Abstract

ATTWOOD, BRIAN CHRISTOPHER. Monte Carlo Simulations of Solid-Fluid Phase Equilibria in Binary and Ternary Mixtures. (Under the direction of Carol K. Hall)

The objective of this research is to study the solid-fluid phase equilibria of binary and ternary mixtures using molecular simulation. Solid-fluid phase equilibria plays an important role in many chemical processes, especially crystallization. This research provides insight into the underlying phenomena that govern these processes.

We first calculate complete phase diagrams, that is showing the solid, liquid, and vapor phases, for 29 binary mixtures of Lennard-Jones molecules characterized by different sets of interaction parameters using the Gibbs Duhem integration technique. The impact of including the possibility of a solid phase on the global phase behavior of such mixtures is investigated by comparing the complete phase behavior calculated by simulation to the global phase diagram calculated from a fluid-phase-only equation of state. Complete phase diagrams from each region of the global phase diagram are presented and compared with the fluid-phase-only phase behavior for the same mixture. It is found that for mixtures in which the components have greatly dissimilar critical temperatures, the presence of the solid phase significantly alters the fluid phase equilibria. In those cases, the phase behavior classification based on experimental observations should differ from that predicted by an equation of state approach.

The Gibbs Duhem integration technique is then extended to calculate ternary phase diagrams at constant temperature and pressure. We calculate solid-fluid phase equilibria for ternary mixtures of Lennard-Jones molecules. The simulation parameters were selected to roughly model a mixture of two diastereomeric molecules in a solvent, where the two “diastereomer”
molecules are of similar melting point and diameter and the solvent has a considerably lower melting point and a slightly smaller diameter. The cross-species well-depth and diameter between the two diastereomers are varied to determine their impact on the phase equilibria. We find that increasing the interspecies diameter up to the diameter of the larger diastereomer results in a slight increase of the solubility of the solid phase. We also find that when the interspecies well-depth is lowered to less than that of either of the diastereomers, the solid phase separates into two solid solutions and consequently there is a region of three-phase coexistence in the ternary phase diagram. Finally we calculate ternary phase diagrams at a series of temperatures for one set of molecular parameters. As the temperature increases, we find that the three-phase region decreases in size until it eventually disappears. For an equimolar mixture of diastereomers, there is a range of temperature and solvent concentration at which only one of the diastereomers will precipitate, thus effecting a separation of the diastereomers. As the temperature is decreased the purity of the precipitate increases.
Monte Carlo Simulations of Solid-Fluid Phase Equilibria in Binary and Ternary Mixtures

by

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Biography

The author was born in Troy, New York on April 27, 1975. He is the eldest son of Richard and Dorothea Attwood and has two brothers, Jason and Kristopher. He received a B.S. degree in chemical engineering from the State University of New York at Buffalo in May, 1997. In August, 1997, he was admitted to North Carolina State University to pursue graduate studies in Chemical Engineering. On June 21, 1998, he married Karen Elizabeth Zawoysky of Clifton Park, New York. He received an M.S. degree in chemical engineering from North Carolina State University in December, 2001.
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To my family and friends, I am especially grateful for the love and encouragement that you have given me while in graduate school. Although I do not get to see you as much as I would like, I think of you often. To my parents, thank you for always expressing your confidence in my ability to succeed and pride in what I have accomplished. To Jason and Kris, at least I got out of school before one of you. Finally, to my wife, Karen, I thank you for always being there to help
me through my defeats and celebrate my successes. You can always make me smile.
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CHAPTER 1

INTRODUCTION

Knowledge of the equilibria between solids and fluids is of vital importance in designing industrial processes based on crystallization, including separations, purification, concentration, solidification, and analysis. Crystallization is widely used in the pharmaceutical industry for product recovery because it yields high purity products with a relatively low energy expenditure compared to distillation or other common methods of separation. Crystallization has economic benefits over distillation for components with melting points near ambient conditions because of its lower energy requirements. The lower operating temperatures typically used in crystallization processes are also important when separating components that would decompose at the temperatures necessary for distillation. Crystallization is also used in the desalination and decontamination of wastewater streams.

One area of crystallization that is of particular interest to us is chiral drug separation. For chiral drugs, crystallization is the only feasible means of separation. Chiral drugs are normally produced as a mixture of two racemates. In general, one of the racemates is the active ingredient; the other is either inactive or has some unwanted activity. While it desirable to separate the racemates, this can not be done through standard techniques because the racemates have identical thermophysical properties. This problem can be circumvented through the use of diastereomeric
crystallization techniques, which are also known as classical resolution\(^3\). The two racemates are first reacted with a chiral resolving agent, forming a pair of diastereomers that are chemically identical but have different physical properties. The diastereomers are then separated using fractional crystallization, taking advantage of the now differing solubilities of the two components. As of yet the design of a diastereomeric separation process is more an art than a science and we hope that this research will provide useful insights into the underlying phenomena.

A prerequisite to efficient use of crystallization is knowledge of the solid-liquid phase equilibria of the components to be separated. The solid-liquid phase diagram for a mixture has many uses in the design of a fractional crystallization process. It can be used to identify feasible operation paths given a known feed stream, choose optimal operating conditions, and solve the related mass balances in a separation operation\(^4\). Although the solid-liquid phase diagram for a particular substance or mixture can be obtained by experiment, limited time and resources generally allow for only a sampling of possible operating conditions for any given system. Theory and molecular-level simulation make it possible to gain insight into the phase equilibria of whole classes of mixtures, rather than just one in particular.

One might think that solid-fluid phase equilibria could be obtained from simulation directly by simply putting a solid and fluid in contact with each other in the simulation box and allowing them to come to equilibrium. Unfortunately this is not the case because, for reasonably-sized systems, the breadth of the interface between the two phases makes it impossible to obtain accurate bulk properties\(^5\). Even if the simulation box is large enough to overcome this problem, system equilibration usually takes a long time due to slow mass transfer across the interface\(^6\). This problem was overcome in 1987 when Panagiotopolous\(^7\) introduced the Gibbs ensemble. In
the Gibbs ensemble the two phases are simulated in separate boxes, each representing one of the phases in equilibrium. Mechanical and thermal equilibrium between the boxes is maintained by conducting the simulations at constant pressure and temperature. Chemical equilibrium is maintained by randomly attempting to insert particles from one phase into the other. This technique does not work well for solid-fluid phase equilibria due to the difficulty of inserting a particle from the liquid phase into the high-density solid phase. Without a sufficient number of these swap moves, chemical equilibria is not maintained and the method fails.

An alternative for calculating solid-fluid equilibria in single or multicomponent systems is the Gibbs-Duhem integration technique of Kofke\textsuperscript{8,9}. Instead of using a particle swap move to maintain chemical equilibrium between the phases, an appropriate form of the Clapeyron equation is integrated to calculate the phase coexistence line. The Gibbs-Duhem integration technique procedure allows one to calculate an entire phase coexistence envelope in one calculation, rather than in the many individual steps required when using Gibbs ensemble simulations. By eliminating the particle exchange move, the Gibbs-Duhem technique also makes it possible to calculate single and multicomponent solid-fluid phase equilibria.

1.1 Overview

This thesis describes research into the fundamentals of solid-fluid phase equilibria by using molecular simulation to analyze the phase change behavior of one of the simplest of all possible mixtures, the Lennard-Jones binary mixture. In this section, we provide a short summary of the remaining chapters of this thesis. All of the chapters are self-contained units complete with literature review and bibliography.
Chapter 2 explores how the solid phase affects the global phase diagram of mixtures composed of molecules of equal diameter. This was done by calculating “complete” phase diagrams, that is including solid, liquid, and vapor phases, at 29 sets of Lennard-Jones parameters using the Gibbs Duhem integration technique. For the systems studied, the well-depth ratio, $\frac{\epsilon_{22}}{\epsilon_{11}}$, ranged from 1.0 to 4.0 and the ratio of the interspecies well-depth to the Lorentz-Berthelot mixing rule well-depth, $[\frac{\epsilon_{12}}{\epsilon_{11} \epsilon_{22}}]^{1/2}$, ranged from 0.5 to 1.875. By using the same parameter definitions as Mazur et al., we are able to compare our results to their predictions for the global phase diagram of Lennard-Jones mixtures. Phase diagrams were calculated for each region of the global phase diagram, except for the type IV phase behavior region. We found that for mixtures in which the two pure components have similar critical temperatures, the solid phase did not significantly alter the vapor-liquid phase equilibria except at low pressure. For mixtures in which the two components had greatly dissimilar critical temperatures, the solid phase interfered with the fluid phase behavior over a greater range of pressures. In those cases, we found that it was possible for the presence of the solid phase to change the classification of the fluid-phase phase behavior.

Chapter 3 explores the role of molecular parameters, such as the Lennard-Jones well-depth and diameter, in the crystallization of ternary mixtures. We investigate a model diastereomeric mixture composed of Lennard-Jones particles. The two model diastereomer particles have similar well-depths ($\epsilon_{11} = 2.00$ vs. $\epsilon_{22} = 2.05$) and diameters ($\sigma_{11} = 1.15$ vs. $\sigma_{22} = 1.175$), while the solvent has a much lower melting point and slightly smaller diameter ($\sigma_{SS} = 1.00$). The cross-species parameters ($\epsilon_{12}$ and $\sigma_{12}$) between the two diastereomers were varied to determine their impact on phase equilibrium. We found that increasing the interspecies
diameter up to the diameter of the large diastereomer resulted in a slight increase of the solubility of the solid phase. We found that decreasing the interspecies well-depth to less than that of either of the diastereomers resulted in an immiscibility in the solid phase and consequently a region of three-phase equilibria (two solid phases and one liquid phase) in the ternary phase diagram. The effect of temperature was then explored by calculating phase diagrams over a range of temperatures for a given set of cross-species well-depths and molecular diameters. It was found that as the temperature increases, the size of the three-phase region decreases until it disappears.

For completeness, an earlier study on the global phase diagram of monomer/dimer mixtures has been included in Appendix A. This work was defended as part of my Master of Science research in September, 2001. In that research, we first extended the Generalized Flory Dimer theory for hard sphere monomer/n-mer mixtures to square-well monomer/n-mer 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 between theory and simulation is very good; this is consistent with the performance of the GFD theory for 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 $\zeta$ is a measure of the difference between the monomer and dimer well depths and $\Lambda$ 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 $\zeta$ and $\Lambda$. 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 is the absence of type IV and type VI behaviors. We also found that the
phase diagram is shifted towards the negative $\zeta$ and $\Lambda$ directions when compared to the van der
Waals global phase diagram for equal diameter spherical molecules.

Chapter 2 and 3 and Appendix A have been adapted from the following publications:

**Chapter 2** B. C. Attwood and C. K. Hall., “Effect of the Solid Phase on the Global Phase

**Chapter 3** B. C. Attwood and C. K. Hall., “Monte Carlo Simulations of Ternary Solid-liquid
Phase Equilibria,” *AIChE Journal*, (in preparation)

**Appendix A** B. C. Attwood and C. K. Hall., “Global Phase Diagram for Monomer/Dimer
1.2 References


CHAPTER 2

EFFECT OF THE SOLID PHASE ON THE GLOBAL

PHASE BEHAVIOR OF BINARY LENNARD-JONES

MIXTURES

2.1 Introduction

Knowledge of the equilibria between solids and fluids is of vital importance in industrial processes based on crystallization, including separations, purification, concentration, solidification, and analysis. Crystallization is widely used in the pharmaceutical industry for product recovery because it yields high purity products with a relatively low energy expenditure compared to distillation or other common methods of separation. Crystallization is also used in the desalination and decontamination of wastewater streams\(^1\), the resolution of racemic mixtures\(^2\), and the separation and purification of numerous organic and inorganic mixtures\(^3\). A prerequisite to efficient use of crystallization is knowledge of the solid-liquid phase equilibria of the components to be separated.

The techniques for calculating phase equilibria of a system based on knowledge of its equation of state are well established. Usually such calculations are carried out for specific values
of the molecular interaction parameters in order to predict the phase equilibrium for a particular fluid or mixture. A different approach was taken in the late sixties by van Konynenburg and Scott\textsuperscript{4–6} who chose to examine the phase behavior predicted for a binary mixture obeying the van der Waals equation of state over the entire range of interaction parameters. Their approach involved calculating the locus of critical points as a function of composition, pressure, and temperature. The type of phase behavior could then be classified into different types based on the projection of the locus of critical points onto the $P$-$T$ plane, as seen in Fig. 2.1.

