL zeta, lambda
REAL x(2), V, TEMP
REAL xstart,xstop,xnum,x1
character*20 output

REAL WD1,WD2,WD12

COMMON /SWBLOCK/ WD1,WD2,WD12,TEMP
COMMON /INPUT/ RRAT,RNL
COMMON x1

integer n,its
logical check,solved

OPEN(unit=5,file='crit.inp',status='old')

C*** Read Ratio of diameters
READ(5,'(F10.5)') RRAT
C*** Read Chain length of component 1
READ(5,'(F10.5)') RNL
C*** Read zeta
READ(5,'(F10.5)') zeta
C*** Read lambda
READ(5,'(F10.5)') lambda
C*** Read volume initial guess
READ(5,'(F10.5)') V
C*** Read temperature initial guess
READ(5,'(F10.5)') TEMP
C*** Read the composition at which to start
READ(5,'(F10.5)') xstart
C*** Read the composition at which to end
READ(5,'(F10.5)') xstop
C** Read number of points in between
READ(5,'(F10.5)') xnum
C*** Read output file name
READ(5,'(A)') output

close(unit=5)

C*** Calculate the well depths from zeta and lambda
wd1 = 1-zeta
wd2 = 1+zeta
```



```

        wd12=1-lambda

        if(xnum.gt.1) then
            xstep=(xstop-xstart)/(xnum-1.)
        else
C*** In case I want to look at just one point
            xstep=(xstop-xstart)*2.
        endif

        open(unit=10,file=output,status='unknown')

        do 150 x1=xstart,xstop,xstep
C*** Call Newton routine to solve the pair of equations for a given composition
            x(1)=V
            x(2)=TEMP
            call newt(x,2,check,its,solved,test)

C*** Check to see if it solved within the given number of maximum iterations
C*** and that it did not converge on a local minimum, then calculate the
C*** compressibility factor and pressure for that mixture
            if (.not.check.and.solved) then
                call xcalc(0.0,V,x1,Pstar)
                write(10,200) TEMP, Pstar, V, x1, test, its
            else
                print*, 'not solved', x1
50         endif
150        continue
200        format(e12.5,1x,e12.5,1x,e11.4,1x,f6.3,1x,e11.4,1x,i4)
            stop
        end

#include <Fcalc.f>
#include <funcva.F>
#include <NEWT.F>
#include <FDJAC.F>
#include <FMIN.F>
#include <LUNLN.F>
#include <subrtns.f>
#include <com_vol_dum.f>
#include <chn_mon_vol.f>
#include <xcalc.f>

```

```

      SUBROUTINE newt(x,n,check,its,solved,test)
C*****
C      Given an initial guess x(1:n) for a root in n dimensions, find the root by a
c      globally convergent Newton's method. The vector of functions to be zeroed,
c      called fvec(1:n) in the routine below, is returned by a user-supplied subroutine
c      that must be called funcv and have the declaration "subroutine funcv(n,x,fvec).
c      The output quantity check is false on normal return and true if the routine has
c      converged to a local minimum of the function fmin defined below. In this case,
c      try new starting points. NP is the expected maximum value of n; MAXITS is the
c      maximum number of iterations; TOFL sets the convergence criterion on function
c      values; TOLMIN sets the criterion for deciding whether spurious convergence to
c      a minimum of fmin has occurred; TOLX is the convergence criterion on dx; STPMX
c      is the scaled maximum step length allowed in line searches.
C*****
      INTEGER n,NP,MAXITS
      REAL x(2),fvec,TOLF,TOLMIN,TOLX,STPMX
      PARAMETER (NP=2,MAXITS=100,TOLF=1.d-04,TOLMIN=1.0d-08,TOLX=1.0d-08,
&      STPMX=0.1d+0)
      INTEGER i,its,j,indx(NP)
      LOGICAL check, solved
      REAL d,den,f,fold,stpmax,sum,temp,test,fjac(NP,NP),g(NP),p(NP),
&      xold(NP),fmin
      EXTERNAL fmin
      COMMON /NEWTV/ fvec(NP),nn
      SAVE /NEWTV/
      COMMON x1

      f=fmin(x)
      test=0.0
      solved=.true.
      do 11 i=1,n
         if(abs(fvec(i)).gt.test)test=abs(fvec(i))
11      continue
      if(test.lt..01d+0*TOLF)then
         check=.false.
         return
      endif
      sum=0.0
      do 12 i=1,n
         sum=sum+x(i)**2
12      continue
      stpmax=STPMX*dmax1(sqrt(sum),dble(n))
      do 21 its=1,MAXITS
         call fdjac(n,x,fvec,NP,fjac)
         do 14 i=1,n
            sum=0.
            do 13 j=1,n
               sum=sum+fjac(j,i)*fvec(j)
13          continue
            g(i)=sum
14          continue
         do 15 i=1,n
            xold(i)=x(i)
15          continue
         fold=f
         do 16 i=1,n
            p(i)=-fvec(i)
16          continue
         call ludcmp(fjac,n,NP,indx,d)
         call lubksb(fjac,n,NP,indx,p)
         call lnsrcb(n,xold,fold,g,p,x,f,stpmax,check,fmin)
         test=0.d+0
         do 17 i=1,n
            if(abs(fvec(i)).gt.test)test=abs(fvec(i))

```

```
17      continue
      if(test.lt.TOLF)then
        check=.false.
        return
```

```

      DOUBLE PRECISION FUNCTION fmin(x)

C*****
c      Returns  $f=(1/2)*F*F$  at x.  subroutine funcv(n,x,f) is a fixed-name,
c      user-supplied routine that returns the vector of the functions at x.  The common
c      block newtv communicates the function values back to newt.
C*****

      INTEGER n,NP, I
      REAL x(n),fvec(NP), sum
      PARAMETER (NP=2)
      COMMON /NEWTV/ fvec(NP),n
      SAVE /NEWTV/

      call funcv(n,x,fvec)
      sum=0.
      do 11 I=1,n
         sum=sum+fvec(I)**2
11      continue
      fmin=0.5d+0*sum
      return
      END

      endif
21      continue
      print*, 'MAXITS exceeded in newt', x1
      solved=.false.
      return
      END

```

```

SUBROUTINE funcv(n,x,fvec)

C*****
C**  Calls the subroutine fcalc, which returns the Helmholtz free energy and its
C**  derivative with respect to V, at various points around the passed values of
C**  temperature and composition. Using those values the values for fvec are
C**  calculated
C*****

      REAL fvec(2), x(2)
      REAL h1,h2,h1i,h2i,V,TEMP
      REAL temp1,temp2
      REAL dadv00,dadv11,dadv1_1,dadv10,dadv_10,dadv01,dadv0_1,dadv02
      REAL a00,a11,a1_1,a10,a_10,a01,a0_1,a02
      REAL da2dv2,da2dx2,da3dv3,da3dx3,da2dvdx,da3dvdx2,da3dv2dx

      COMMON /SWBLOCK/ WD1,WD2,WD12, TEMP
      COMMON x1

      V=x(1)
      TEMP=x(2)
      h1=1.d-4
      temp1=x1+h1
      h1i=1./(temp1-x1)
      h2=1.d-4*V
      temp2=V+h2
      h2i=1./(temp2-V)

      call fcalc(V,dadv00,a00,x1)
      call fcalc(V+h2,dadv11,a11,x1+h1)
      call fcalc(V+h2,dadv1_1,a1_1,x1-h1)
      call fcalc(V+h2,dadv10,a10,x1)
      call fcalc(V-h2,dadv_10,a_10,x1)
      call fcalc(V,dadv01,a01,x1+h1)
      call fcalc(V,dadv0_1,a0_1,x1-h1)
      call fcalc(V,dadv02,a02,x1+2*h1)

C***  Calculate points derivatives in equations 37 and 38 in section 3 from the
C***  values of the Helmholtz free energy and it derivative with respect to composition
C***  calculated above

      da2dv2=(dadv10-dadv_10)*0.5d+0*h2i
      da2dx2=(a01-2.d+0*a00+a0_1)*h1i*h1i
      da3dv3=(dadv10-2.d+0*dadv00+dadv_10)*h2i*h2i
      da3dx3=(a02-3.*a01+3.*a00-a0_1)*h1i*h1i*h1i
      da2dvdx=(dadv01-dadv0_1)*0.5d+0*h1i
      da3dvdx2=(dadv01-2.d+0*dadv00+dadv0_1)*h1i*h1i
      da3dv2dx=(dadv11-dadv1_1-dadv01+dadv0_1)*0.5d+0*h2i*h1i

C***  Evaluate the LHS of eqautions 37 and 38

      fvec(1)=(da2dv2*da2dx2-da2dvdx**2)
      fvec(2)=(da3dv3*da2dx2**2-3d+0*da3dv2dx*da2dvdx*da2dx2
&          +3.d+0*da3dvdx2*da2dvdx**2-da3dx3*da2dv2*da2dvdx)

      return
      end

```

```

SUBROUTINE fcalc(Vout,dadv,A,XC)

REAL D1,D2,D12
REAL WD1,WD2,WD12,TEMP
REAL VS11,VS22,VS12
REAL RRAT,RNL

COMMON /DIABLOCK/D1,D2,D12
COMMON /SWBLOCK/ WD1,WD2,WD12,TEMP
COMMON /VBLOCK/ VS11,VS22,VS12
COMMON /INPUT/ RRAT, RNL

PARAMETER(N=2,NN=100)
REAL R(N),X(N),AR(N,N),E(N),X2(N),F(N),
& BB(N),S(N),RB(N),XN(N),YN(N),ZN(N),WN(N),
& Zh1(N,2000),Zh2(N,2000),
& AX(N),AY(N),AZ(N),AW(N),AM1(N),AM2(N),
& AM(N),AN(N),AO(N),
& ZAT1(2000),ZAT2(2000),ZATMDD(2000),ZATMDM(2000),
& BB2(N), S2(N), RB2(N), eta(NN)
REAL PI, XC,etain,RAD,YNL,YNU
INTEGER Neta

Neta=100
PI = 4.0*ATAN(1.0)

C*** Diameter of component 2
R(1)=1.0
R(2) = RRAT

C** The site fraction of each component
X(1)=RNL*XC/(RNL*XC+(1.-XC))
X(2)=1.-X(1)

C** The mole fraction of dimers and monomers in a hypothetical
C** dimer monomer mixture fluid formed by breaking the alternative
C** bonds of the chain
X2(1)=RNL*XC/(RNL*XC+2.0*(1.-XC))
X2(2)=1.-X2(1)

D1 = R(1)
D2 = R(2)
D12 = (D1+D2)*0.5

C*** Volume of the attractive well
VS12=4./3.*PI*(1.5**3-1)*D12**3
VS11=4./3.*PI*(1.5**3-1)*D1**3
VS22=4./3.*PI*(1.5**3-1)*D2**3

etain=PI*(xc*rn1*d1**3+(1.-xc)*d2**3)/6./Vout

C*** Calculate C, the total volume fraction of the system
C=0.0
DO 10 I=1,N
    C=C+X(I)*R(I)**3
10 CONTINUE

C*** Calculate the Fractional occupation fraction F(i) of each component
DO 199 I=1,N
    E(I)=(X(I)*R(I)**3/C)
    F(I)=E(I)
199 CONTINUE

```

```

C*** Excluded volume convention
C*** VE1L = Volume excluded by monomer of comp 1 to monomer of comp 1
C*** VE2L = Volume excluded by dimer of comp 1 to monomer of comp 1
C*** VE3L = Volume excluded by trimer of comp 1 to monomer of comp 1
C*** VENL = Volume excluded by chain of comp 1 to monomer of comp 1
C***
C*** VE2U = Volume excluded by dimer of comp 1 to monomer of comp 2
C*** VENU = Volume excluded by chain of comp 1 to monomer of comp 2

C*** Calculate the Excluded Volume of the chain to chain segment
VE1L=4./3.*PI
VE2L=9./4.*PI
CALL VOLC(D1,D1,RNL,VENL)

C*** Calculate the volume excluded by component 1 to component 2

RAD=(1.0+RRAT)/2.0

C*** Volume Excluded by a monomer of component 1 to monomer of comp 2
VE1U=VE1L*(RAD)**3

C*** Volume excluded by a dimer of component 1 to a monomer of
C*** component 2. The distance between the centers of the two beads is D1
DIS = D1

C*** Function EXC calculates the common volume between two spheres of radii
C*** R1, R2 and with their centers DIS apart
VE2U = 2*VE1L*RAD**3 - EXC(RAD,RAD,DIS)

IF (RNL .GT. 2) THEN
  CALL VOLC(D1,D2,RNL,VENU)
ELSE
  VENU=VE2U
ENDIF

C*** Calculate the excluded volume ratios
C*** Mixture excluded volume ratio calculated as the volume fraction
C*** average of excluded volume ratios

C*** chain to chain segment excluded volume ratio
YNL=(VENL-VE2L)/(VE2L-VE1L)
C*** chain to monomer excluded volume ratio
YNU=(VENU-VE2U)/(VE2U-VE1U)
C*** Mixture excluded volume ratio
RAT=YNL*F(1)+YNU*F(2)

C*** Calculate the Hard Monomer mixture insertion factors

C*** Geometric factors for monomers of component 1
BB(1)=4./3.*PI*R(1)**3
S(1)=4.*PI*R(1)**2
RB(1)=R(1)

C*** Geometric factors for monomers of component 2
BB(2)=4./3.*PI*R(2)**3
S(2)=4.*PI*R(2)**2
RB(2)=R(2)

C*** Geometric factors for dimers of component 1
BB2(1)=8./3.*PI*R(1)**3
S2(1)=8.*PI*R(1)**2

```

```

RB2(1)=1.5*R(1)

C*** Geometric factors for dimers of component 2
BB2(2)=BB(2)
S2(2)=S(2)
RB2(2)=RB(2)

C*** Calculate the insertion factor for monomer 1 and 2
C*** at Eta ranging from      Eta = etain/Neta --> eatin   Increment = etain/Neta

      do 50 J=1,Neta
      eta(J)=eta*real(J)/real(Neta)
50    continue

      CALL SPTZ(BB,RB,S,X,eta,Zh1,Neta)

C*** Calculate the insertion factors for Dimers and Monomers over the range above
CALL SPTZ(BB2,RB2,S2,X2,eta,Zh2,Neta)

C*** Calculate the SW contribution to the compressibility
C*** factor from coordination number models.
      call monmon(x,eta,zat1,zat2,Neta)
      call dimmon(x2,eta,zatmdd,zatmdm,Neta)

C*** Calculate the (Z-1)/eta at eta=eta/Neta
      Z_1on1=(XC*((RAT+1.0)*(Zh2(1,1)+ZATMDD(1)))-
&          RAT*(Zh1(1,1)+ZAT1(1)))+(1.-XC)*(Zh2(2,1)+ZATMDM(1))
&          - 1.)/eta(1)

C*** Calculate the (Z-1)/eta at eta=2*eta/Neta
      Z_1on2=(XC*((RAT+1.0)*(Zh2(1,2)+ZATMDD(2)))-
&          RAT*(Zh1(1,2)+ZAT1(2)))+(1.-XC)*(Zh2(2,2)+ZATMDM(2))
&          - 1.)/eta(2)

C**   Extrapolate to eta=0
      Z_1on0=(Z_1on1*eta(2)-Z_1on2*eta(1))/(eta(2)-eta(1))

C*** Numerically integrate from eta=0 -> eta=eta
      helm=0.5*Z_1on0*eta(1)

      helm=0.5*(XC*((RAT+1.0)*(Zh2(1,1)+ZATMDD(1)))-
&          RAT*(Zh1(1,1)+ZAT1(1)))+(1.-XC)*(Zh2(2,1)+ZATMDM(1))
&          - 1.)/eta(1)*eta(2)+helm

      DO 101 J=2,neta-1
      helm=0.5*(XC*((RAT+1.0)*(Zh2(1,J)+ZATMDD(J)))-
&          RAT*(Zh1(1,J)+ZAT1(J)))+(1.-XC)*(Zh2(2,J)+ZATMDM(J))
&          - 1.)/eta(J)*(eta(J+1)-eta(J-1))+helm
101    continue

      helm=0.5*(XC*((RAT+1.0)*(Zh2(1,neta)+ZATMDD(neta)))-
&          RAT*(Zh1(1,neta)+ZAT1(neta)))+(1.-XC)*(Zh2(2,neta)
&          +ZATMDM(neta))-1.)/eta(neta)*(eta(neta)-eta(neta-1))
&          +helm

C*** Calculate the compressibility
      zgfd=XC*((RAT+1.0)*(Zh2(1,neta)+ZATMDD(neta)))-
&          RAT*(Zh1(1,neta)+ZAT1(neta)))+(1.-XC)*(Zh2(2,neta)
&          +ZATMDM(neta))

C*** Calculate the Helmholtz free energy
      if(xc*(1.-xc).eq.0.0d+0) then
        A=(helm-log(Vout))*Temp
      else

```



```

        A=(helm-log(Vout)+xc*dlog(xc)+(1.-xc)*dlog((1.-xc)))*Temp
    endif

C*** The derivative of the Helmholtz free energy with respect to volume
C*** equals -P which equals Z*T/V
        dadv=-zgfd/Vout*Temp

    return
end

```

```

      SUBROUTINE VOLC(DIA1,DIA2,CHNLEN,VOL)

C*****
C*** Calculate the excluded volume of chain to a monomer
C*****

      REAL DIA1,DIA2,CHNLEN,VOL
      REAL A,B,C,RAT
      PI = 4.0*ATAN(1.0)

      RAT = DIA2/DIA1

      IF (RAT .GT. 1.0) THEN

          A = EXP(0.5109851)
          B = EXP(0.9529611)
          C = EXP(-7.802438)

          VOL = A*RAT**2.542618 + B*CHNLEN*RAT**1.241169 -
&              C*CHNLEN**2 * RAT**3.164862

      ELSE

          A = 1.56763
          B= 4.749
          C=2.99416
          D=0.515413
          V3 = A + B*RAT + C*RAT*RAT + D*RAT**3
          V2 = PI*(RAT**3 + 4.5*RAT**2 + 6*RAT + 2)/6