For their analysis of mixtures of equal-sized components, Scott and van Konynenburg\textsuperscript{4,6} considered two dimensionless interaction parameters, $\zeta$ and $\Lambda$, 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 $\Lambda = (a_{11} + a_{22} - 2a_{12})/(a_{22} + a_{11})$. For equal sized molecules, $\zeta$ is related to the differences in critical temperatures or pressures of the pure components and $\Lambda$ is related 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 fluid 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 even though 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 found 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 the parameter $b$ independent of concentration (implying that the molecules are of equal size) and the parameter $a$ a quadratic function of composition. 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 revisited the global phase diagram 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 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. 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 is qualitatively similar to that of the van der Waals equation of state, except that Type VI phase behavior is also predicted. Dieters and Pegg calculated the global phase diagram for the Redlich-Kwong equation of state 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 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 size, some unusual new phase behavior was found involving four-phase states and high density instabilities.

In recent years, a number of investigators\textsuperscript{15–19} have calculated closed-loops of immiscibility for equations of state based on isotropic potentials, a result that continues to be debated in the literature. Yelash and Kraska\textsuperscript{15} found that even a simple equation of state composed of the Carnahan-Starling repulsion and the van der Waals attraction exhibited several types of closed-loop phase behavior. One disadvantage of the global phase diagrams found in the literature is that they are based on equations of state that are only applicable for fluid phases.

In this chapter, we consider how including the possibility of a solid phase influences the global phase behavior of a binary mixture of equal-diameter Lennard-Jones molecules. We calculate “complete” phase diagrams, that is including solid, vapor, and liquid phases, for 29 sets of interaction parameters using the Gibbs Duhem integration technique developed by Kofke\textsuperscript{20,21}. Since we have used the same interaction parameters as Mazur et al., we are able to compare our results to their predictions for the global phase diagram of Lennard-Jones mixtures. It is important to point out that our goal is not to remap the global phase diagram, since that is not our focus and is extremely expensive computationally, but instead to sample the behavior in different regions of the global phase diagram. By calculating temperature-composition phase diagrams at a number of pressures for each set of interaction parameters we are able to see how the solid phase influences the type of phase behavior exhibited by the fluid phases. That is, we seek to determine those sets of parameters for which the classification of the fluid phase behavior with the solid phase included would differ from the classification that would be determined based solely on the
fluid phase equation of state.

For certain sets of parameters we consider our results in light of the classification scheme for complete phase diagrams developed by Valyashko. Valyashko proposed a scheme of twelve types based on analysis of experimental data and the method of continuous topological transformation. Valyashko proposed two main groups of complete phase behavior. In group 1 systems, a continuous three-phase (SLV) curve in P-T-x space connects the triple points of the two components. In group 2 systems, the three-phase (SLV) curve is interrupted by the locus of L-V critical points, resulting in a discontinuity in both of the curves. Further subclasses are determined by considering the presence and location of the liquid-liquid immiscibility region and the locus of the three-phase (SLV) coexistence curve.

Highlights of our results are as follows. We find that for mixtures in which the components have similar critical temperatures, inclusion of the solid phase does not significantly alter the types of fluid phase equilibria observed. This is because for these mixtures the melting point of both components is below the boiling point of either component. As such, the solid phase can only impact the observed vapor-phase behavior at low pressures close to the triple point of one or both of the components. Since the phase behavior classification scheme is based mainly on the locus of the vapor-liquid critical points this low pressure interaction does not alter the classification of these mixtures. However, as the difference in critical temperatures increases, the solid phase of the component with the higher critical temperature can coexist with the vapor phase of the component with the lower critical temperature. This results in some interesting new behavior, such as the formation of a vapor-solid eutectic point. This interference between the solid phase and the vapor-liquid equilibria also serves to obscure features of the
fluid-phase equilibria that are necessary in the classification of the type of phase behavior, such as the presence of liquid-liquid immiscibility at low temperatures. It is seen that in those cases the solid phase effectively alters the classification of the fluid phase behavior that would be seen in experiment from what would have been predicted based on a fluid-phase-only equation of state.

The remainder of this chapter is organized as follows. In Section 2 we briefly review the Gibbs-Duhem technique for binary mixtures. In Section 3 we present our results and discuss their significance. Section 4 concludes the chapter with a brief summary.

2.2 Method

2.2.1 Gibbs Duhem integration technique

The Gibbs Duhem integration technique is based upon integrating an appropriate form of the Clapeyron equation which describes how the field variables vary as a function of each other at equilibrium. One can calculate the properties of two coexisting phases as a function of almost any variable of interest. For a mixture of $c$ components, the Gibbs-Duhem equation can be expressed as

$$
\frac{d \ln \left[ \sum_{i=1}^{c} \tilde{f}_i \right]}{d \beta} = h_r \, d \beta + Z d \ln p - \sum_{i=1}^{c} \frac{x_i}{\xi_i} \, d \xi_i \tag{2.1}
$$

where $p$ is the pressure, $Z$ is the compressibility factor, $x_i$ and $f_i$ are the mole fraction and fugacity of species $i$, $h_r$ is the residual molar enthalpy, $\beta = 1/kT$ with $T$ the temperature and $k$: 
Boltzmann’s constant, and $\xi_i$ is the fugacity fraction, defined as

$$\xi_i = \frac{\hat{f}_i}{\sum_{n=1}^{c} f_n}.$$  \hspace{1cm} (2.2)

For binary mixtures equation 2.1 reduces to the following

$$d \ln(f_1 + f_2) = h_r d\beta + Z d \ln p - \frac{x_2 - \xi_2}{\xi_2(1 - \xi_2)} d\xi_2.$$ \hspace{1cm} (2.3)

since $x_1 = 1 - x_2$ and $\xi_1 = 1 - \xi_2$.

The Gibbs-Duhem equation can be applied to two phases, $\alpha$ and $\gamma$, in equilibrium, by writing Eq. 2.3 for each of the phases. Since the fugacity, and hence the fugacity fraction, of each of the components is identical in phases $\alpha$ and $\gamma$, we can set the right-hand sides of those two equations equal to get

$$h^\alpha d\beta + Z^\alpha d \ln p - \frac{x_2^\alpha - \xi_2}{\xi_2(1 - \xi_2)} d\xi_2 = h^\gamma d\beta + Z^\gamma d \ln p - \frac{x_2^\gamma - \xi_2}{\xi_2(1 - \xi_2)} d\xi_2.$$ \hspace{1cm} (2.4)

At this point one has a choice as to which variable to hold constant and which variable to integrate with respect to. In the calculation of temperature-composition diagrams we hold pressure constant and integrate Eq. 2.4 with respect to the fugacity fraction of component 2. Solving for $d\beta/d\xi_2$ we get

$$\frac{d\beta}{d\xi_2} = \frac{x_2^\alpha - x_2^\gamma}{(h^\alpha - h^\gamma)\xi_2(1 - \xi_2)}.$$ \hspace{1cm} (2.5)

By starting with values of $\beta$ and $\xi_2$ at a known equilibrium point, we can calculate $\beta$ as a function of $\xi_2$ for the rest of the coexistence curve by integrating Eq. 2.5. To start the integration,
an initial value for the integrand is needed. In general, we start the integration at one of the pure components, i.e. $\xi_2 = 0$ or 1. Because the right-hand side of Eq. 2.5 is undefined at either of these conditions, we obtain its value by calculating its limit as $\xi_2 \to 0$ or 1. Assuming the mixtures to be ideal as $\xi_2 \to 0$, the following approximations are made

$$\hat{f}_2 = x_2 H_2$$ \hspace{1cm} (2.6)

$$\hat{f}_1 = f_1^o$$ \hspace{1cm} (2.7)

where $f_1^o$ is the fugacity of pure component 1; these approximations are based on Henry’s law and the Lewis Randall rule, respectively. Thus we can write

$$\frac{d\beta}{d\xi_2}|_{\xi_2=0} = \frac{\left( \frac{f_1^o}{H_2} \right)^\alpha - \left( \frac{f_1^o}{H_2} \right)^\gamma}{h_1^\alpha - h_1^\gamma}$$ \hspace{1cm} (2.8)

The quantity $f_1^o/H_2$ can be evaluated during an NPT simulation (at the boiling temperature of pure component 1 for the desired pressure) on pure component 1 by performing trial identity switches of randomly chosen atoms. The value of $f_1^o/H_2$ can then be calculated from

$$\frac{f_1^o}{H_2} = \langle \exp(\Delta U_{switch}/kT) \rangle_{NPT}$$ \hspace{1cm} (2.9)

where $\langle \rangle$ denotes the ensemble average and $U_{switch}$ is the potential energy change upon switching particle identities. The values of $(f_1^o/H_2)^\alpha$ and $(f_1^o/H_2)^\gamma$ can be calculated by conducting a simulation at the density of the $\alpha$ and $\gamma$ phases respectively. If we are starting the integration for $0 < \xi_2 < 1$, the above steps are unnecessary and we can simply use Eq. 2.5 to calculate
the initial value of the integrand. In either case, the values of the compositions and enthalpies in Eq. 2.5 will either be known from a prior Gibbs-Duhem integration or can be calculated by an NPT\(\xi_2\) simulation at the desired temperature, pressure, and fugacity fraction.

Once the initial condition is calculated, the integration is carried out using a standard predictor-corrector algorithm. A step, \(\Delta \xi_2\), in the fugacity fraction value is taken and the predictor formula is used to find the new value for the inverse temperature, i.e.

\[
\beta_1 = \beta_0 + \int_{\xi_2=0}^{\xi_2=\Delta \xi_2} \frac{d\beta}{d\xi_2} d\xi_2
\]

\[\text{(2.10)}\]

A separate semigrand ensemble (constant NPT\(\xi_2\)) Monte Carlo simulation is then performed for each of the coexisting phases to evaluate the enthalpy and composition at the new fugacity fraction and temperature. After the simulations have equilibrated, the integrand is recalculated, the corrector formula is applied to find the “corrected” inverse temperature, and more simulations are performed at the new value for the temperature. This corrector step is repeated until the inverse temperature converges to its final value. A production run of simulations is then carried out to calculate the final values for the enthalpies and compositions of the coexisting phases. These values are then used in the predictor formula to calculate the inverse temperature at the next value of the fugacity fraction. Continuing this process we can calculate the entire phase coexistence envelope, starting at phase equilibrium for either of the pure components.

For certain sets of parameters, there is a range of pressures for which two two-phase coexistence envelopes, e.g. vapor-liquid and liquid-solid, overlap over a range of temperatures resulting in three-phase equilibria, e.g. vapor-liquid-solid coexistence, at the point of intersection. A new type of two-phase equilibria, e.g. solid-vapor, will occur in the range of temperatures
for which the envelopes overlap. The solid-vapor coexistence envelope is calculated by conducting a Gibbs Duhem integration starting at the values of temperature and $\xi_2$ at the point of overlap of the vapor-liquid and liquid-solid coexistence envelopes. The solid and vapor phases at that temperature are used as the initial coexisting phases to start the integration. This procedure is explained in greater detail in a paper by Lamm and Hall\textsuperscript{23}.

A different approach is needed to calculate low-temperature liquid-liquid immiscibility with an UCST, as would be found in type II phase behavior at higher pressures, because those curves do not originate at either of the pure components. One way to calculate an initial point for starting the integration would be to use Gibb’s ensemble simulation to calculate the properties of the coexisting liquids at one temperature. We have developed an alternative approach that makes use of the Gibb Duhem integration technique, as illustrated in Fig. 2.2 for the system $\zeta = 0.2$ and $\Lambda = 0.175$. Our approach starts by calculating a temperature-composition diagram at a pressure ($P^* = 0.04$) lower than the desired pressure, where there is three-phase coexistence (Fig. 2.2(a)). We then choose a temperature ($T^* = 0.99$) below the three-phase coexistence temperature at which two liquids are in equilibrium (solid circles on Fig. 2.2(a)). After that a Gibbs Duhem pressure integration can be conducted at constant temperature ($T^* = 0.99$) up to the pressure ($P^* = 0.05$) of interest (open circles Fig. 2.2(b)) using the following form of the Clapeyron equation

$$\frac{dP^*}{d\xi_2} = \frac{x_2^\beta - x_2^\gamma}{(Z^\alpha - Z^\gamma)\xi_2(1 - \xi_2)}. \quad (2.11)$$

The resulting two coexisting liquid state points can then be used as initial conditions (open circles Fig. 2.2(c)) for calculating the remainder of the liquid-liquid immiscibility curve.
2.2.2 Simulations

As mentioned previously, semigrand ensemble Monte Carlo (NPT\(\mathcal{C}_2\)) simulations are used to evaluate the properties of the coexisting phases during the integration of the Gibbs-Duhem equation. In this section, we briefly describe how these simulations are conducted.

There are three types of moves in the semigrand ensemble: particle displacement, volume change, and identity exchange. The particle displacement and volume change moves are carried out in the same manner as in isothermal-isobaric (NPT) simulations. The identity exchange move involves choosing a random molecule in the system and switching its identity. The change in the configurational energy of the system caused by the identity change is then evaluated. The overall acceptance probability, \(P\), for these moves is

\[
P = \min[1, \exp(-\beta(U^{\text{trial}} - U^{\text{old}}) - \beta P(V^{\text{trial}} - V^{\text{old}}) + N \ln \frac{V^{\text{trial}}}{V^{\text{old}}} + \ln \frac{\xi^{\text{trial}}}{\xi^{\text{old}}})] \quad (2.12)
\]

where \(U^{\text{trial}}\) and \(U^{\text{old}}\) are the configurational energies, \(V^{\text{trial}}\) and \(V^{\text{old}}\) are the volumes of the trial and existing states respectively, \(N\) is the total number of molecules, and \(\xi^{\text{trial}}\) and \(\xi^{\text{old}}\) refer to the fugacity fractions of the trial and existing identities of the molecule during the identity exchange moves. At each step, the type of move is randomly chosen with a weighting such that for every volume change move there are 20 particle displacements and 20 identity exchange moves. After an appropriate number of equilibrium moves, running averages of the composition and enthalpy (as calculated by \(h = U/N + PV/N\)) are calculated for use in evaluating the integrand in the Gibbs Duhem technique.

Other details of the simulation are as follows. Prior theoretical calculations\(^{24}\) and molecular
simulations\textsuperscript{25} have shown that by choosing diameter ratios \(0.85 \leq \sigma_{11}/\sigma_{22} \leq 1.0\) we can assume that the most stable configuration for the solid phase will be that of a substitutionally disordered fcc lattice. By using an fcc lattice as an initial configuration for the solid phase, an fcc lattice will be maintained in the solid phase throughout the simulation without any additional constraints on the simulation. The simulations are performed on a system of 500 molecules in a cubic box with periodic boundary conditions. The molecules interact via the Lennard-Jones potential

\[
 u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] \tag{2.13}
\]

where \(u_{ij}\) is the potential energy of the interaction between atoms \(i\) and \(j\), \(r\) is the distance between atoms \(i\) and \(j\), \(\epsilon_{ij}\) is the Lennard-Jones well-depth, and \(\sigma_{ij}\) is the Lennard-Jones diameter. The potential interactions are truncated at half the box length and standard long-range corrections\textsuperscript{26} are applied to the potential energy and pressure calculations.

### 2.3 Results and Discussion

We have calculated complete phase diagrams at conditions indicated by the circles on the Mazur et al. global phase diagram shown in Fig. 2.3. The small dots indicate sets of parameters at which complete phase diagrams have been calculated for at least one pressure and the larger dots indicate sets of parameters at which complete phase diagrams have been calculated at more than one pressure. We have not calculated the phase behavior in region IV because that region is very small. In addition, it is difficult to be sure that a chosen set of parameters will lie within the Mazur et al. region IV because their global phase diagram is based on an approximate
equation of state. In each of the phase diagrams presented here, the upper row of diagrams show
the phase behavior calculated using the Gibbs Duhem technique for the fluid and solid phases,
the middle row is a schematic of the upper row of diagrams presented when necessary, and the
bottom row shows the phase behavior calculated when considering only the fluid phases. The
fluid-phase-only diagrams were calculated by simply omitting the calculation of the solid-fluid
phase coexistence. In this way we are able to calculate metastable fluid phase equilibria below
the freezing point of the mixtures. In the fluid-phase-only diagrams, the dotted lines indicate
portions of the diagram whose presence is inferred rather than calculated. In these cases the
fluid phase was sufficiently unstable compared to the solid phase that it spontaneously solidified
during the simulation. Table 2.1 lists the temperature and compositions of the coexisting phases
for each of the three-phase coexistence lines found in Figs. 2.4-2.13. In both the figures and the
table, \( P^* = \frac{P \sigma_{11}^3}{\epsilon_{11}} \) and \( T^* = \frac{kT}{\epsilon_{11}} \).

Fig. 2.4 shows a series of temperature-composition phase diagrams at decreasing pressures
for \( \zeta = 0.2 \) and \( \Lambda = -0.1 \), which is in the type I region on the Mazur et al. global phase
diagram. In terms of the fluid-phase-only phase behavior classification, Type I phase behavior
is characterized by a single vapor-liquid phase coexistence envelope terminated at either end by
the pure component boiling points at the pressure of interest. We find that at high pressures (e.g.
\( P^* = 0.05 \), Fig. 2.4(a)), the solid does not affect the fluid phase equilibria because the vapor-
liquid phase coexistence envelope occurs at a significantly higher temperature than the solid-
liquid phase coexistence envelope. At intermediate pressures (e.g. \( P^* = 0.005 \) Fig. 2.4(b) ),
the solid-liquid phase coexistence envelope intersects with the descending vapor-liquid phase coex-
existence envelope and a pair of three-phase lines (VL$_2$S and VL$_3$S) are formed, which separate re-
gions of vapor-liquid, liquid-solid, and vapor-solid phase coexistence. Between these two three-phase lines lies a range of temperatures at which there is coexistence between a solid phase and a vapor phase. As the pressure decreases further, the range of temperatures at which vapor-solid equilibria occurs broadens until the triple point pressure of pure component 2 ($P^* = 0.00165$) is reached. Below this there is no longer solid-liquid and vapor-liquid equilibria for pure component 2, but only solid-vapor equilibria. At low pressures (e.g. $P^* = 0.001425$, Fig. 2.4(c)), which is below the triple point pressure of component 2, the phase coexistence is predominantly solid-vapor. Without including the possibility of a solid phase, we would be unable to see any of the three phase (SLV) coexistence curves in region I. The complete phase behavior can be classified as type 1a according to Valyashko’s scheme based on examining the temperature-composition phase diagrams shown in Fig. 2.4. An experimental system which has similar complete phase behavior is silver nitrate + water.

Fig. 2.5 shows a temperature-composition phase diagram at $P^* = 0.002$ for $\zeta = 0.0$ and $\Lambda = -0.5$, which is in the type I-A region on the Mazur et al. global phase diagram. Because the mixture is symmetric ($a_{11} = a_{22}$) the diagram is symmetric about $x_2 = 0.5$. In terms of fluid-phase-only phase behavior classification, Type I-A differs from Type I in that Type I-A exhibits an azeotrope in the vapor-liquid phase coexistence envelope. When including the solid phase, we find that there is an azeotrope in the solid-liquid phase coexistence envelope as well. Because of the presence of the azeotrope there are two regions of vapor-solid phase coexistence, in contrast with the single region of vapor-solid phase coexistence seen in Figs. 2.4(a) and 2.4(b).

Fig. 2.6 shows a temperature-composition phase diagram at $P^* = 0.002$ for $\zeta = 0.2$ and $\Lambda = 0.1$, which is in the type II region on the Mazur et al. global phase diagram. In terms of
fluid-phase-only phase behavior classification, the fluid phase equilibria is similar to that of type I except that type II has low temperature liquid-liquid immiscibility. The pressure $P^* = 0.002$ is just above the triple point of component 2. Two three-phase coexistence lines (VL$_2S_2$ and VL$_1S_2$) separate regions of vapor-liquid and liquid-solid coexistence from a region of vapor-solid coexistence, while one three-phase coexistence line (L$_1S_1S_2$) separates regions of liquid-solid coexistence from the region of solid-solid coexistence. It can be seen that for this set of parameters and at this particular pressure and temperature, liquid-liquid immiscibility is metastable compared to the liquid-solid and solid-solid phase equilibria since liquid-liquid immiscibility is present in the fluid-phase-only diagram, but not in the complete phase diagram.

Fig. 2.7 shows a series of temperature-composition phase diagrams at decreasing pressures for $\zeta = 0.05$ and $\Lambda = 0.25$, which is in the type II-A region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, Type II-A phase behavior is the same as type II with the addition of an azeotrope in the vapor-liquid coexistence curves. At the highest pressure ($P^* = 0.08$, Fig. 2.7(a)) we can see that below $T^* = 0.755$ the liquid-liquid immiscibility becomes less stable than liquid-solid phase coexistence. The interference between the solid phase and liquid phases results in the formation of two three-phase coexistence lines (L$_1L_2S_2$) and (S$_1L_1S_2$) separating liquid-liquid, liquid-solid, and solid-solid phase coexistence. We are unable to calculate the liquid-liquid immiscibility curve all the way up to the UCST because as the critical point is approached, density fluctuations cause the simulation to become unstable. The dashed line indicates where we expect the curve would be, approximately. The liquid-liquid coexistence curves in this case were calculated by the method described in Section 2.2.1. As the pressure is lowered ($P^* = 0.01$, Fig. 2.7(b)) the vapor-liquid coexistence
envelope interferes with the liquid-liquid coexistence curves and a third three-phase line ($L_1VL_2$) is produced. As the pressure decreases further the $L_1VL_2$ line decreases in temperature and the $L_1L_2S_2$ increases in temperature until they eventually coincide to form a four phase ($L_1VL_2S_2$) line at one value of the pressure (the quadruple point). We have not located the quadruple point directly because this involves guessing the exact temperature at which it occurs. (An alternative approach would be to conduct two Gibbs Duhem integrations along the two three-phase lines ($L_1VL_2$ and $L_1L_2S_2$) to find the pressure at which they merge. This is beyond the scope of this paper.) At the lowest pressure shown ($P^* = 0.00116, \text{Fig. 2.7(c)}$), which is below the triple point of component 2, there are two three-phase lines ($S_1L_1V$) and ($S_2VS_2$). The liquid-liquid immiscibility has been completely obscured by the presence of the solid phase. In addition, a solid-vapor eutectic point, a vapor in equilibrium with two solid phases, has been formed. The interesting phenomena here are the changes in the three-phase lines as the pressure decreases and the formation of a vapor-solid eutectic point, neither of which would be seen without including the possibility of the solid phase. The complete phase behavior can most closely be classified as type 1b' according to Valyashko’s scheme based on examining the temperature-composition phase diagrams shown in Fig. 2.7. Based on the series of phase diagrams shown in Fig. 2.7, the experimental system ethane + $n$-tetrasocane exhibits the most similar phase behavior although there is no azeotrope in the vapor-liquid phase equilibria.$^{28}$

Fig 2.8 shows a series of temperature-composition phase diagrams at decreasing pressures for $\zeta = 0.4$ and $\Lambda = 0.3$, which is in the type III region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, Type III phase behavior differs from types I and II in that there is not a continuous locus of critical points from one pure
component critical point to the other. At the highest pressure ($P^* = 0.15$, Fig. 2.8(a)), which is above the critical pressure of pure component one, we see that the interference of the solid phase with the vapor-liquid equilibria results in two three-phase coexistence lines ($VL_2S_2$ and $VS_1S_2$) separating regions of vapor-liquid, vapor-solid, and solid-solid phase coexistence. At the two lower pressures ($P^* = 0.05$, Fig. 2.8(b) and $P^* = 0.005$, Fig. 2.7(c)), which are below the critical pressure of component 2, a third three-phase coexistence line ($VL_1S_2$) is formed and liquid-solid phase coexistence appears. One feature of type III phase behavior that we do not see in this series of graphs is liquid-liquid immiscibility. Because the melting point of component two is above the boiling point of component one, we find liquid-solid and solid-solid phase coexistence occurring in the region where we would have expected liquid-liquid immiscibility. We did find a small set of parameter sets in the type III region where liquid-liquid immiscibility was not completely hidden by the liquid-solid and solid-solid phase equilibria. Figure 2.9 is one such set of parameters, with $\zeta = 0.3$ and $\Lambda = 0.2$. It can be seen that for a narrow range of temperature there are two liquids in equilibrium with each other. We could not find a set of parameters in the type III region in which the UCST of the liquid-liquid immiscibility was stable with respect to the solid-liquid and solid-solid phase equilibria. The complete phase behavior can most closely be classified as type 2a according to Valyashko’s scheme based on examining the temperature-composition phase diagrams shown in Fig. 2.8. An experimental system which has similar complete phase behavior is sodium sulfate and water\textsuperscript{27}.

Fig. 2.10 shows a temperature-composition phase diagram at $P^* = 0.10$ for $\zeta = 0.2$ and $\Lambda = 0.3$, which is in the type III-A region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, Type III-A phase behavior is distinguished
from type III by the presence of an azeotrope in the vapor-liquid phase diagram at high pressures. It can be seen in Fig. 2.10, that the interference of the solid phase with the vapor-liquid equilibrium results in the formation of two additional three-phase coexistence lines (L₁L₂S₂ and S₁L₁S₂) separating regions of liquid-liquid, liquid-solid, and solid-solid phase equilibria. Although we investigated the phase behavior at a number of different pressures, we never located a UCST for the liquid-liquid immiscibility, which indicates that this set of parameters may actually be in the Type III-H region.