          VOL = V3 + (V3 - V2)*(CHNLEN - 3)

      ENDIF

      VOL = VOL*DIA1**3

      RETURN
      END

```

```

      FUNCTION  EXC(D1,D2,R)

C*****
C**  This function calculates the volume common to two
C**  spheres of radii D1 and D2 whose centers are R apart.
C*****

      REAL  D1,D2,R,PI,EXC,t0

      PI = 4.0*ATAN(1.0)

      t0 = 2.0/3.0*pi*d1**3+pi*(d1**2-d2**2
&  +r**2)*(-10*d1**2*r**2+d1**4-
#  2*d1**2*d2**2+d2**4-2*d2**2*r**2+r**4)
#  /r**3/24+2.0/3.0*pi*d2**3-pi
#*(-r**2+d1**2-d2**2)*(-10*d2**2*r**2+r**4
#  -2*d1**2*r**2+d1**4-2*d1*
#  *2*d2**2+d2**4)/r**3/24

      EXC = t0

      return
      end

```

```

SUBROUTINE SPTZ(B,R,S,X,eta,PINS,neta)

C*****
C*** This subroutine calculates the insertion factors for various components
C*** in mixtures of hard convex bodies using the Scaled Particle
C*** theory
C***
C*** Input Arrays
C***
C*** B(i) = Volume of each component
C*** R(i) = Radius of curvature of each component
C*** S(i) = Surface area of each component
C*** X(i) = Molefraction of each component
C***
C*** Output Array
C*** PINS(i,j) Insertion factor of component I at Eta = j
C***
C*** WN,XN,YN,ZN Various exponents in insertion probability
C*** expression (See Gulati, Wichert and Hall JCP 1996)
C***
C*** AM,AN,AO,AM1,AM2 are intermediate arrays used to evaluate
C*** insertion factors
C*****

PARAMETER (NCOMP=2)
REAL B(NCOMP),R(NCOMP),S(NCOMP), X(NCOMP)
REAL C(NCOMP),WN(NCOMP),XN(NCOMP),YN(NCOMP)
REAL ZN(NCOMP),AM(NCOMP),AN(NCOMP),AM1(NCOMP)
REAL AM2(NCOMP), AO(NCOMP)
REAL PINS(NCOMP,neta),eta(neta)

BT=0.0
ST=0.0
RT=0.0
CT=0.0

DO 19 I=1,NCOMP
  BT=BT+X(I)*B(I)
  ST=ST+X(I)*S(I)
  RT=RT+X(I)*R(I)
  CT=CT+X(I)*R(I)**2
19 CONTINUE

DO 25 I=1,NCOMP

  AM(I)=(R(I)*ST+S(I)*RT+B(I))/BT
  AO(I)=1./3.*B(I)/BT*CT*ST**2/BT**2
  AN(I)= 1./6.*R(I)**2*ST**2/BT**2+1./3.*CT*S(I)*ST/BT**2
  &
  &+B(I)/BT**2*RT*ST
  AM1(I)=(BT*(R(I)**2*ST**2+2.*CT*S(I)*ST)-2.*CT*ST**2*B(I))
  &
  &/(9.0*BT**3)
  AM2(I)=CT*ST**2*B(I)/(9.0*BT**3)

  XN(I)=-AM(I) - AM1(I)
  YN(I)=2.0*AM(I)- AN(I) +5./2.*AM1(I)
  ZN(I)=AN(I)-AM(I)-AO(I)-3./2.*AM1(I)+AM2(I)
  WN(I)=-1.0*AM1(I)

25 CONTINUE

```

```

DO 100 II=1,neta
DO 30 I=1,NCOMP
PINS(I,II)=(-1.0-WN(I)-YN(I)-3.0*ZN(I))*ALOG(1-ETA(II))
&      /ETA(II)+((-YN(I)-3.0*ZN(I)-WN(I))+ETA(II)
&      *(-XN(I)/2.0+5./2.*YN(I)+15./2.*ZN(I)+
&      3.0*WN(I))+ETA(II)**2
&      *(-XN(I)/2.-5./2.*YN(I)-11./2.*ZN(I)-3.*WN(I))+
&      ETA(II)**3*WN(I))/(1.-ETA(II))**3
30      CONTINUE
100     CONTINUE

RETURN
END

```

```

      SUBROUTINE MONMON(X,eta,Zat1,Zat2,neta)

C*****
C*** This subroutine determines the compressibility factor
C*** of a square well monomer-monomer mixture by
C*** numerical integration, given a coordination number model.
C*** the high density correction is similar to
C*** Vimalchand, et.al. Species one is the dimer.
C***
C*** The parameters in our coordination number model
C*** are determined by least sqrs fit.
C*****

      REAL D1,D2,D12
      REAL WD1,WD2,WD12
      REAL VS11,VS22,VS12
      REAL AMN,BMN,CMN,ADI,BDI,CDI

      COMMON/DIABLOCK/D1,D2,D12
      COMMON/SWBLOCK/WD1,WD2,WD12,TEMP
      COMMON/VBLOCK/VS11,VS22,VS12
      COMMON/GEOBLOCK/AMN,BMN,CMN,ADI,BDI,CDI

      INTEGER nstep,II,
      REAL X(2),eta(neta),PI,stp,tot1,areal
      REAL chp1(0:neta),chp2(0:neta),zat1(neta),zat2(neta)
      REAL RHO,RHO1,RHO2,RHOS

      PI=4.0*ATAN(1.0)
      nstep=50

C*** Parameters determined by least square fit
      AMN=0.919
      BMN=0.791
      CMN=0.339
      ADI=0.919
      BDI=0.791
      CDI=0.339

      D12=(D1+D2)/2.0
      CHP1(0)=0.0
      CHP2(0)=0.0
      ZDIFFS=0.0

      DO 50 II=1,neta
         stp=eta(neta)/real(neta)

C*** Species 1 if the chain in a chain monomer mixture.
C***
C*** Rho = Number density
C*** Rhos = Reduced density

      RHO=ETA(II)*6./PI/(X(1)*D1**3+X(2)*D2**3)
      RHO1=RHO*X(1)
      RHO2=RHO*X(2)
      RHOS=RHO1*D1**3+RHO2*D2**3

C*** Integrate over the inverse temperature
C*** Initialize integral sum
      tot1=0.0

      call intv(rho,x,rhos,tinv,tot1,rho1,rho2)
      step=1./real(nstep)/temp

```

```

C***  Chpl(ii) = -ln P_1(eta)
      chpl(ii)=totl/2.0*step

C***  Integrate the chemical potentials to get the attractive contribution
C***  to the compressibility factor
      areal=0.0
      do 999 ij=1,ii
        areal=areal+(chpl(ij)+chpl(ij-1))
999    continue
      zatl(ii)=chpl(ii)-1./eta(II)*areal/2.*stp
50    continue
      return
      end

```

```

Subroutine Intv(Rho,X,Rhos,Tinv,totl,Rho1,Rho2)

C*****
C** This subroutine integrates the expression U-dU/dx with respect to 1/T
C** from 1/T=0 -> 1/T. This subroutine gets called a lot and profiling the
C** program revealed that most of the time was being spent here. Hence I
C** did a lot of optimizing by hand and now it is not very reader friendly.
C*****

REAL D1,D2,D12
REAL WD1,WD2,WD12
REAL VS11,VS22,VS12
REAL AMN,BMN,CMN,ADI,BDI,CDI

COMMON /DIABLOCK/D1,D2,D12
COMMON/SWBLOCK/WD1,WD2,WD12,TEMP
COMMON/VBLOCK/VS11,VS22,VS12
COMMON/GEObLOCK/AMN,BMN,CMN,ADI,BDI,CDI
REAL X(2)

REAL Alp,Alpp,Zt,Ztpd
REAL ZtdRho1,ZtdRho1S,ZtpdRho1S,ZtdRho2,ZtdRho2S,ZtpdRho2
REAL D13,D123,D23,RhoD13,RhoD123,RhoD23,D1oD2
REAL nstep,xi,tinv
REAL Om11,Om12,Om22,Omg,Omgp
REAL Den1,Den12,Den2
REAL Va,Vb,Vc,Val,Vbl,Vcl
REAL Vil,Vipl,Vi2

C*** Calculate Alpha and Alpha'
Alp=1.-Rhos/Sqrt(2.)
Alpp=-1./Sqrt(2.)