Fig. 2.11 shows a temperature-composition phase diagram at $P^* = 0.05$ for $\zeta = 0.2$ and $\Lambda = 0.5$, which is in the type III-H region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, Type III-H phase behavior is distinguished from type III by the presence of a heteroazeotrope in the vapor-liquid phase diagram, that is a vapor-liquid eutectic. It differs from Type III-A in the following way. While Type III-A also has a heteroazeotrope at low pressure, as the pressure is increased the vapor-liquid equilibria separates from the liquid-liquid equilibria and the heteroazeotrope is replaced by an azeotrope. In Type III-H phase equilibria, the heteroazeotrope is not replaced by an azeotrope at any pressure. In this figure we can see that the increased value of $\Lambda$ compared to that in Fig. 2.10, (i.e. decreased attractions between the two components) has caused the two components to become more immiscible.

Fig 2.12 shows a series of temperature-composition phase diagrams at decreasing pressures for $\zeta = 0.6$ and $\Lambda = -0.1$, which is in the type V region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, the unique feature of type V phase behavior is a region of liquid-liquid immiscibility with an LCST below the vapor-
liquid coexistence envelope, as depicted by the dashed lines in the bottom $T - x$ diagram at $P^* = 0.15$ (Fig. 2.12(a)). However, we found that interference by the solid obscured the region in which this liquid-liquid immiscibility is supposed to occur. The consequence of this is that although the equation of state might predict that this system should exhibit type V phase behavior, experimentally it would appear to behave more like a type I mixture. As indicated in the fluid-phase-only diagrams by the dashed line, we were unable to calculate the complete fluid phase coexistence envelopes at the two lowest pressures. This occurred because the coexisting vapor and liquid phases became so unstable as the vapor-solid coexistence region was entered during our simulations, that the liquid phase spontaneously crystallized resulting in coexisting vapor and solid phases. This prevented us from confirming the existence of the liquid-liquid immiscibility expected for type V phase behavior. Similar attempts to find the LCST at $\zeta = 0.6$ and $\Lambda = -0.3$ or $\Lambda = -0.5$ were also unsuccessful. The complete phase behavior can be classified as type 2a according to Valyashko’s scheme based on examining the temperature-composition phase diagrams shown in Fig. 2.12. An experimental example of a system which exhibits similar phase behavior is carbon dioxide + $n$-tetrasocane.  

Fig. 2.13 shows a temperature-composition phase diagram at $P^* = 0.005$ for $\zeta = 0.4$ and $\Lambda = -0.5$, which is in the type V-A region on the Mazur et al. global phase diagram. In terms of the fluid-phase-only phase behavior classification, Type V-A phase behavior is similar to Type V phase behavior with the additional feature of an azeotrope in the vapor-liquid phase coexistence envelope. In Fig. 2.13, it can be seen that there is an azeotrope in both the vapor-liquid and solid-liquid phase coexistence envelopes. Furthermore, we see that the interference of the solid phase with the vapor-liquid equilibria results in two three-phase coexistence lines ($VL_2S$ and $VL_3S$).
separating regions of vapor-liquid, vapor-solid, and liquid-solid phase coexistence.

### 2.4 Conclusions

Our general conclusions are that for mixtures in which the components have similar critical temperatures, i.e. $\zeta < 0.3$, inclusion of the solid phase does not alter how the phase behavior of the mixture would be classified based solely on the fluid phase behavior. This is because the classification scheme is based primarily on the locus of gas phase critical points. For values of $\zeta$ close to zero, the influence of the solid phase is only felt at temperatures and pressures well below the critical point of either species, which means that it does not alter the topology of the locus of critical points. This is seen to be especially true in regions I and II. For mixtures in which the components have greatly dissimilar critical temperatures, i.e. $\zeta > 0.4$, the fluid phase behavior type may be different from what is expected because the solid phase for the component with the higher critical point can exist in equilibrium with supercritical phases of the other component. When this happens, the coexistence between a vapor rich in one species and a solid rich in the other species can alter the topology of the locus of vapor-liquid critical points. This was seen in the figures presented for region V.

### 2.5 Summary

The Gibbs Duhem integration technique was used to calculate composition-temperature phase diagrams at 29 different points on the global phase diagram for binary mixtures of Lennard-Jones molecules. We presented phase diagrams calculated in each region of the global phase diagram, with the exception of region IV. We compared our results to the global phase
diagram calculated by Mazur et al. using a polynomial equation of state for binary mixtures of Lennard-Jones molecules. We found that for mixtures of components with similar critical temperatures, i.e. $\zeta < 0.3$, the phase behavior was essentially the same as in the fluid-phase-only case. For mixtures in which the components had greatly dissimilar critical temperatures, $\zeta > 0.4$, interaction between the vapor and solid phases could significantly alter the fluid-only phase behavior. This was manifested in interesting types of solid-fluid phase behavior, such as a vapor-solid eutectic point, that is - a vapor in equilibrium with two immiscible solids. We found that a mixture that would be expected to have type V phase behavior according to a fluid-phase equation of state might experimentally exhibit type I phase behavior. This is because the phase behavior features unique to type V phase behavior occur below the freezing point of the mixtures. We also found that while the Gibbs Duhem integration technique does make it possible to calculate metastable phase behavior below the freezing point of the mixtures, the calculations are limited by the stability of the coexisting metastable phases.
2.6 References


Table 2.1: Three phase coexistence data from the figures discussed in Section 2.3. For each three phase line the temperature, the identity of each of the phases, and their respective mole fractions of component 2 are given.

<table>
<thead>
<tr>
<th>$\epsilon_{22}$</th>
<th>$\epsilon_{12}$</th>
<th>$P^*$</th>
<th>$T^*$</th>
<th>Phases</th>
<th>$x_2$</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.500</td>
<td>1.375</td>
<td>0.005</td>
<td>0.873</td>
<td>V-L-S-S</td>
<td>0.014, 0.364, 0.462</td>
<td>Fig. 2.4(b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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CHAPTER 3

SOLID-LIQUID PHASE BEHAVIOR OF TERNARY MIXTURES

3.1 Introduction

Knowledge of the equilibria between solids and fluids is of vital importance in designing industrial processes based on crystallization, including separations, purification, concentration, solidification, and analysis. Crystallization is widely used in the pharmaceutical industry for product recovery because it yields high purity products with a relatively low energy expenditure compared to distillation or other common methods of separation. For chiral drugs, crystallization is the only feasible means of separation. Chiral drugs are normally produced as a mixture of two racemates. In general, one of the racemates is the active ingredient; the other is either inactive or has some unwanted activity. While it desirable to separate the racemates, this cannot be done through standard techniques because the racemates have identical thermophysical properties. This problem can be circumvented through the use of diastereomeric crystallization techniques, which are also known as classical resolution\(^1\). The two racemates are first reacted with a chiral resolving agent, forming a pair of diastereomers that are chemically identical but have differ-
ent physical properties. The diastereomers are then separated using fractional crystallization, taking advantage of the now-differing solubilities of the two components. Crystallization has economic benefits over distillation for components with melting points near ambient conditions because of lower energy requirements. The lower operating temperatures typically used in crystallization processes are also important when separating components that would decompose at the temperatures necessary for distillation \(^2\). Crystallization is also used in the desalination and decontamination of wastewater streams \(^3\).

A prerequisite to efficient use of crystallization is knowledge of the solid-liquid phase equilibria of the components to be separated. The solid-liquid phase diagram for a mixture has many uses in the design of a fractional crystallization process. It can be used to identify feasible operation paths given a known feed stream, choose optimal operating conditions, and solve the related mass balances in a separation operation \(^4\). Although the solid-liquid phase diagram for a particular substance or mixture can be obtained by experiment, limitations on time and resources generally allow for only a small sampling of possible operating conditions for any given system. Theory and molecular-level simulation can overcome some of these limitations by making it possible to gain insight into the phase equilibria of whole classes of mixtures, rather than just one in particular. In this work, we use simulation to gain a fundamental understanding of how molecular size and attractions affect the solid-fluid phase equilibria of ternary mixtures of Lennard-Jones molecules.

In this chapter, we seek to gain a fundamental understanding of what role molecular parameters, such as the Lennard-Jones well-depth and diameter, play in crystallization of ternary mixtures. The system investigated is that of a model diastereomeric mixture, composed of Lennard-
Jones particles. The two diastereomer molecules have similar Lennard-Jones well-depths and diameters and, hence, melting points, while the solvent has a much lower melting point to prevent it from crystallizing with the diastereomers. Ternary phase diagrams for the system are calculated at constant temperature and pressure using the Gibbs Duhem integration technique. The Gibbs Duhem integration technique is well-suited for calculating solid-liquid phase equilibria because it does not require the insertion of molecules into dense liquid and solid phase as do other popular simulation techniques such as the Gibbs ensemble. By varying the cross-species well-depths and molecular diameters associated with the two diastereomers we learn how these two parameters affect the resulting ternary phase behavior. The effect of temperature is then explored by calculating phase diagrams over a range of temperatures for a given set of cross-species well-depths and molecular diameters.

Highlights of the results are the following. The ternary Gibbs Duhem integration technique that we developed is well-behaved in that when there is no liquid-liquid or solid-solid immiscibility, the coexistence curves connect one initial coexistence point to the other in a continuous curve. When all of the interspecies interactions conform to the Lorentz-Berthelot rules, the mixture phase separates into one solid phase and one liquid phase over a range of compositions. In this case, the curves on the ternary phase diagram indicating the composition of the solid and liquid phases extend continuously from the diastereomer 1 – solvent edge of the diagram to the diastereomer 2 – solvent edge of the diagram. When the interspecies diameter is increased to that of the larger diastereomer, the resulting phase diagram is similar, except that there is an increase in the solubility of the diastereomers in the solvent. When the interspecies well-depth is lowered to less than that of either of the diastereomers, two solid phases are formed along the diastere-
omer 1 – diastereomer 2 edge of the diagram. The immiscibility between the solid phases extends into the ternary phase diagram and results in the formation of a three-phase region. When ternary phase diagrams are calculated at a series of temperatures, it is found that as the temperature increases, the size of the three-phase region decreases until it disappears. It is also found that at low temperatures a solvent-rich solid is formed which disappears as the temperature increases. At high temperatures the pure solvent forms a gas and a region of equilibrium forms between solvent-rich vapor and diastereomer-rich liquid. For a limited range of concentration of solvent and temperature one of the diastereomers will precipitate from an equimolar mixture of the diastereomers in the solvent. This implies that for that range of temperature and composition one of the diastereomers can be separated from the mixture. The purity of the precipitate is found to increase as the temperature decreases.

The remainder of this chapter is organized as follows. In Section 2 we briefly review the Gibbs-Duhem technique for ternary mixtures. In Section 3 we present our results and discuss their significance. Section 4 concludes the chapter with a brief summary.

### 3.2 Method

The Gibbs-Duhem integration technique is based upon integrating an appropriate form of the Clapeyron equation, which determines how the field variables vary as a function of each other at equilibrium. One can calculate the properties of two coexisting phases as a function of almost any variable of interest. For a mixture of \( c \) components, the Gibbs-Duhem equation\(^5\) can be expressed as

\[
\begin{align*}
\text{d} \ln \left[ \sum_{i=1}^{c} f_i \right] = & \ h_r \ \text{d} \beta + Z \ln p - \sum_{i=1}^{c} \frac{x_i}{\xi_i} \text{d} \xi_i \\
\end{align*}
\]  

(3.1)
where $p$ is the pressure, $Z$ is the compressibility factor, $x_i, f_i$ are the mole fraction and fugacity of species $i$, $h_r$ is the residual molar enthalpy, $\beta = 1/kT$ where $T$ is the temperature, and $\xi_i$ is the fugacity fraction, defined as

$$\xi_i = \frac{f_i}{\sum_{n=1}^{c} f_n}.$$  

(3.2)

For ternary mixtures equation 3.1 reduces to the following

$$d \ln (f_1 + f_2 + f_3) = h_r d \beta + Z d \ln p - \frac{x_1}{\xi_1} d \xi_1 - \frac{x_2}{\xi_2} d \xi_2 - \frac{x_3}{\xi_3} d \xi_3.$$  

(3.3)

The Gibbs-Duhem equations can be applied to two phases, $\alpha$ and $\gamma$, in equilibrium, by writing Eq. 3.3 for each of the phases. Since the fugacity, and hence the fugacity fraction, of each of the components is identical in phases $\alpha$ and $\gamma$, we can set the right hand sides of those two equations equal to get

$$h_\alpha^0 d \beta + Z^0 d \ln p - \frac{x_1}{\xi_1} d \xi_1 - \frac{x_2}{\xi_2} d \xi_2 - \frac{x_3}{\xi_3} d \xi_3 = h_\gamma^0 d \beta + Z^\gamma d \ln p - \frac{x_1}{\xi_1} d \xi_1 - \frac{x_2}{\xi_2} d \xi_2 - \frac{x_3}{\xi_3} d \xi_3.$$  

(3.4)

At this point there are several integration pathways to choose, depending upon which properties are held fixed and which are allowed to vary. Since we are interested in calculating ternary phase diagrams at constant temperature and pressure, we choose to hold temperature and pressure fixed, which results in

$$\frac{x_1^0}{\xi_1} d \xi_1 + \frac{x_2^\alpha}{\xi_2} d \xi_2 + \frac{x_3^\alpha}{\xi_3} d \xi_3 = \frac{x_1^\gamma}{\xi_1} d \xi_1 + \frac{x_2^\gamma}{\xi_2} d \xi_2 + \frac{x_3^\gamma}{\xi_3} d \xi_3.$$  

(3.5)

Using the relations $x_3 = 1 - x_1 - x_2$ and $\xi_3 = 1 - \xi_1 - \xi_2$, we can eliminate $x_3$ and $\xi_3$ from
Eq. 3.5 and write
\[
\frac{d\xi_1}{d\xi_2} = -\frac{\Delta x_2 (1 - \xi_1)\xi_1 + \Delta x_1 \xi_1 \xi_2}{\Delta x_1 (1 - \xi_2) + \Delta x_2 \xi_1 \xi_2}
\] (3.6)

where \(\Delta x_i = x_i^\alpha - x_i^\gamma\).

The initial condition is typically be two phases, \(\alpha\) and \(\gamma\), in equilibrium at a chosen temperature and pressure and \(\xi_2 = 0\), as indicated by the large dots in Fig. 3.1. Each phase is a binary mixture of components 1 and 3, since \(x_2^\alpha, x_2^\gamma \to 0\) as \(\xi_2 \to 0\). The initial condition fugacity fractions and compositions used in Eq. 3.6 can be determined by carrying out a binary Gibbs Duhem integration for a mixture of components 1 and 3, as explained in a previous paper. The right hand side of Eq. 3.6 is be undefined as \(\xi_2 \to 0\). To remedy this, we divide the top and bottom of the right hand side of Eq. 3.6 by \(\xi_2\) to get
\[
\frac{d\xi_1}{d\xi_2} = -\frac{\Delta x_2 (1 - \xi_1)\xi_1 + \Delta x_1 \xi_1 \xi_2}{\Delta x_1 (1 - \xi_2) + \Delta x_2 \xi_1 \xi_2}
\] (3.7)

which can be written in terms of Henry’s constants since as \(\xi_2 \to 0\) (and hence \(x_2 \to 0\) for the \(\alpha\) and \(\gamma\) phases) \(f_2 \to x_2 H_2\), where \(H_2\) is the Henry’s constant of component 2 in the mixture. It follows then that
\[
\left.\frac{d\xi_1}{d\xi_2}\right|_{\xi_2=0} = -\left[\left(\frac{x_2 H_2}{f_2 + f_3}\right)^\alpha - \left(\frac{x_2 H_2}{f_2 + f_3}\right)^\gamma\right](1 - \xi_1)\xi_1 + \Delta x_1 \xi_1
\] (3.8)

Here we have made use of the fact that \(\xi_2^\alpha = \xi_2^\gamma\). Recognizing that \(\Delta x_2 = 0\) when \(\xi_2 = 0\), this can be further reduced to
\[
\left.\frac{d\xi_1}{d\xi_2}\right|_{\xi_2=0} = -\left[\left(\frac{f_2}{H_2} + \frac{f_3}{H_2}\right)^\alpha - \left(\frac{f_2}{H_2} + \frac{f_3}{H_2}\right)^\gamma\right](1 - \xi_1)\xi_1 + \Delta x_1 \xi_1
\] (3.9)
where $f_1/H_2$ and $f_3/H_2$ can be calculated by conducting an NPT simulation on each of the mixtures. We can calculate $(f_1/H_2)^{\alpha}$ and $(f_3/H_2)^{\alpha}$ by calculating the change in potential energy upon switching a particle of component 1 to component 2 and a particle of component 3 to component 2, respectively, at the temperature, pressure, and composition of phase $\alpha$. The values of $(f_1/H_2)^{\alpha}$ and $(f_3/H_2)^{\alpha}$ can be calculated from

$$\frac{f_i}{H_2} = \left\langle \exp\left(\frac{\Delta U_{i\rightarrow 2}}{kT}\right) \right\rangle_{NPT}$$

(3.10)

where $\left\langle \right\rangle$ denotes the ensemble average and $U_{i\rightarrow 2}$ is the potential energy change upon switching the identity of a particle from component $i$ ($i=1$ or 3) to component 2. The same procedure can then be used to calculate the values of $(f_1/H_2)^{\gamma}$ and $(f_3/H_2)^{\gamma}$.

Once the initial condition is calculated, the integration is carried out using a standard predictor-corrector algorithm. A step, $\Delta \xi_2$, in the fugacity fraction of component 2 is taken and the predictor formula is used to find the new value for the fugacity fraction of component 1, $\xi_1$, i.e.

$$\xi_1^1 = \xi_1^0 + \int_{\xi_2=0}^{\xi_2=\Delta \xi_2} \frac{d\xi_1}{d\xi_2} d\xi_2$$

(3.11)

A separate semigrand ensemble (constant NPT$\xi_2$) Monte Carlo simulation is then performed for each of the coexisting phases to evaluate the enthalpy and composition at the new $\xi_1$ and $\xi_2$. After the simulations have equilibrated, the integrand is recalculated, the corrector formula is applied to find the “corrected” $\xi_1$, and more simulations are performed at the new value of $\xi_1$. This corrector step is repeated until $\xi_1$ converges to its final value. A production run of simulations is then carried out to calculate the final values for the enthalpies and compositions of the coexisting
phases. These values are then used in the predictor formula to calculate $\xi_1$ at the next value of $\xi_2$. Continuing this process we can calculate the entire phase coexistence envelope.

Semigrand ensemble Monte Carlo simulations are used to evaluate the properties of the coexisting phases during the integration of the Gibbs-Duhem equation. There are three types of moves in the semigrand ensemble: particle displacement, volume change, and identity exchange. The particle displacement and volume change moves are carried out in the same manner as in isothermal-isobaric (NPT) simulations. The identity exchange move involves choosing a random molecule in the system and changing its identity to that of one of the other species in the mixture chosen at random (for the binary case, this is simply be the other species). The change in the configurational energy of the system caused by the identity change is then evaluated. The overall acceptance probability, $P$, for any of these moves is

$$P = \min[1, \exp(-\beta(U^{\text{trial}} - U^{\text{old}}) - \beta P(V^{\text{trial}} - V^{\text{old}}) + N \ln \frac{V^{\text{trial}}}{V^{\text{old}}} + \ln \frac{\xi^{\text{trial}}}{\xi^{\text{old}}})] \quad (3.12)$$

where $U^{\text{trial}}$ and $U^{\text{old}}$ are the configurational energies, $V^{\text{trial}}$ and $V^{\text{old}}$ are the volumes of the trial and existing states respectively, $N$ is the total number of molecules, and $\xi^{\text{trial}}$ and $\xi^{\text{old}}$ refer to the fugacity fractions of the trial and existing identities of the molecule during the identity exchange moves. At each step, the type of move is randomly chosen with a weighting such that for every volume change move there are 20 particle displacements and 20 identity exchange moves. After an appropriate number of equilibrium moves, a running average of the composition and enthalpy (as calculated by $h = U/N + PV/N$) is calculated for use in calculating the integrand in the Gibbs Duhem technique.

Other details of the simulations are as follows. Each simulation box contains 2048
molecules. A cell structured neighbor list is used to increase the efficiency of the simulations. Prior theoretical calculations and molecular simulations, have shown that by choosing diameter ratios $0.85 \leq \sigma_{11}/\sigma_{22} \leq 1.0$ we can assume that the most stable configuration for the solid phase is a substitutionally disordered fcc lattice. By using an fcc lattice as an initial configuration for the solid phase, the fcc lattice is maintained in the solid phase throughout the simulation without any additional constraints on the simulation. The simulations are conducted in a cubic box with periodic boundary conditions. The molecules interact via the Lennard-Jones potential

$$u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]$$  \hspace{1cm} (3.13)

where $u_{ij}$ is the potential energy of the interaction between atoms $i$ and $j$, $r$ is the distance between atoms $i$ and $j$, $\epsilon_{ij}$ is the Lennard-Jones well-depth, and $\sigma_{ij}$ is the Lennard-Jones diameter. The potential interactions are truncated at half the box length and standard long range corrections are applied to the potential and pressure calculations.

### 3.3 Results

We have calculated ternary phase diagrams for two different mixtures. The pure component properties and interspecies interaction parameters between the solvent and “diastereomers” (see Table 3.1) are the same for both mixtures since the parameters were chosen to model a diastereomeric mixture. The two diastereomer molecules have similar size and melting point, much like the diastereomers in a real mixture would. The solvent well-depth and size were chosen so that the solvent would have a lower melting point than the diastereomers and be somewhat smaller.
The cross-species parameters between the diastereomers was varied, as explained below. Both of
the diagrams were calculated at a constant pressure, $P^* \equiv P\sigma_{SS}^3/\epsilon_{SS} = 0.04$, and temperature,
$T^* \equiv kT/\epsilon_{SS} = 1.000$. To determine the initial conditions for the Gibbs Duhem calculation
of the ternary phase diagrams, three binary, component 1 – solvent (Figure 3.2), component 2
– solvent (Figure 3.3), and component 1 – component 2 (Figure 3.4), temperature-composition
phase diagrams were calculated. This gave us the properties of the coexisting phases along the
edges of the diagrams, as described in Section 3.2.

Figure 3.5 is the ternary phase diagram calculated when $\epsilon_{12} = 2.025$ and $\sigma_{12} = 1.163$,
which corresponds to the Lorentz-Berthelot mixing rules, $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$ and $\sigma_{12} = (\sigma_{11} +
\sigma_{22})/2$. The diagram shows a liquid phase in the solvent rich region, a single solid phase in the
solvent poor region, and a two-phase solid-liquid region in between. In the diagram, the upper
line indicates the composition of the liquid in equilibrium and the lower line indicates the com-
position of the solid. Tie lines connect approximately every fifth set of coexisting points to make
the diagram easier to read. Mixtures in the two-phase region will phase separate into a liquid
and solid phase with compositions determined by the tie line that crosses the total composition
of the system. Mixtures whose composition is in the region below the solid line will exist as
a substitutionally disordered fcc lattice crystal. One can see that the solid rich in component 1
(lower right corner) contains slightly more solvent than the solid rich in component 2 (lower left
corner). This can be explained by the greater difference in size and well-depth between com-
ponent 2 and the solvent than between component 1 and the solvent. As was shown in Chapter
2, as the difference between the well-depths (and hence critical points) of two components in a
binary mixture becomes greater, the two components become less miscible with each other.
Figure 3.6 is the ternary phase diagram calculated when $\epsilon_{12} = 2.025$ and $\sigma_{12} = 1.175$, which means the interspecies diameter is equal to the diameter of the second component. Physically this means that there will be greater repulsion at close range between a species of component 1 and a species of component 2 than there was in the previous case (Fig. 3.5). This diagram looks fairly similar to Fig. 3.5 except that the solubility of the mixture is slightly greater than the solubility of the mixture in Fig. 3.5, i.e. the liquid in coexistence with the solid is richer in both components, as indicated by the minimum in the liquid curve. Since $\sigma_{12}$ in Figure 3.6 is larger than in Figure 3.6 the molecules no longer pack as tightly in the solid, which leads to a decreased effective attraction between components 1 and 2. Consequently, the enthalpic penalty for entering the liquid phase is no longer as great and the solid becomes more soluble.

Figures 3.7-3.12 are ternary phase diagrams calculated at a series of temperatures, $kT/\epsilon_{SS} = 0.67, 0.75, 1.00, 1.25, 1.35$, and 1.38, for a mixture with $\epsilon_{12} = 1.822$ and $\sigma_{12} = 1.163$. The lower graph in each figure is a schematic of the actual data presented in the upper graph. In this case, the intraspecies diastereomeric attraction, $\epsilon_{12}$, is stronger than the interspecies diastereomeric attraction, or in terms of deviation from Lorentz-Berthelot mixing rules, $k_{12} = 0.9$, where $\epsilon_{12} = (1 - k_{12})(\epsilon_{11}\epsilon_{22})^{1/2}$. The horizontal lines on Figures 3.2-3.4 indicate the series of temperatures at which the ternary phase diagrams are calculated.