Zt=Amn+Bmn*Rhos-Cmn*Rhos**4
Ztp=Bmn-4.*Cmn*Rhos**3

Ztd=Adi+Bdi*Rhos-Cdi*Rhos**4
Ztpd=Bdi-4.0*Cdi*Rhos**3

ZtdRho1=Ztd*Rho1
ZtdRho1S=Ztd*Rho1*Rho1
ZtpdRho1S=Ztpd*Rho1*Rho1
ZtdRho2=Ztd*Rho2
ZtdRho2S=Ztd*Rho2*Rho2
ZtpdRho2S=Ztpd*Rho2*Rho2
ZtpdRho2=Ztpd*Rho2

D13=D1**3
D123=D12**3
D23=D2**3
RhoD13=Rho*D13
RhoD123=Rho*D123
RhoD23=Rho*D23
D1oD2=D1/D2

nstep=50
do 10 i=0,nstep

step=1./real(nstep)/temp
xi=real(i)/real(nstep)
tinv=1.*xi/temp

Om11=Exp(Alp*Wd1*Tinv)

```



```

Oml2=Exp(Alp*Wd12*Tinv)
Om22=Exp(Alp*Wd2*Tinv)

C*** Calculate the Omega Sum [xi*xj*exp(alp*Eij/kT)]
Omg=X(1)**2*Om11+2.*X(2)*X(1)*Oml2+X(2)**2*Om22

C*** Calculate Omega Prime = d Omega/d Rho1*
Omgp=(X(1)**2*Alpp*Wd1*Tinv*Om11+
&      2.0*X(1)*X(2)*Alpp*Wd12*Tinv*Om12+
&      X(2)**2*Alpp*Wd2*Tinv*Om22)*D13+
&      (2.*X(1)*X(2)*Om11+
&      2.*(2.*X(2)**2-X(2))*Om12-
&      2.*X(2)**2*Om22)/Rho

Den1=1+RhoD13*(Omg-1)
Den12=1+RhoD123*(Omg-1)
Den2=1+RhoD23*(Omg-1)

If(D1 .le. D2) Then
    Va=Om11*( (ZtdRho1+
&      (D13*ZtpdRho1S+ZtdRho1+D13*
&      ZtdRho1S*Alpp*Wd1*Tinv))/Den1-
&      ZtdRho1S*(D13*(Omg-1)
&      +RhoD13*Omgp)/Den1**2)
    Val=1./((0.296*(D1oD2)+0.704)*Va

    Vb1=Om12/(0.13*(D1oD2)+0.87)*((ZtdRho2+Rho1*D13
&      *(ZtpdRho2+ZtdRho2*
&      Alpp*Wd12*Tinv))/Den12-
&      ZtdRho1*Rho2*(D123*(Omg-1)
&      +RhoD123*Omgp)/Den12**2)

    Vc1=Om22*(D13*(ZtpdRho2S+ZtdRho2S*
&      Alpp*Wd2*Tinv)/Den2-
&      ZtdRho2S*(D23*(Omg-1)+RhoD23*Omgp)/
&      Den2**2)
    Else
    Va=(Ztd*Rho1*Om11+Rho1
&      *(D13*Ztpd*Rho1*Om11+Ztd*Om11+D13*Ztd*Om11*
&      Rho1*Alpp*Wd1*Tinv))/Den1-
&      Ztd*Rho1**2*Om11*(D13*(Omg-1)
&      +Rho*D13*Omgp)/Den1**2
    Val=Va

    Vb1=1./((0.13*(D2/D1)+0.87)*((Ztd*Rho2*Om12+Rho1*D13
&      *(Ztpd*Rho2*Om12+Ztd*Om12*
&      Rho2*Alpp*Wd12*Tinv))/Den12-
&      Ztd*Rho1*Rho2*Om12*(D123*(Omg-1)
&      +Rho*D123*Omgp)/Den12**2)

    Vc1=1./((0.296*(D2/D1)+0.704)*
&      D13*Rho2*(Ztpd*Rho2*Om22+Ztd*Om22*
&      Rho2*Alpp*Wd2*Tinv)/Den2-
&      Ztd*Rho2*Rho2*Om22*(D23*(Omg-1)+Rho*D23*Omgp)/
&      Den2**2)
Endif

Va=Val*Wd1*Vs11/2.
Vb=Vb1*Wd12*Vs12/2.
Vc=Vc1*Wd2*Vs22/2.

Vil=Va+2.*Vb+Vc
if(i .eq. 0) then
    vip1=vil

```

```
        goto 10
    endif

    tot1=tot1-(vil+vip1)
    vip1=vil
10  continue
    Vi2=0.
End
```

```

      SUBROUTINE DIMMON(X,eta,ZATMDD,ZATMDM,neta)
C** This program determines the compressibility factor
C** of a square well monomer-dimer mixture by numerical integration,
C** given a coordination number model.
C** the high density correction is similar to
C** Vimalchand, et.al.
C** Species one is the dimer.

C** the parameters in our coordination number model
C** are determined by least sqrs fit.

      REAL D1,D2,D12
      REAL WD1,WD2,WD12
      REAL VS11,VS22,VS12
      REAL AMN,BMN,CMN,ADI,BDI,CDI
      REAL ACR,BCR,CCR

      COMMON/DIABLOCK/D1,D2,D12
      COMMON/SWBLOCK/WD1,WD2,WD12,TEMP
      COMMON/GEOBLOCK/AMN,BMN,CMN,ADI,BDI,CDI
      COMMON/BLO_LOC/ACR,BCR,CCR
      REAL X(2),eta(neta)

      REAL CHP1(0:neta),CHP2(0:neta)
      REAL ZATMDD(neta),ZATMDM(neta)

      PI=4.0*ATAN(1.0)
      NSTEP=50
C*** Amn, Bmn, Cmn are the parameters for Monomers
C*** Adi, Bdi, Cdi are the parameters for Dimers
C*** Acr, Bcr, Ccr are the parameters for monomer-dimer interaction (Cross interaction)

      AMN=0.919
      BMN=0.791
      CMN=0.339
      ADI=1.754
      BDI=4.986
      CDI=1.951

      RAT=D2/D1
      D12=(D1+D2)/2.0

      IF(RAT .GE. 1) THEN
        ACR=3.207+D1/D2*-2.226
      ELSE
        ACR=3.010+D2/D1*-2.028
      ENDIF

      IF(RAT .GE. 1) THEN
        BCR=-1.347+D1/D2*4.166
      ELSE
        BCR=0.017+D2/D1*2.802
      ENDIF

      IF(RAT .GE. 1) THEN
        CCR=-1.795+D1/D2*3.544
      ELSE
        CCR=-1.997+D2/D1*3.746
      ENDIF

      CHP1(0)=0.0
      CHP2(0)=0.0

```

```

ZDIFFS=0.0

DO 50 II=1,neta
    stp=eta(neta)/real(neta)

C***  X(1) is the molefraction of dimer
        RHO=ETA(II)*6./PI/(2.0*X(1)*D1**3+X(2)*D2**3)
        RHO1=RHO*X(1)
        RHO2=RHO*X(2)
        RHOS=2.0*RHO1*D1**3+RHO2*D2**3

C***  Integrate over the inverse temperature
        tot1=0.0
        tot2=0.0

        call intv2(rho,X,rhos,tinv,tot1,tot2,rho1,rho2)

        step=1./real(nstep)/temp

        chp1(ii)=tot1/2.0*step
        chp2(ii)=tot2/2.0*step

C**  Integrate the chemical potentials to get the attractive
C**  contribution to the compressibility factor
        areal=0.0
        area2=0.0
        do 999 ij=1,ii
            areal=areal+(chp1(ij)+chp1(ij-1))
            area2=area2+(chp2(ij)+chp2(ij-1))
999    continue

        zatmdd(ii)=chp1(ii)-1./eta(II)*areal/2.*stp
        zatmdm(ii)=chp2(ii)-1./eta(II)*area2/2.*stp

        zatt=zatmdd(ii)*X(1)+zatmdm(ii)*X(2)
50    continue
return
end

```

```

SUBROUTINE INTV2(RHO,X,RHOS,TINV,tot1,tot2,RHO1,RHO2)

C*****
C** This subroutine integrates the expression U-dU/dx with respect to 1/T
C** from 1/T=0 -> 1/T. This subroutine gets called a lot and profiling the
C** program revealed that most of the time was being spent here. Hence I
C** did a lot of optimizing by hand and now it is not very reader friendly.
C*****

REAL D1,D2,D12
REAL WD1,WD2,WD12
REAL VS11,VS22,VS12
REAL AMN,BMN,CMN,ADI,BDI,CDI
REAL ACR,BCR,CCR

COMMON /DIABLOCK/D1,D2,D12
COMMON/SWBLOCK/WD1,WD2,WD12,TEMP
COMMON/VBLOCK/VS11,VS22,VS12
COMMON/GEObLOCK/AMN,BMN,CMN,ADI,BDI,CDI
COMMON/BLO_LOC/ACR,BCR,CCR
REAL X(2)

REAL D13,D123,D23
REAL ALP,ALPP
REAL ZT,ZTRho2SD13,ZTRho2SD23
REAL ZTP,ZTPRho2SD13,ZTD,ZTDRho1,ZTDRho1SD13,ZTDRho2SD13
REAL ZTPD,ZTPDRho1SD13,ZTC,ZTCRho2,ZTCR1R2D123,ZTPC
REAL tot1,tot2,nstep,xi,tinv
REAL Om11,Om12,Om22,OMG,Omgp,OMGOMGP
REAL Den1,Den12,Den2
REAL VA,VB,VC,VA1,VB1,VC1,VA2,VB2,VC2
REAL Vi1,Vip1,Vi2

D13=D1**3
D123=D12**3
D23=D2**3

ALP=1.-RHOS/SQRT(2.)
ALPP=-1./SQRT(2.)

ZT=AMN+BMN*RHOS-CMN*RHOS**4
ZTRho2SD13=ZT*Rho2*Rho2*D13
ZTRho2SD23=ZT*Rho2*Rho2*D23

ZTP=BMN-4.0*CMN*RHOS**3
ZTPRho2SD13=ZTP*Rho2*Rho2*D13

ZTD=ADI+BDI*RHOS-CDI*RHOS**4
ZTDRho1=ZTD*Rho1
ZTDRho1SD13=ZTD*Rho1*Rho1*D13
ZTDRho2SD13=ZTD*Rho2*Rho2*D13

ZTPD=BDI-4.0*CDI*RHOS**3
ZTPDRho1SD13=ZTPD*Rho1*Rho1*D13

ZTC=ACR+BCR*RHOS-CCR*RHOS**4
ZTCRho2=ZTC*Rho2
ZTCR1R2D123=ZTC*Rho1*Rho2*D123

ZTPC=BCR-4.0*CCR*RHOS**3

tot1=0.
tot2=0.
nstep=50

```

```

do 10 i=0,nstep
  step=1./real(nstep)/temp
  xi=real(i)/real(nstep)
  tinv=1./temp*xi
C*** Calculate Omega
  Om11=Exp(Alp*Wd1*Tinv)
  Om12=Exp(Alp*Wd12*Tinv)
  Om22=Exp(Alp*Wd2*Tinv)
  OMG=X(1)**2*Om11+2.*X(2)*X(1)*Om12+X(2)**2*Om22

  DEN1=1+RHO*D13*(OMG-1)
  DEN12=1+RHO*D123*(OMG-1)
  DEN2=1+RHO*D23*(OMG-1)

C*** Calculate Omega Prime
  OMGP=(X(1)**2*ALPP*WD1*TINV*Om11+
&      2.0*X(1)*X(2)*ALPP*WD12*TINV*Om12+
&      X(2)**2*ALPP*WD2*TINV*Om22)*D13+
&      (2.*X(1)*Om11+2.*(2.*X(2)-1.)*Om12-
&      2.*X(2)*Om22)*X(2)/RHO

  OMGOMGP=(OMG-1)+Rho*OMGP
C*** d Rhos/d Rho1 = D13
C*** d Rho/ d Rho1 = 1

  VA1=(2.0*ZTDRHO1*Om11+(ZTPDRHO1SD13
&      *Om11+ZTDRho1SD13*Om11*ALPP*WD1*TINV))/DEN1
&      -ZTDRHO1SD13*Om11*OMGOMGP/DEN1**2

  VB1=(ZTCRHO2*Om12+RHO1*RHO2*D13*(ZTPC*Om12
&      +ZTC*Om12*ALPP*WD12*TINV))/DEN12-
&      ZTCR1R2D123*Om12*OMGOMGP/DEN12**2

  VC1=(ZTPRHO2SD13*Om22+ZTRho2SD13*Om22*
&      ALPP*WD2*TINV)/DEN2-
&      ZTRHO2SD23*Om22*OMGOMGP/DEN2**2

  VA=VA1*WD1*VS11/2.
  VB=VB1*WD12*VS12/2.
  VC=VC1*WD2*VS22/2.
  Vi1=VA+2.*VB+VC

  OMGP=(X(2)**2*ALPP*WD2*TINV*Om22+
&      2.*X(1)*X(2)*ALPP*WD12*TINV*Om12+
&      X(1)**2*ALPP*WD1*TINV*Om11)*D23+
&      (2.*X(2)*X(1)*Om22+
&      2.*(2.*X(1)**2-X(1))*Om12-
&      2.*X(1)**2*Om11)/RHO

  VA2=(2.0*ZT*RHO2*Om22+RHO2**2*D23*(ZTP*Om22
&      +ZT*Om22*ALPP*WD2*TINV))/DEN2-
&      ZT*RHO2**2*Om22*((OMG-1)*D23
&      +RHO*D23*OMGP)/DEN2**2

  VB2=(ZTC*RHO1*Om12+RHO2*RHO1*D23*(ZTPC*Om12+
&      ZTC*Om12*ALPP*WD12*TINV))/DEN12-
&      ZTC*RHO1*RHO2*Om12*(D123*(OMG-1)
&      +RHO*D123*OMGP)/DEN12**2

  VC2=D23*RHO1**2*(ZTPD*Om11+ZTD*Om11*
&      ALPP*WD1*TINV)/DEN1-
&      ZTD*RHO1*RHO1*Om11*(D13*(OMG-1)+RHO*D13*OMGP)/
&      DEN1**2

```

```

VA=VA2*WD2*VS22/2.
VB=VB2*WD12*VS12/2.
VC=VC2*WD1*VS11/2.

Vi2=VA+2.*VB+VC

if(i .eq. 0) then
    vip1=vil
    vip2=vi2
    goto 10
endif

C**  tot is the total attractive interaction for
C**  the square well fluid.
        tot1=tot1-(vil+vip1)
        tot2=tot2-(vi2+vip2)
        vip1=vil
        vip2=vi2
10    continue
    RETURN
END

```

```

SUBROUTINE ludcmp(a,n,np,indx,d)

C*****
c   Given a matrix a(1:n,1:n) with physical dimension np by np, this routine replaces
c   it by the LU decomposition of a rowwise permutation of itself, a and n are input.
c   a is output arranged to be used by lubksb. indx(1:n) is an output vector that
c   records the row permutation effected by the partial pivoting; d is output as +/-1
c   depending on whether the number of row interchanges was even or odd, respectively
c   This routine is used in combination with lubksb to solve linear equations or
c   invert a matrix. NMAX=largest expected nm and TINY=a small number.
C*****

      INTEGER n,np,indx(n),NMAX
      REAL d,a(np,np),TINY
      PARAMETER (NMAX=2,TINY=1.0d-20)
      INTEGER i,imax,j,k
      REAL aamax,dum,sum,vv(NMAX)

      d=1.d+0
      do 12 i=1,n
         aamax=0.d+0
         do 11 j=1,n
            if (dabs(a(i,j)).gt.aamax) aamax=dabs(a(i,j))
11          continue
            if (aamax.eq.0.d+0) pause 'singular matrix in ludcmp'
            vv(i)=1.d+0/aamax
12          continue
         do 19 j=1,n
            do 14 i=1,j-1
               sum=a(i,j)
               do 13 k=1,i-1
                  sum=sum-a(i,k)*a(k,j)
13              continue
               a(i,j)=sum
14              continue
            aamax=0.d+0
            do 16 i=j,n
               sum=a(i,j)
               do 15 k=1,j-1
                  sum=sum-a(i,k)*a(k,j)
15              continue
               a(i,j)=sum
               dum=vv(i)*abs(sum)
               if (dum.ge.aamax) then
                  imax=i
                  aamax=dum
               endif
16              continue
            if (j.ne.imax)then
               do 17 k=1,n
                  dum=a(imax,k)
                  a(imax,k)=a(j,k)
                  a(j,k)=dum
17              continue
               d=-d
               vv(imax)=vv(j)
            endif
            indx(j)=imax
            if(a(j,j).eq.0.)a(j,j)=TINY
            if(j.ne.n)then
               dum=1.d+0/a(j,j)
               do 18 i=j+1,n
                  a(i,j)=a(i,j)*dum
18              continue
            endif

```



```
        endif
19    continue
    return
END
```

```

SUBROUTINE lubksb(a,n,np,indx,b)

C*****
c   Solves the set of n linear equations  $A \cdot X = B$ . Here a is input not as the matrix A
c   but rather as its LU decomposition determined by the routine ludcmp. indx is
c   input as the permutation vector returned by ludcmp. b(1:n) is input as the right-
c   hand side vector B, and returns with the solution vector X. a, n, np and indx are
c   not modified by this routine and can be left in place for successive calls with
c   different right-hand sides b. This routine takes into account the possibility
c   that b will begin with many zero elements, so it is efficient for use in matrix
c   inversion.
C*****

      INTEGER n,np,indx(n)
      REAL a(np,np),b(n)
      INTEGER i,ii,j,ll
      REAL sum

      ii=0
      do 12 i=1,n
         ll=indx(i)
         sum=b(ll)
         b(ll)=b(i)
         if (ii.ne.0d+0)then
            do 11 j=ii,i-1
               sum=sum-a(i,j)*b(j)
11          continue
            else if (sum.ne.0.d+0) then
               ii=i
            endif
            b(i)=sum
12      continue
      do 14 i=n,1,-1
         sum=b(i)
         do 13 j=i+1,n
            sum=sum-a(i,j)*b(j)
13          continue
            b(i)=sum/a(i,i)
14      continue
      return
      END

```

```

SUBROUTINE lnsrch(n,xold,fold,g,p,x,f,stpmax,check,func)