Figure 3.7 is the ternary phase diagram calculated at a reduced temperature of $kT/\epsilon_{SS} = 0.67$. At this temperature in the binary component 1 – component 2 phase diagram, the solids formed at low temperature phase separate into two solid solutions. In both the component 1 – solvent and component 2 – solvent binary phase diagrams there are two regions of solid-liquid phase equilibria, one with a solvent-rich solid and one with a solid rich in component 1 (or 2).
It can be seen in Figure 3.7 that the solid-solid immiscibility in the absence of solvent (bottom of diagram) is decreased upon the addition of the solvent and that the solid-solid immiscibility curves intersect with the solid-liquid coexistence curves originating from the component 1 – solvent and component 2 – solvent edges of the ternary phase diagram, resulting in a three-phase region. Mixtures within the three-phase region will phase separate into two solid phases and one liquid phase whose compositions are given by the vertices of the triangle forming the three-phase region. There also exists a region of solid-liquid phase equilibrium near the pure solvent vertex of the ternary phase diagram.

Figure 3.8 is the ternary phase diagram calculated at a reduced temperature of $kT/\epsilon_{SS} = 0.75$. At this temperature in the binary component 1 – component 2 phase diagram, the solids formed at low temperature phase separate into two solid solutions, although the solids are not as pure as at $kT/\epsilon_{SS} = 0.67$ (Figure 3.7). In both the component 1 – solvent and component 2 – solvent binary phase diagrams there is only one region of solid-liquid phase equilibria. As a result there is no longer a solid rich in solvent in the ternary phase diagram. The diastereomers have become more soluble in the solvent as indicated by the higher mole fraction of diastereomers in the liquid coexisting with the solid, and the region of three phase coexistence is smaller than at the previous temperature.

Figure 3.9 is the ternary phase diagram calculated at a reduced temperature of $kT/\epsilon_{SS} = 1.00$. At this temperature in the binary component 1 – component 2 phase diagram, the solids formed at low temperature phase separate into two solid solutions. In both the component 1 – solvent and component 2 – solvent binary phase diagrams there is one region of solid-liquid phase equilibria. Figure 3.9 is similar to Figure 3.8 except that the diastereomers are again more
soluble and the solids are less pure, resulting in a three-phase region smaller than at the previous temperature.

Figure 3.10 is the ternary phase diagram calculated at a reduced temperature of $kT/\varepsilon_{SS} = 1.25$. At this temperature in the binary component 1 – component 2 phase diagram, the solids formed at low temperature phase separate into two solid solutions of even lower purity that at $kT/\varepsilon_{SS} = 1.00$ (Figure 3.9). In both the component 1 – solvent and component 2 – solvent binary phase diagrams there is one region of solid-liquid phase equilibria and one region of vapor-liquid phase equilibria. Because of the vapor-liquid equilibria present in the binary phase diagrams, a region of vapor-liquid phase equilibria forms at high concentrations of solvent. The region of three phase phase equilibria is even smaller than it was at the previous temperature.

Figure 3.11 is the ternary phase diagram calculated at a reduced temperature of $kT/\varepsilon_{SS} = 1.35$. At this temperature in the binary component 1 – component 2 phase diagram, there are two regions of solid-liquid phase equilibria, which means that there are two pairs of curves emanating from the component 1 – component 2 edge of the ternary phase diagram. In both the component 1 – solvent and component 2 – solvent binary phase diagrams there is one region of solid-liquid phase equilibria and one region of vapor-liquid phase equilibria. Because there is no longer any solid-solid phase coexistence in the binary component 1 – component 2 phase diagram, the three-phase region has disappeared. At high concentrations of solvent there is a region of vapor-liquid phase coexistence; the liquid phase solvent concentration here is lower than in the previous case. At low concentrations of solvent there are two separate regions of solid-liquid phase equilibria.

Figure 3.12 is the ternary phase diagram calculated at a reduced temperature of $kT/\varepsilon_{SS} = 1.38$. At this temperature in the binary component 1 – component 2 phase diagram, there is one
region of solid-liquid phase equilibria. In the component 1 – solvent binary phase diagram there is only one region of vapor-liquid equilibria, while in the component 2 – solvent binary phase diagram there is one region of solid-liquid equilibria and one region of vapor-liquid equilibria. At high concentrations of solvent in the ternary phase diagram there is a region of vapor-liquid phase coexistence and the concentration of solvent in the liquid phase is again lower than at the previous temperature. At low concentrations of solvent there is now only one region of solid-liquid phase equilibria.

To apply the previous figures to the process of classical resolution, one must consider that a racemic mixture will, in most cases, be an equimolar mixture of the two racemates. Consequently, the mixture that results from reacting the enantiomers with the resolving agent will be an equimolar mixture of the two diastereomers. In terms of the ternary diagrams that have been presented, the composition of the mixtures will fall upon a line that extends from the pure solvent vertex of the ternary phase diagram to the middle of the component 1 – component 2 edge of the diagram. In Figures 3.7 - 3.10, we see that there exists a range of solvent concentration along this line where the mixture phase separates into a liquid and a solid rich in component 2. It is for this range of solvent concentration that separation of the diastereomers is possible. It can be seen the purity of the solid phase with respect to component 2 increases as the temperature is decreased.

3.4 Summary

We extended the Gibbs Duhem integration technique to calculate ternary phase equilibria at constant temperature and pressure. We then used the Gibbs Duhem technique to calculate
ternary phase equilibria for a model diastereomeric system composed of two “diastereomers” of similar size and melting point and a “solvent” of slightly smaller size and lower melting temperature. The cross-species well-depth and diameter between the two diastereomers were varied to determine their impact on the resulting phase equilibria. We found that increasing the interspecies diameter up to that of the larger component resulted in a slight increase in the solubility of the solvent. We found that when the interspecies well-depth was lowered to below that of either of the diastereomers, two immiscible solid phases were formed resulting in a region of three-phase equilibria in the ternary phase diagram. We then calculated a series of ternary phase diagrams at various temperatures for the same set of intermolecular parameters. It was found that as the temperature increases, the size of the three-phase region decreases until it disappears. It was also found that at low temperatures a solvent-rich solid is formed which disappears as the temperature increases. At high temperatures a solvent-rich gas was formed and this resulted in a region of equilibrium between solvent-rich vapor and diastereomer-rich liquid. For a limited range of concentration of solvent and temperature, one of the diastereomers will precipitate from an equimolar mixture of the diastereomers in the solvent. The purity of the precipitate is found to increase as the temperature decreases.
3.5 References


Table 3.1: Lennard-Jones parameters used in Figures 1-2

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## 3.6 Figures

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Figure 3.1: Schematic of ternary Gibbs Duhem integration. The dots indicate the compositions of the initial coexisting phases. The dashed lines indicate the coexistence curves.
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Figure 3.5: Ternary phase diagram calculated at $T^* = 1.00$, $P^* = 0.040$ and $\epsilon_{12} = 2.025$, $\sigma_{12} = 1.163$. 
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Figure 3.7: Ternary phase diagram calculated at $T^* = 0.67$, $P^* = 0.040$ and $\epsilon_{12} = 1.822$, $\sigma_{12} = 1.163$. The upper graph is data calculated by the Gibbs Duhem integration technique and the bottom graph is a schematic of the upper graph.
Figure 3.8: Ternary phase diagram calculated at $T^* = 0.75$, $P^* = 0.040$ and $\epsilon_{12} = 1.822$, $\sigma_{12} = 1.163$. The upper graph is data calculated by the Gibbs Duhem integration technique and the bottom graph is a schematic of the upper graph.
Figure 3.9: Ternary phase diagram calculated at $T^* = 1.00$, $P^* = 0.040$ and $\epsilon_{12} = 1.822$, $\sigma_{12} = 1.163$. The upper graph is data calculated by the Gibbs Duham integration technique and the bottom graph is a schematic of the upper graph.
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Figure 3.12: Ternary phase diagram calculated at $T^* = 1.38$, $P^* = 0.040$ and $\epsilon_{12} = 1.822$, $\sigma_{12} = 1.163$. The upper graph is data calculated by the Gibbs Duhem integration technique and the bottom graph is a schematic of the upper graph.
CHAPTER 4

FUTURE WORK

Work is currently being done in this research group to apply the Gibbs Duhem integration technique to the calculation of solid-liquid phase equilibria for a more realistic model of a diastereomeric mixture. The ultimate goal is to predict the phase behavior of a pair of diastereomers, (2S,3R)-3-chloro-2-butanol and (2R,3R)-3-chloro-2-butanol, in ethanol. Once this goal is achieved, the Gibbs Duhem technique could prove useful as a general design tool for diastereomeric crystallization operations.

Towards that ultimate goal we propose that the following intermediate steps be taken. The first is to use the Gibbs Duhem integration technique to calculate solid-fluid phase equilibria for a system of pure Lennard-Jones dumbbells. (Up until now, our research group has only used the Gibbs Duhem technique to calculate the phase equilibria of spherical molecules.) Dumbbells represent the simplest case of a non-spherical molecule and thus are a good first step in modeling non-spherical molecules more realistically. The dumbbell molecules will add a layer of complexity to the calculation because the most stable crystal structure of the solid phase will need to be calculated rather than assumed, as we were able to do in the case of spherical molecules of similar diameter. The most stable crystal structure can be determined by using the free energy calculation method developed by Frenkel and Ladd\textsuperscript{1}. This method involves thermodynamically
integrating the free energy over a reversible path from an Einstein crystal to the system of interest.

Once we have successfully calculated phase diagrams for pure and binary systems of dumbbells, we will proceed in the same manner to calculate phase diagrams for our model diastereomers, (2S,3R)-3-chloro-2-butanol and (2R,3R)-3-chloro-2-butanol. We will first calculate solid-liquid phase equilibria for just one of the diastereomers in order to determine how to treat the chlorine and hydroxyl groups. We plan on modeling the diastereomers using an united atom representation with fixed bond angles and lengths. The diastereomers will interact via Lennard-Jones potentials. The Lennard-Jones parameters will be adopted from Jorgensen’s optimized (OPLS) Lennard-Jones parameters$^2$. After we are satisfied with the results for the pure diastereomer phase diagram calculations, we will then use the knowledge and pure component equilibria data gained from that step to calculate binary phase diagrams for mixtures of the two diastereomers. Finally we will calculate phase diagrams for a ternary system of our model diastereomers and ethanol. The research presented in this dissertation will provide the basis for making the transition from binary to ternary mixtures.

Another possibility for future work would be to calculate the effect of the solid phase on the fluid-phase equilibria for binary mixtures of dissimilar sized molecules. Based on previous research in this group$^3$, we would expect to see a greater variety of solid-liquid phase behavior than is seen when considering molecules of equal diameter as in Chapter 2. This in turn would allow for a greater variety of ways in which the solid phase would interfere with the fluid-phase equilibria. Diameter ratios from $\sigma_{11}/\sigma_{22} = 0.85$ to $\sigma_{11}/\sigma_{22} = 1.00$ could easily be incorporated using the computer code and procedure outlined in Chapter 2 because we could assume that the
solid phase crystallized into a disordered solid-solution on an fcc lattice. For even lower diameter ratios, more calculations would be required to determine the most stable crystal structure for the solid phase. However, some of the work needed to develop a procedure for such a case would coincide with that needed for the work on diastereomeric mixtures. Calculating phase diagrams for mixtures of molecules of greatly dissimilar diameters would result in even more interesting types of solid-fluid equilibria, including polymorphism.
4.1 References


Appendices
A.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 equilibria of a particular system. A different approach was taken in the late sixties by van Konynenburg and Scott\textsuperscript{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, \( \left( \frac{\partial^2 G}{\partial x_i^2} \right)_{p,T} = 0 \) and \( \left( \frac{\partial^3 G}{\partial x_i^3} \right)_{p,T} = 0 \), 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\textsuperscript{1,2} used two dimensionless parameters, \( \zeta \) and \( \Lambda \), 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, \( \zeta \) is related to the differences in critical temperatures or pressures of the pure components and \( \Lambda \) 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 diagram 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 bond-
ing, e.g. hydrogen bonding. More recently, Yelash et al.\textsuperscript{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\textsuperscript{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\textsuperscript{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 \textsuperscript{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\textsuperscript{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 \textsuperscript{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 \textsuperscript{17}, alternating, block, and random heteronuclear square-well chain fluids \textsuperscript{18–20}, hard-chain networks\textsuperscript{21} and gels\textsuperscript{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 Konyenburg 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 $\zeta$-$\Lambda$ space, with $\zeta$ and $\Lambda$ each ranging from -0.9 to 0.9. For this range of $\zeta$ and $\Lambda$, 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\textsuperscript{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 $\zeta$. 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 $\Lambda$ direction.