C*****
c   Given an n-dimensional point xold(1:n) the value of the function and gradient
c   there, fold and g(1:n), and a direction p(1:n), finds a new point x(1:n) along
c   the direction p from xold where the function func has decreased sufficiently.
c   The new function value is returned as f. stpmax is an input that limits the
c   step size. p is usually the Newton direction. The output check is false on
c   normal exit and true when x is too close to xold. In minimization this usually
c   signals convergence. In zero finding the result must be checked to determine
c   if may be spurious. ALF ensures sufficient decrease in function value and TOLX
c   is the convergence critierion on delta(x).
C*****

REAL D1,D2,D12
REAL RRAT,RNL,x1

COMMON /DIABLOCK/ D1,D2,D12
COMMON /INPUT/ RRAT,RNL
COMMON x1

INTEGER n,i,its
LOGICAL check
REAL f,fold,stpmax,g(n),p(n),x(n),xold(n),func,ALF,TOLX,d1,d2
Real a,alam,alam2,alamin,b,disc,f2,fold2,rhs1,rhs2,slope,
&      sum,temp,test,tmp1am
PARAMETER (ALF=1.d-4,TOLX=1.d-7)
EXTERNAL func

check=.false.
PI = 4.0d+0*daTAN(1.0d+0)
its=0
sum=0.d+0
do 11 i=1,n
    sum=sum+p(i)*p(i)
11 continue
sum=dsqrt(sum)
if(sum.gt.stpmax)then
    do 12 i=1,n
        p(i)=p(i)*stpmax/sum
12 continue
endif
slope=0.d+0
do 13 i=1,n
    slope=slope+g(i)*p(i)
13 continue
test=0.
do 14 i=1,n
    temp=dabs(p(i))/dmax1(dabs(xold(i)),1.d+0)
    if(temp.gt.test)test=temp
14 continue
alamin=TOLX/test
alam=1.d+0
1 continue
do 15 i=1,n
    x(i)=xold(i)+alam*p(i)
15 continue
eta=PI*(x1*RNL*D1**3+(1-x1)*D2**3)/6d+0/x(1)
if(eta.gt.0.70d+0) then
    print*, 'eta>0.7'
    alam=0.5*alam
    goto 1
elseif(eta.lt.0.0) then
    print*, 'eta<1'

```

```

        alam=0.5*alam
        goto 1
elseif(x(2).lt.0.0d+0) then
    print*, 'T<0'
    alam=0.5*alam
    goto 1
elseif(alam.lt.alamin)then
    do 16 i=1,n
        x(i)=xold(i)
16      continue
        check=.true.
        return
endif
f=func(x)
if(f.le.fold+ALF*alam*slope)then
    return
else
    if(alam.eq.1.d+0)then
        tmplam=-slope/(2.d+0*(f-fold-slope))
    else
        rhs1=f-fold-alam*slope
        rhs2=f2-fold2-alam2*slope
        a=(rhs1/alam**2-rhs2/alam2**2)/(alam-alam2)
        b=(-alam2*rhs1/alam**2+alam*rhs2/alam2**2)/(alam-alam2)
        if(a.eq.0.d+0)then
            tmplam=-slope/(2.d+0*b)
        else
            disc=b*b-3.d+0*a*slope
            tmplam=(-b+dsqrt(disc))/(3.d+0*a)
        endif
        if(tmplam.gt..5d+0*alam)tmplam=.5d+0*alam
    endif
endif
alam2=alam
f2=f
fold2=fold
alam=dmax1(tmplam,.1d+0*alam)
goto 1

END

```

B.2 Code listing for calculating coexistence points

```
PROGRAM TXDIAG

REAL D1,D2,D12
REAL WD1,WD2,WD12, TEMP
REAL Vs11,Vs22,Vs12
REAL RRAT, RNL
REAL INC, Xc

COMMON /DIABLOCK/ D1,D2,D12
COMMON /SWBLOCK/ WD1,WD2,WD12, TEMP
COMMON /VBLOCK/ Vs11,Vs22,Vs12
COMMON /INPUT/ RRAT, RNL
COMMON /params/ INC
COMMON xc

INTEGER i, j, k, l, jtot, M, NL, its, N(2)
CHARACTER*20 fileout
LOGICAL muout, supcrit, posslp
REAL TEMP1, TEMP2
REAL PI, h, step
REAL Vstart, V1, Vold, Vnew, Vo, outnew, outold
REAL m1, m2, Mu2out, Mulout, MU1(2000), Mu2(2000)
REAL Mulint, Mu2int
REAL R(2), numpts, p
REAL X(2,2000), Gx(2000,2)
REAL xcol, xco2

OPEN(UNIT=5, FILE='swmdmix.inp', STATUS='UNKNOWN', FORM='FORMATTED')

C*** Read Ratio of diameters
READ(5, '(F15.10)') RRAT
C*** Read Chain Length
READ(5, '(I3)') NL
C*** Read the well depth of the chains
READ(5, '(F15.10)') WD1
C*** Read the well depth of monomers
READ(5, '(F15.10)') WD2
C*** Read the cross well depth
READ(5, '(F15.10)') WD12
C*** Read the starting temperature
READ(5, '(F15.10)') TEMP1
C*** Read the stopping temperature
READ(5, '(F15.10)') TEMP2
C*** Read the number of points to calculate
READ(5, '(F15.10)') numpts
C*** Read the pressure
READ(5, '(F15.10)') P
C*** Read output file name
READ(5, '(A)') fileout

close(unit=5)

muout=.true.
open(unit=3, file=fileout, status='unknown')

PI=4.0*ATAN(1.0)
neta=2000
ftol=1.d-5

C*** Real chain length
RNL = REAL(NL)
```

```

C*** Diameter of component 1 set to 1
      R(1)=1.0
C*** Real chain length
      RNL = REAL(NL)
C*** Diameter of component 2
      R(2) = RRAT

      D1 = R(1)
      D2 = R(2)
      D12 = (D1+D2)*0.5

      VS12=4./3.*PI*(1.5**3-1)*D12**3
      VS11=4./3.*PI*(1.5**3-1)*D1**3
      VS22=4./3.*PI*(1.5**3-1)*D2**3

      do 550 temp=temp1,temp2,(temp2-temp1)/(numpts-1.)
        jtot=0
        h=0.0001
        J=0
C*** Calculate the volume of the mixture for the desired pressure for the range
C*** of compositions and the Gibbs free energy of mixing
        do K=1,2
          N(K)=0
        enddo

step=0.005
I=0
xc=0.0
  5 if(xc.le.1.0) then
    I=I+1
    Vstart=PI*(xc*rnl*d1**3+(1.-xc)*d2**3)/6./0.65
    V1=Vstart+0.2
    L=0
    its=0
C*** Calculate the pressure for a given composition and temperature at a very high density
    call xcalc(P,Vstart,xc,outold)
    Vold=Vstart

    supcrit=.false.
    posslp=.false.
    if(P.gt.0.14*(xc*WD1+(1.-xc)*WD2)) supcrit=.true.
    if(Temp.gt.(xc*1.85*WD1+(1.-xc)*1.35*WD2)) supcrit=.true.

C** If the pressure or temperature is above the respective critical value, then there will
C*** only be one solution for the volume at that pressure, thus we can be more aggressive
C*** bracketing the solution and quit after finding it. Since solutions with positive slopes
C*** indicate mechanically unstable systems, we look only for a change from + to - pressure.
    if(supcrit) then
      10 do 15 Vnew=Vstart+1.0,25.,1.0
        call xcalc(P,Vnew,xc,outnew)
        if (outold*outnew.lt.0.0) then
          call zero(P,Vold,outold,Vnew,outnew,Vo)
          L=L+1
          X(1,I)=xc
          X(2,I)=L
          call helmint(Vo,Gx(I,L),xc)
          goto 70
        endif
        outold=outnew
        Vold=Vnew
      15 continue
      Vstart=Vnew
      do 20 Vnew=Vstart,500.,10.
        call xcalc(P,Vnew,xc,outnew)

```

```

    if (outold*outnew.lt.0.0) then
        call zero(P,Vold,outold,Vnew,outnew,Vo)
        L=L+1
        X(1,I)=xc
        X(2,I)=L
        call helmint(Vo,Gx(I,L),xc)
        goto 70
    endif
    outold=outnew
    Vold=Vnew
    20    continue
        goto 70
    endif

C***  If we are below the critical pressure and temperature there may be 1 or 2 solutions
C***  Take smaller steps to bracket the solution...
    do 40 Vnew=Vstart+0.2,7.0,0.2
        call xcalc(P,Vnew,xc,outnew)
        if (outnew.lt.0.0.AND.outold.gt.0.0) then
            call zero(P,Vold,outold,Vnew,outnew,Vo)
            L=L+1
            X(1,I)=xc
            X(2,I)=L
            call helmint(Vo,Gx(I,L),xc)
        endif
C***  And look for the slope to change to positive
        if(outnew.gt.outold) posslp=.true.
        outold=outnew
        Vold=Vnew
    40    continue

        if(L.eq.0) then
C*****if we haven't found a solution below this volume, then there will be only one
C*****solution and we should proceed as in the supercritical case above
            Vstart=7.0
            goto 10
        elseif(L.eq.1.AND..NOT.posslp) then
C*****if we have found one solution but have not hit the local minimum, then there
C*****only be one solution and we can stop
            goto 70
        elseif(L.eq.2) then
C*****if two solutions have been found, then we can stop
            goto 70
        endif

C***  If one solution has been found and we have passed the local minimum, then continue
    do 45 Vnew=7.0,40.,1.0
        call xcalc(P,Vnew,xc,outnew)
        if(outnew.lt.outold) then
            call zero(P,Vold,outold,Vnew,outnew,Vo)
            L=L+1
            X(1,I)=xc
            X(2,I)=L
            call helmint(Vo,Gx(I,L),xc)
            goto 70
        endif
        Vold=Vnew
        outold=outnew
    45    continue

C***  If the second solution has not been found by this point use the supercritical search
        Vstart=Vnew
        Vold=Vnew
        outold=outnew

```

```

        goto 10

70      xc=REAL(I)*step
      goto 5
endif

C*** For each value of composition keep only the more stable volume , i.e. that with the
C*** lowest Gibb's free energy
do J=1,I
  if(X(2,J).eq.2) then
    if(Gx(J,1).gt.Gx(J,2)) Gx(J,1)=Gx(J,2)
  endif
enddo

C*** Calculate the chemical potentials
do k=2,I-1
  Mul(k-1)=Gx(k,1)+(1.d+0-X(1,k))*(Gx(k+1,1)-
    &      Gx(k-1,1))/(X(1,k+1)-X(1,k-1))
  Mu2(k-1)=Gx(k,1)-X(1,k)*(Gx(k+1,1)-Gx(k-1,1))
    &      /(X(1,k+1)-X(1,k-1))
  X(1,k-1)=x(1,k)
enddo

K=1
100 if (K.lt.(I-3)) then
  M=K+2
  110 if (M.lt.(I-2)) then
C**  **If the two points of the points are far apart enough move on to the next pair
    if(abs(Mul(M+1)-Mul(M)).gt.1.) goto 120
    if(abs(Mul(K+1)-Mul(K)).gt.1.) goto 120
C**  **Calculate the point of intersection of the lines
    m1=(Mul(M+1)-Mul(M))/(Mu2(M+1)-Mu2(M))
    m2=(Mul(K+1)-Mul(K))/(Mu2(K+1)-Mu2(K))
    Mu2int=(Mul(K)-Mul(M)+m1*Mu2(M)-m2*Mu2(K))/(m1-m2)
    Mulint=m1*(Mu2int-Mu2(M))+Mul(M)
C**  **Test to see that the lines intersect along the segements between successive points..
    test1=(Mu2int-Mu2(M))*(Mu2int-Mu2(M+1))
    test2=(Mu2int-Mu2(K))*(Mu2int-Mu2(K+1))
    test3=(Mulint-Mul(M))*(Mulint-Mul(M+1))
    test4=(Mulint-Mul(K))*(Mulint-Mul(K+1))
    if((test1.lt.0.0).AND.(test2.lt.0.0).AND.
      &      (test3.lt.0.0).AND.(test4.lt.0.0)) then
      xco1=(Mulint-Mul(M))/(Mul(M+1)-Mul(M))*
        &      (X(1,M+1)-X(1,M))+X(1,M)
      xco2=(Mulint-Mul(K))/(Mul(K+1)-Mul(K))*
        &      (X(1,K+1)-X(1,K))+X(1,K)
C**  **If they do then record the interoplated compositions and skip the point of higher
C**  **to search for any other phase coexistence points
      write(3,*) temp, xco1, xco2
      K=M
      goto 100
    endif
    120      M=M+1
      goto 110
    endif
    K=K+1
    goto 100
  endif
print*, 'done T=',temp
550 continue
end

```



```
#include <Monchnhelm.f>
#include <xcalc.f>
#include "com_vol_dum.f"
#include "chn_mon_vol.f"
#include "subrtns.f"
#include "zerofind.f"
```

```

SUBROUTINE xcalc(P,V,xc,out)

C*****
C** This subroutine calculates the pressure P and the difference between the
C** desired pressure and calculated pressure and returns this as OUT. The
C** subroutines used here are the same as those used in Section B.1
C*****

REAL D1,D2,D12
REAL WD1,WD2,WD12, TEMP
REAL Vs11,Vs22,Vs12
REAL RRAT, RNL
REAL INC, Xc

COMMON /DIABLOCK/ D1,D2,D12
COMMON /SWBLOCK/ WD1,WD2,WD12,TEMP
COMMON /VBLOCK/ VS11,VS22,VS12
common /input/ RRAT, RNL

PARAMETER(N=2,NE=2000)
REAL R(N),X(N),AR(N,N),E(N),X2(N),F(N),
& BB(N),S(N),RB(N),XN(N),YN(N),ZN(N),WN(N),
& Zh1(N,2000),Zh2(N,2000),
& AX(N),AY(N),AZ(N),AW(N),AM1(N),AM2(N),
& AM(N),AN(N),AO(N),
& ZAT1(NE),ZAT2(NE),ZATMDD(NE),ZATMDM(NE),
& BB2(N), S2(N), RB2(N), eta(NE)
REAL OUT,PI,etamax,V,ZGFD
INTEGER Neta

PI = 4.0*ATAN(1.0)

etamax=PI*(xc*rnl*d1**3+(1.-xc)*d2**3)/6d+0/V

C*** Check for an unphysically high density and return if it is
if (etamax.gt.0.75) then
    out=1000.
    goto 100
endif

C*** Initialize the array of value of eta
Neta=INT(etamax/0.0005)
do 50 J=1,Neta
    eta(J)=etamax*REAL(J)/REAL(neta)
50 continue

C*** Diameter of component 2
R(1)=1.0
R(2) = RRAT

C** The site fraction of each component
X(1)=RNL*XC/(RNL*XC+(1.-XC))
X(2)=1.-X(1)

C** The mole fraction of dimers and monomers in a hypothetical
C** dimer monomer mixture fluid formed by breaking the alternative
C** bonds of the chain
X2(1)=RNL*XC/(RNL*XC+2.0*(1.-XC))
X2(2)=1.-X2(1)

C*** Calculate C, the total volume fraction of the system
C=0.0
DO 10 I=1,N

```

```

      C=C+X(I)*R(I)**3
10  CONTINUE

C*** Calculate the Fractional occupation fraction F(i) of each component
DO 199 I=1,N
      E(I)=(X(I)*R(I)**3/C)
      F(I)=E(I)
199 CONTINUE

C*** Calculate the Excluded Volume of the chain to chain segment
VE1L=4./3.*PI
VE2L=9./4.*PI
CALL VOLC(D1,D1,RNL,VENL)

C*** Calculate the volume excluded by component 1 to component 2

RAD=(1.0+RRAT)/2.0

C*** Volume Excluded by a monomer of component 1 to monomer of comp 2
VE1U=VE1L*(RAD)**3

C*** Volume excluded by a dimer of component 1 to a monomer of
C*** component 2. The distance between the centers of the two beads is D1
DIS = D1

C*** Function EXC calculates the common volume between two spheres of radii
C*** R1, R2 and with their centers DIS apart
VE2U = 2*VE1L*RAD**3 - EXC(RAD,RAD,DIS)

      IF (RNL .GT. 2) THEN
        CALL VOLC(D1,D2,RNL,VENU)
      ELSE
        VENU=VE2U
      ENDIF

C*** Calculate the excluded volume ratios
C*** Mixture excluded volume ratio calculated as the volume fraction
C*** average of excluded volume ratios

C*** chain to chain segment excluded volume ratio
YNL=(VENL-VE2L)/(VE2L-VE1L)
C*** chain to monomer excluded volume ratio
YNU=(VENU-VE2U)/(VE2U-VE1U)
C*** Mixture excluded volume ratio
RAT=YNL*F(1)+YNU*F(2)

C*** Calculate the Hard Monomer mixture insertion factors

C*** Geometric factors for monomers of component 1
BB(1)=4./3.*PI*R(1)**3
S(1)=4.*PI*R(1)**2
RB(1)=R(1)

C*** Geometric factors for monomers of component 2
BB(2)=4./3.*PI*R(2)**3
S(2)=4.*PI*R(2)**2
RB(2)=R(2)

C*** Dimer Geometric factors
BB2(1)=8./3.*PI*R(1)**3
S2(1)=8.*PI*R(1)**2
RB2(1)=1.5*R(1)
BB2(2)=BB(2)
S2(2)=S(2)

```

```

      RB2(2)=RB(2)

C*** Calculate the insertion factor for monomer 1 and 2
C*** at Eta ranging from      Eta = 0.0 --> 0.5  Increment = 0.005

      CALL SPTZ(BB,RB,S,X,eta,Zh1,neta)

C*** Calculate the insertion factors for Dimers and Monomers
C*** at Eta ranging from      Eta=0.0 --> 0.5  Increment = 0.005
      CALL SPTZ(BB2,RB2,S2,X2,eta,Zh2,neta)

C*** Calculate the SW contribution to the compressibility
C*** factor from coordination number models.
      call monmon(x,eta,zat1,zat2,neta)
      call dimmon(x2,eta,zatmdd,zatmdm,neta)

C*** Calculate the total compressibility factor of the chain monomer
C*** mixture.