The remainder of this paper is organized as follows. In Section A.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 A.3 the method used to calculate the global phase diagram is described. In Section A.4, the global phase diagram resulting from the GFD prediction for square-well monomer/dimer mixtures is presented. Section A.5 concludes the paper with a brief summary.

A.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

\[
\frac{P(\eta, n)}{kT} = \frac{\eta}{v_n} [1 - \ln p_n(\eta)] + \frac{1}{v_n} \int_0^n \ln p_n(\eta')d\eta',
\]  
(A.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 \(\sigma\) is the segment diameter. The insertion factor is defined as

\[
p_n(\eta) = \left< e^{\eta' \left( -\frac{U}{kT} \right)} \right>,
\]  
(A.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\textsuperscript{23} by

$$\frac{-\mu^*_n(\eta)}{kT} = \ln p_n(\eta)$$

(A.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

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

(A.4)

Because equation (A.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.
A.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

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

\[= p_1^{hs}(\eta) - Y_n p_2^{hs}(\eta) Y_n + 1, \quad (A.6)\]

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, \(v_c(n)\) is the volume excluded by an \(n\)-mer to a monomer, and

\[Y_n = \frac{v_c(\eta) - v_c(2)}{v_c(2) - v_c(1)}. \quad (A.7)\]

Eq. (A.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

\[
p_n(\eta) = \begin{pmatrix}
\text{Probability of inserting bead 1} \\
\text{Conditional probability of inserting bead 2 given bead 1} \\
\text{Conditional probability of inserting bead 3 given beads 1 and 2} \\
\vdots \\
\text{Conditional probability of inserting bead n given beads 1, ..., n - 1}
\end{pmatrix}.
\]

(A.8)

The first term on the right hand side of Eq. (A.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.
(A.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. (A.5).

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

\[
Z_{n}^{h*}(\eta) = (Y_n + 1)Z_2^{h*}(\eta) - Y_nZ_1^{h*}(\eta),
\]  
(A.9)

where \( Z_2^{h*}(\eta) \) and \( Z_1^{h*}(\eta) \) 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\textsuperscript{24} and Tildesley-Street\textsuperscript{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

\[ v_e(n) \approx v_e(3) + (n - 3)[v_e(3) - v_e(2)], \tag{A.10} \]

for $2 \leq n \leq 8$ and

\[ v_e(n) \approx v_e(1)[10.094 + 0.6374(n - 15)], \tag{A.11} \]

for $n > 8$.\(^{26} \)

### A.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, $p^{sw}_n(\eta)$ is given by

\[
\begin{align*}
    p^{sw}_n(\eta) &= p^{sw}_1(\eta) \left[ \frac{p^{sw}_2(\eta)}{p^{sw}_1(\eta)} \right] \frac{(v_e(n) - v_e(1))}{(v_e(2) - v_e(1))}, \\
    &= p^{sw}_1(\eta) Y_n p^{sw}_2(\eta) Y_n + 1, \tag{A.12}
\end{align*}
\]

where $p^{sw}_1$ is the insertion factor for a square-well monomer in a square-well monomer fluid, $p^{sw}_2$ 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. (A.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. A.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,

$$Z^{sw}_n(\eta) = (Y_n + 1)Z^{sw}_2(\eta) - Y_n Z^{sw}_1(\eta), \quad (A.14)$$

is the Generalized Flory-Dimer equation of state for square-well chain fluids, where $Z^{sw}_2(n)$ and $Z^{sw}_1(n)$ 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, coordination number models, or by using the RISM theory with the mean-spherical approximation closure.

**A.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

$$\frac{P(\eta_a, \eta_b)}{kT} = \frac{x_a \eta}{\bar{V}} \left[ 1 - \ln p_a(\eta_a, \eta_b) \right] + \frac{x_a}{\bar{V}} \int_0^\eta \ln p_a(\eta'_a, \eta_b) d\eta' + \frac{x_b \eta}{\bar{V}} \left[ 1 - \ln p_b(\eta_a, \eta_b) \right] + \frac{x_b}{\bar{V}} \int_0^\eta \ln p_b(\eta'_a, \eta'_b) d\eta', \quad (A.15)$$

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 $\bar{\eta} = x_a \nu_a + x_b \nu_b$ 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

\[ \eta_a' = x_a \frac{v_a}{\theta} \eta_a' ; \quad \eta_b' = x_b \frac{v_b}{\theta} \eta_b' \]  

(A.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 \(a\) and length \(n_a\) into a mixture at total volume fraction \(\eta\) and composition \(x_a\) containing species \(a\) and \(b\) chains of lengths \(n_a\) and \(n_b\), respectively, is denoted as \(p(\eta, x_a)^{(n_a, n_b)}\). 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. (A.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

\[ p(\eta, x_a)^{(n_a, 1)} \approx \left( p(\eta, x_a)^{(n_a, 1)} \right) - (Y'_{n_a})_{\text{mix}} \times \left( p(\eta, x_a)^{(n_a, 1)} \right)^{(Y'_{n_a})_{\text{mix} + 1}} \]  

(A.17)

where \(p(\eta, x_a)^{(n_a, 1)}\) is the factor for inserting a monomer of species \(a\) into the chain/monomer mixture, \(p(\eta, x_a)^{(n_a, 1)}\) is the factor for inserting a dimer of species \(a\) into the chain/monomer mixture, and \((Y'_{n_a})_{\text{mix}}\) is the volume excluded in the mixture by a molecule of species \(a\) and length \(n_a\). 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

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

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 created by breaking every other bond along the chain

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

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

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

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

\[
Z^{GFD}(\eta, x_a)^{n_a, 1} = \frac{P(\eta, x_a)\mathcal{V}}{\eta k T} \quad (A.21)
\]

\[
= x_a \{1 - [(Y_{n_a}^a)_{mix} + 1] \ln p^{(2,1)}_{a2} + (Y_{n_a}^a)_{mix} \ln p^{(1,1)}_{a1}\}
\]

\[
+ \frac{x_a}{\eta} [(Y_{n_a}^a)_{mix} + 1] \times \int_0^\eta \ln p^{(2,1)}_{a2} d\eta'
\]

\[
- \frac{x_a}{\eta} (Y_{n_a}^a)_{mix} \times \int_0^\eta \ln p^{(1,1)}_{a1} d\eta' + x_b [1 - \ln p^{(2,1)}_{b1}]
\]

\[
+ \frac{x_b}{\eta} \int_0^\eta \ln p^{(2,1)}_{b1} d\eta'.
\]

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

\[
\gamma(\eta, y_a)^{[n_a, 1]} = 1 - \ln p(\eta, y_a)^{[n_a, 1]} + \frac{1}{\eta} \int_0^\eta \ln p(\eta', y_a)^{[n_a, 1]} d\eta', \quad (A.22)
\]

where the subscripts and superscripts on \(\gamma\) 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 \(\gamma\) notation, the equation of state can then be written as

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

The \(\gamma\)’s can written in the form

\[
\gamma(\eta, y_a)^{[n_a, 1]} = \gamma^{hs}(\eta, y_a)^{[n_a, 1]} + \gamma^{sw}(\eta, y_a)^{[n_a, 1]} \quad (A.24)
\]
where \( \gamma^{hs} \) is the hard sphere, or repulsive, contribution to the compressibility factor and \( \gamma^{sw} \) is the square-well, or attractive, contribution to the compressibility factor. Eq. (A.23) can then be written as

\[
Z^{GFD} = \exp\left[a \left[ \left( (Y_{\alpha}^\sigma)^{m_{\text{mix}}} + 1 \right) \left( \gamma^{hs}(\eta, y_{\alpha})_{a_2}^{(2,1)} + \gamma^{sw}(\eta, y_{\alpha})_{a_2}^{(2,1)} \right) - (Y_{\alpha}^\sigma)^{m_{\text{mix}}} \right] \left( \gamma^{hs}(\eta, y_{\alpha})_{\alpha_1}^{(1,1)} + \gamma^{sw}(\eta, y_{\alpha})_{\alpha_1}^{(1,1)} \right) \right] + b \left[ \left( \gamma^{hs}(\eta, y_{\alpha})_{b_1}^{(2,1)} + \gamma^{sw}(\eta, y_{\alpha})_{b_1}^{(2,1)} \right) \right],
\]

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

\[
\gamma(\eta, y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} = -[1 + W(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} + Y(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} + 3Z(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})}] \ln(1 - \eta) \eta
\]

\[
\quad + \left\{ -[X(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} / 2 + (5/2)Y(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} + (15/2)Z(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})}] \right\}
\]

\[
\quad + \eta \left[ X(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} / 2 + (5/2)Y(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} + (11/2)Z(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} \right] - \eta^2 \left[ X(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} / 2 + (5/2)Y(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} + (11/2)Z(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} \right] + \eta^3 \left[ W(y_{\alpha})_{i}^{(n_{\alpha}, n_{b})} \right] \right\} \left( 1 - \eta \right)^{-3},
\]

where the coefficients \( W, X, Y, \) and \( Z \) are determined from SPT and are listed in Table A.1. The shape parameter ratios and shape parameters required to calculate \( W, X, Y, \) and \( Z \) can be found in Tables A.2 and A.3, respectively.
The square well contribution to the compressibility factor of the mixture, \( \gamma_s \), 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\(^\text{29}\) and to apply the high density correction of Vimalchand et al.\(^\text{31}\). 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

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

where \( \lambda_i \) 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

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

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 \( V_{n,ij} (\equiv \frac{4}{3} \pi (\chi^3 - 1) \sigma_{ij}) \) is the volume of the coordination shell. The inter-species hard-core diameter, \( \sigma_{12} \), is defined as \( \frac{1}{2} (\sigma_{11} + \sigma_{22}) \), while the inter-species well-depth, \( \epsilon_{12} \), normally defined to be \( (\epsilon_{11} \epsilon_{22})^{1/2} \), is allowed to vary. The parameter \( Z_l \) differs from that of Lee and Chao due to the application of the high density correction of Vimalchand et al and is defined as

\[
Z_l = A + B \rho^* - C (\rho^*)^4, \tag{A.29}
\]

where the coefficients \( A, B, \) and \( C \) depend on the types of components in the mixture and can be found in Table A.4. Because Vimalchand et al. did not apply the high density correction to the model of Lee and Chao, the coefficients in Table A.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

\[
U = - \sum_i \sum_j \frac{N_i}{2} z_{ij} \epsilon_{ij}. \tag{A.30}
\]

The Helmholtz energy, \( A \), is obtained by integrating the equation

\[
\frac{\partial (A/T)}{\partial (1/T)}_{N,V} = U \tag{A.31}
\]

to get an expression for the Helmholtz energy,

\[
A = T \int_0^{1/T} U d(1/T'). \tag{A.32}
\]

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 $x_i$

$$\ln p(\eta, y_a)_{i_{n_i}} = \left( \frac{\partial A}{\partial N_i} \right)_{T, V, N_j \neq i}$$

$$= A - x_i \left( \frac{\partial A}{\partial x_i} \right)_{T, V, x_j \neq i}$$

$$= T \int_0^{1/T} \left[ U - x_i \left( \frac{\partial U}{\partial x_i} \right)_{T, V, x_j \neq i} \right] d(1/T)' .$$

The resulting expressions for $\ln p(\eta, y_a)_{i_{n_i}}$ can then be substituted in Eq. (A.22) to calculate $\gamma^{sw}(\eta, y_a)_{i_{n_i}}$ for $i_{n_i} = a_1, a_2, b_1$ which, along with the expressions for $\gamma^{hs}(\eta, y_a)_{i_{n_i}}$ 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. (A.23).

### A.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 A.2.3 with discontinuous molecular dynamics simulations of monomer-dimer and monomer-chain mixtures. Figure A.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 A.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 A.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.