      ZGFD=XC*((RAT+1.0)*(Zh2(1,neta)+ZATMDD(neta))-
&      RAT*(Zh1(1,neta)+ZAT1(neta)))+(1.-XC)*
&      (Zh2(2,neta)+ZATMDM(neta))

      Pstar = ZGFD*TEMP/V

      OUT=Pstar-P

100  return
      end

```

```

      SUBROUTINE zero(P,Vold,outold,Vnew,outnew,Vo)

C*****
C**  Once the solution has been bracketed this subroutine narrows it
C**  down by alternately halve the bracketed region and attempt to
C**  interpolate to the answer
C*****

      REAL Vold,Vnew,Vzero,Vhalf,outold,outnew,outhalf
      REAL Vo, outo, P
      common xc

      ftol=1.d-5

10    Vhalf=(Vnew+Vold)*0.5
      call xcalc(P,Vhalf,xc,outhalf)
      if(outhalf*outnew.lt.0.0) then
         Vo=-outhalf*(Vnew-Vhalf)/(outnew-outhalf)+Vhalf
      else
         Vo=outhalf*(Vhalf-Vold)/(outhalf-outold)+Vold
      endif
      call xcalc(P,Vo,xc,outo)
      if(outo.lt.-ftol) then
         Vnew=Vo
         outnew=outo
         goto 10
      elseif(outo.gt.ftol) then
         Vold=Vo
         outold=outo
         goto 10
      else
         return
      endif
      end

```

```

      SUBROUTINE helmint(Vout,Gex,xc)

C*****
c      This program calculates the Gibb's free energy
c      of a chain-monomer mixture from the mcs1 and SPT equation
c      of state and the generalized flory dimer theory.
c      the sw contribution to the compressibility factor
c      is calculated by a coordination number model.
C*****

      REAL D1,D2,D12
      REAL WD1,WD2,WD12, TEMP
      REAL Vs11,Vs22,Vs12
      REAL RRAT, RNL
      REAL INC, Xc

      COMMON /DIABLOCK/ D1,D2,D12
      COMMON /SWBLOCK/ WD1,WD2,WD12,TEMP
      COMMON /VBLOCK/ VS11,VS22,VS12
      COMMON /input/ RRAT,RNL

      PARAMETER(N=2)
      REAL R(N),X(N),AR(N,N),E(N),X2(N),F(N),
&      BB(N),S(N),RB(N),XN(N),YN(N),ZN(N),WN(N),
&      Zh1(N,2000),Zh2(N,2000),
&      AX(N),AY(N),AZ(N),AW(N),AM1(N),AM2(N),
&      AM(N),AN(N),AO(N),
&      ZAT1(2000),ZAT2(2000),ZATMDD(2000),ZATMDM(2000),
&      BB2(N), S2(N), RB2(N), eta(1000)
      REAL PI,etain,Vout,ZGFD,Gex
      INTEGER Neta

      Neta=50
      PI = 4.0*aTAN(1.0)

      etain=PI*(xc*rn1*d1**3+(1.-xc)*d2**3)/6./Vout
C*** Diameter of component 2
      R(1)=1.0
      R(2) = RRAT

C** The site fraction of each component
      X(1)=RNL*XC/(RNL*XC+(1.-XC))
      X(2)=1.-X(1)

C** The mole fraction of dimers and monomers in a hypothetical
C** dimer monomer mixture fluid formed by breaking the alternative
C** bonds of the chain
      X2(1)=RNL*XC/(RNL*XC+2.0*(1.-XC))
      X2(2)=1.-X2(1)

C*** Calculate C, the total volume fraction of the system
      C=0.0
      DO 10 I=1,N
        C=C+X(I)*R(I)**3
      10 CONTINUE

C*** Calculate the Fractional occupation fraction F(i) of each component
      DO 199 I=1,N
        E(I)=(X(I)*R(I)**3/C)
        F(I)=E(I)
      199 CONTINUE

C*** Calculate the Excluded Volume of the chain to chain segment

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      VE1L=4./3.*PI
      VE2L=9./4.*PI
      CALL VOLC(D1,D1,RNL,VENL)

C*** Calculate the volume excluded by component 1 to component 2

      RAD=(1.0+RRAT)/2.0

C*** Volume Excluded by a monomer of component 1 to monomer of comp 2
      VE1U=VE1L*(RAD)**3

C*** Volume excluded by a dimer of component 1 to a monomer of
C*** component 2. The distance between the centers of the two beads is D1
      DIS = D1

C*** Function EXC calculates the common volume between two spheres of radii
C*** R1, R2 and with their centers DIS apart
      VE2U = 2*VE1L*(RAD)**3 - EXC(RAD,RAD,DIS)

      IF (RNL .GT. 2) THEN
        CALL VOLC(D1,D2,RNL,VENU)
      ELSE
        VENU=VE2U
      ENDIF

C*** chain to chain segment excluded volume ratio
      YNL=(VENL-VE2L)/(VE2L-VE1L)
C*** chain to monomer excluded volume ratio
      YNU=(VENU-VE2U)/(VE2U-VE1U)
C*** Mixture excluded volume ratio
      RAT=YNL*F(1)+YNU*F(2)

C*** Calculate the Hard Monomer mixture insertion factors
C*** Geometric factors for monomers of component 1
      BB(1)=4./3.*PI*R(1)**3
      S(1)=4.*PI*R(1)**2
      RB(1)=R(1)

C*** Geometric factors for monomers of component 2
      BB(2)=4./3.*PI*R(2)**3
      S(2)=4.*PI*R(2)**2
      RB(2)=R(2)
C*** Dimer Geometric factors
      BB2(1)=8./3.*PI*R(1)**3
      S2(1)=8.*PI*R(1)**2
      RB2(1)=1.5*R(1)
      BB2(2)=BB(2)
      S2(2)=S(2)
      RB2(2)=RB(2)

C*** Calculate the insertion factor for monomer 1 and 2
C*** at Eta ranging from Eta = 0.0 --> 0.5 Increment = 0.005
      Neta=INT(etain/0.0005)
      do 50 J=1,neta
        eta(J)=etain*REAL(J)/REAL(neta)
50    continue

      CALL SPTZ(BB,RB,S,X,eta,Zh1,neta)
C*** Calculate the insertion factors for Dimers and Monomers
C*** at Eta ranging from Eta=0.0 --> 0.5 Increment = 0.005
      CALL SPTZ(BB2,RB2,S2,X2,eta,Zh2,neta)

C*** Calculate the SW contribution to the compressibility
C*** factor from coordination number models.

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call monmon(x,eta,zat1,zat2,neta)
call dimmon(x2,eta,zatmdd,zatmdm,neta)

Z_lon1=(XC*((RAT+1.0)*(Zh2(1,1)+ZATMDD(1)))-
&      RAT*(Zh1(1,1)+ZAT1(1)))+(1.-XC)*(Zh2(2,1)+ZATMDM(1))
&      - 1.)/eta(1)

Z_lon2=(XC*((RAT+1.0)*(Zh2(1,2)+ZATMDD(2)))-
&      RAT*(Zh1(1,2)+ZAT1(2)))+(1.-XC)*(Zh2(2,2)+ZATMDM(2))
&      - 1.)/eta(2)

Z_lon0=(Z_lon1*eta(2)-Z_lon2*eta(1))/(eta(2)-eta(1))

helm=0.5*Z_lon0*eta(1)

helm=0.5*(XC*((RAT+1.0)*(Zh2(1,1)+ZATMDD(1)))-
&      RAT*(Zh1(1,1)+ZAT1(1)))+(1.-XC)*(Zh2(2,1)+ZATMDM(1))
&      - 1.)/eta(1)*eta(2)+helm

DO 101 J=2,neta-1
    helm=0.5*(XC*((RAT+1.0)*(Zh2(1,J)+ZATMDD(J)))-
&      RAT*(Zh1(1,J)+ZAT1(J)))+(1.-XC)*(Zh2(2,J)+ZATMDM(J))
&      - 1.)/eta(J)*(eta(J+1)-eta(J-1))+helm
101 continue

    helm=0.5*(XC*((RAT+1.0)*(Zh2(1,neta)+ZATMDD(neta)))-
&      RAT*(Zh1(1,neta)+ZAT1(neta)))+(1.-XC)*(Zh2(2,neta)
&      +ZATMDM(neta))-1.)/eta(neta)*(eta(neta)-eta(neta-1))
&      +helm

    zgfd=XC*((RAT+1.0)*(Zh2(1,neta)+ZATMDD(neta)))-
&      RAT*(Zh1(1,neta)+ZAT1(neta)))+(1.-XC)*(Zh2(2,neta)
&      +ZATMDM(neta))
    Pstar = ZGFd*TEMP*Eta(neta)

    if(xc*(1.-xc).eq.0.0d+0) then
        Gex=helm-log(Vout)+zgfd
    else
        Gex=helm-log(Vout)+zgfd+xc*dlog(xc)+(1.-xc)*dlog((1.-xc))
    endif
200 format(f8.5,1x,f10.7,1x,f10.7,1x,f10.7)
    return
end

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