A.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\textsuperscript{2,11}, 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, $\epsilon_{ii}$, and on the inter-species interaction energies, $\epsilon_{ij}$. 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

\begin{equation}
\zeta = \frac{\epsilon_{22} - \epsilon_{11}}{\epsilon_{22} + \epsilon_{11}} \quad \text{(A.34)}
\end{equation}

\begin{equation}
\Lambda = \frac{\epsilon_{11} - 2\epsilon_{12} + \epsilon_{22}}{\epsilon_{22} + \epsilon_{11}}. \quad \text{(A.35)}
\end{equation}

to define the parameter space for our global phase diagram. The type of phase behavior exhibited at each point $\zeta, \Lambda$ 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 A.4 shows characteristic projections of the locus of critical points onto the $P - T$ plane for Types I-VI phase behavior\textsuperscript{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

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

(A.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. (A.36) from functions of the Gibbs free energy to functions of the Helmholtz free energy, leading to the following critical point equations

\[
A_{2V}A_{2x} - A_{Vx}^2 = 0
\]

(A.37)

\[
A_{3V}A_{2x}^2 - 3A_{2Vx}A_{Vx}A_{2x} + 3A_{V2x}A_{Vx}^2 - A_{3x}A_{2V}A_{Vx} = 0
\]

(A.38)

where,

\[
A_{mVnVx} \equiv \left( \frac{\partial^{n+m} A}{\partial^m V \partial^n x} \right)_{T}.
\]

(A.39)

The Helmholtz free energy can be expressed in terms of the mixture compressibility factor, packing fraction, and mole fraction as \(^{32}\)

\[
\frac{A}{RT} - \frac{A^0}{RT} = \int_0^\eta \frac{Z - 1}{\eta'} d\eta' - \ln \frac{V}{V^o} + \sum_i x_i \ln x_i,
\]

(A.40)

where \( A^0 \) and \( V^o \) are reference state conditions that are independent of volume and composition. Thus, when the partial derivatives in Eqs.(A.37) and (A.38) are performed \( A^0 \) and \( V^o \) will drop
out of the resulting expressions.

The compressibility factor used in equation Eq. (A.40) was calculated using the Generalized Flory Dimer equation of state for square-well chain/monomer mixtures derived in Section A.2.3. Eqs. (A.37) and (A.38) were then solved numerically using Newton’s method\textsuperscript{33} for the critical temperature and volume at fixed values of $\zeta$, $\Lambda$, 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. (A.37) and (A.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. (A.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 $\Lambda$ and $\zeta$, 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 $\alpha$ and $\beta$, 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 $\mu_i^j$ 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.
This required an iterative solution because Eq. (A.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

\[
\frac{G}{RT} - \frac{G^0}{RT} = \int_0^\eta \frac{Z - 1}{\eta'} d\eta' - \ln \frac{V}{V^0} + Z - 1 + \sum_i x_i \ln x_i, \quad (A.41)
\]

where \(G^0\) and \(V^0\) 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

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

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

The final step in the calculation involved finding values of the composition at which \(\mu_i^0 = \)
$\mu_i^\beta$. The algorithm essentially boiled down to plotting a parametrized curve of $\mu_1$ versus $\mu_2$ with composition as the parameter; this is represented schematically in Figure A.5. Point A in Figure A.5 represents a point at which $\mu_1$ and $\mu_2$ have the same value at two different values of composition. Three phase coexistence would be represented in Figure A.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 A.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 $\mu_1$ versus $\mu_2$ 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 $\varsigma - \Lambda$ 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 A.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 $\Lambda$ and $\varsigma$ 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.
A.4 Global Phase Diagram for Monomer/Dimer Mixtures

Figure A.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 A.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 A.6 should be no greater than 0.05 units in the \( \Lambda \) or \( \zeta \) directions.

Figure A.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\(^3\). Comparison of Figures A.6 and A.7 reveals the absence of Type IV and Type VI behaviors on Figure A.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\(^1\) 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 A.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 $\Lambda$ 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.
A.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 $\Lambda$ and $\zeta$ 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 $\zeta$ and $\Lambda$ 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.
A.6 References


Table A.1: Values of the density-independent coefficients of Equations A.27, determined using Boublik’s equation of state\textsuperscript{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, $\omega$ and $\psi$, and their derivatives $\omega'$ and $\psi'$ with respect to $N_i$, the number of species $i$ molecules. The shape parameter ratios and their derivatives are defined in Table A.2.

<table>
<thead>
<tr>
<th>$W(y_n)<em>{i}^{(n</em>{a}, n_{b})}$</th>
<th>$-\psi'_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X(y_n)<em>{i}^{(n</em>{a}, n_{b})}$</td>
<td>$-\psi'_i - \omega'_i - (\omega + 1)(b_i / b)$</td>
</tr>
<tr>
<td>$Y(y_n)<em>{i}^{(n</em>{a}, n_{b})}$</td>
<td>$\psi'_i + 2\omega'_i - 3(\psi - \omega - 2)(b_i / b)$</td>
</tr>
<tr>
<td>$Z(y_n)<em>{i}^{(n</em>{a}, n_{b})}$</td>
<td>$(\psi - 1)(b_i / b) - \omega'_i$</td>
</tr>
</tbody>
</table>

Table A.2: The shape parameter ratios, $\omega$ and $\psi$, and their derivatives, $\omega'$ and $\psi'$ 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 ($\bar{\tau} = \sum_i y_i \tau_i$) of the shape parameters for the individual species and $c$ is the mole fraction average of the radius of curvature squared $c = \sum_i y_i \bar{c}_i^2$. The species shape parameters for monomers and dimers are defined in Table A.3.

\[
\begin{align*}
\omega &= \bar{\tau} s / b \\
\psi &= \frac{(c s^2)}{(9 b^2)} \\
\omega'_i &= \partial (N \omega) / \partial N_i = (r_i s + \bar{r} s_i - (b_i / b) \bar{r} s) / b \\
\psi'_i &= \partial (N \psi) / \partial N_i = \frac{(r_i^2 s^2 + 2 c s s_i - 2(b_i / b) c s^2)}{(9 b^2)}
\end{align*}
\]
Table A.3: Species shape parameters for monomers and dimers determined from the segment radius, \( r_i = \sigma_i/2 \).  

<table>
<thead>
<tr>
<th>shape</th>
<th>( b_i )</th>
<th>( s_i )</th>
<th>( \tilde{r}_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>monomer</td>
<td>( 4\pi r_i^3/3 )</td>
<td>( 4\pi r_i^2 )</td>
<td>( r_i )</td>
</tr>
<tr>
<td>dimer</td>
<td>( 8\pi r_i^4/3 )</td>
<td>( 8\pi r_i^2 )</td>
<td>( (3/2)r_i )</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>interacting species</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>monomer/monomer</td>
<td>0.919</td>
<td>0.791</td>
<td>0.339</td>
</tr>
<tr>
<td>dimer/dimer</td>
<td>1.754</td>
<td>4.986</td>
<td>1.951</td>
</tr>
<tr>
<td>dim/mon (( \sigma_r \geq 1.0 ))</td>
<td>3.207-2.226( \sigma_r )</td>
<td>-1.347+4.166( \sigma_r )</td>
<td>-1.795+3.544( \sigma_r )</td>
</tr>
<tr>
<td>dim/mon (( \sigma_r &lt; 1.0 ))</td>
<td>3.010-2.028( \sigma_r^{-1} )</td>
<td>0.017-2.802( \sigma_r^{-1} )</td>
<td>-1.997+3.746( \sigma_r^{-1} )</td>
</tr>
</tbody>
</table>
A.7 Figures

A.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. 117

A.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. 118

A.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. 119

A.4 Six classifications of phase behavior 120

A.5 Schematic of a parametrized plot of $\mu_1$ vs. $\mu_2$ 121

A.6 The global phase diagram predicted by the Generalized Flory Dimer theory for a mixture of square-well monomer and dimers. 122

A.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 Konynenberg and Scott 123
Figure A.1: Comparison of GFD equation of state to molecular dynamics simulation results for mixtures of monomers and dimers at $\varepsilon_{22}/\varepsilon_{11} = 0.5, 1.0$ and 1.5, equal segment diameters and equal volume fractions $x_1 v_1 = x_2 v_2$ of the two species.
Figure A.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 $x_2 = 0.111, 0.333, \text{ and } 0.667$ and equal segment diameters.
Figure A.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 A.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 A.5: Schematic of a parametrized plot of $\mu_1$ vs. $\mu_2$ with composition as the parameter. Point A represents the value of $\mu_1$ and $\mu_2$ at coexistence.
Figure A.6: The global phase diagram predicted by the Generalized Flory Dimer theory for a mixture of square-well monomer and dimers.
Figure A.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.
In this appendix, we provide the source code for the programs that were used in preparing this thesis. The following code was used to calculate the ternary phase diagrams presented in Chapter 3. It can easily be modified to calculate binary or higher-order phase diagrams of any number of phases, with proper modification to the integrand subroutine and the initial condition. The parameters NPHASE (number of phases), NCOMP (number of components), NOP (number of particles in each phase), HENRY (set if special initial condition is needed), and CELLLIST (activates neighbor list optimization) are declared at compile time. The code was run on our cluster of Alpha and Athlon processor machines.
program GDI_VLE_P
#include "mainhead4.f"

C*** Put this statement at the beginning of what you want to time
    DELTA = DTIME(TARRAY)

c Set up file for clean program termination
    call term_fil()

c Read in data file (initial condition).
    call rd_data(input,npoints,hen,hh)

c Read in particle configuration files for each phase.
    cnfile='liquid.xyz'
    call readcn(cnfile,1)
    cnfile='vapor.xyz'
    call readcn(cnfile,2)

c Get number of each species in initial configuration
    do i=1,NPHASE
        do k=1,NCOMP
            N(k,i)= 0
        enddo
    enddo

doi=1,NPHASE
    do j=1,NOP
        do k=1,NCOMP
            if(species(j,i).eq.k) N(k,i)=N(k,i)+1
        enddo
    enddo
enddo

c These files are for recording the program output for plotting in xmgr.
    open(unit=17,file=run//'_liq',status='unknown')
    open(unit=18,file=run//'_vap',status='unknown')

c These files are for output to use with Sigmaplot
    open(unit=19,file=run//'_liq_sig',status='unknown')
    open(unit=20,file=run//'_vap_sig',status='unknown')
    write(17,'(i5,'# x_1 T +/- x_1')
    write(18,'(i5,'# x_v T +/- x_v')

    open(unit=7,file=run//'.out',status='unknown')
    WRITE(7, 'Lennard-Jones parameters')

do i=1,NCOMP
    do j=1,NCOMP
        WRITE(7,110) i,j,eps(i,j),i,j,sigmas(i,j)
    enddo
enddo
WRITE(7, *) 'fugacity fraction, species 1 and 2'
WRITE(7,*), xi(1), xi(2)
WRITE(7,*), 'fug_frac(1), fug_frac(2)
WRITE(7,*), x(1,1), x(2,1), avx(1,1), avx(2,1)
WRITE(7,*), n(1,1), n(2,1), n(1,2), n(2,2)
WRITE(7,*), n(1,2), n(2,2)

c output file for XMGR
write(17,*), 0.5*(1.0+avx(1,1)-avx(2,1)), sqrt(3.0/2.0*avx(3,1))
write(18,*), 0.5*(1.0+avx(1,2)-avx(2,2)), sqrt(3.0/2.0*avx(3,2))

c output file for sigmaplt
write(19,*), avx(1,1), avx(2,1), avx(3,1)
write(20,*), avx(1,2), avx(2,2), avx(3,2)

c PRELIM CALCULATIONS ON LJ PARAMETERS
do i=1,NCOMP
  do j=1,NCOMP
    eps_4(i,j) = 4.0*eps(i,j)
    sig2(i,j) = sigmas(i,j)*sigmas(i,j)
  end do
end do
$, \text{sig3} (i,j) = \text{sig2} (i,j) \ast \text{sigmas} (i,j)$. 

Enddo 
Enddo 

write(7,*)
write(7,*)
write(7,120)

** Use initial condition to estimate next coexistence point ******
*****************************************************************************

Calculate G-D integrand using initial condition information.

two, binary component phases

simcount = 0 

depend(simcount) = fug_frac(1)
indpnd(simcount) = fug_frac(3)

ifdef HENRY

F(simcount) = -((hen(1,1)+hen(2,1))-(hen(1,2)+hen(2,2)))*
  (1-depend(simcount))*depend(simcount)+(avx(1,1)-avx(1,2))*
  depend(simcount))/(avx(1,1)-avx(1,2))

#else
call integrnd(F(simcount),depend(simcount),indpnd(simcount))
#endif

Write integrand to file (for keeping track of step size).

open(unit=27,file=run//'int',status='unknown')
write(27,*)) indpnd(simcount),F(simcount),hh

open(unit=37,file=run//'corr.log',status='unknown')
write(37,*)) simcount
write(37,*)) '# update BETA'

Increment independent variable.

indpnd(1) = indpnd(simcount)+ hh

c Use trapezoid predictor to estimate new dependent variable. 

depend(1) = depend(simcount) + hh*F(simcount)

call flush(7)

*****************************************************************************

One complete loop gives one phase point.

Input npoints from main input file.

do 150 simcount = 1,npoints

Check to see if we are being stopped

call chk_term(quitnow)

c if we are, then skip through the rest of the loops
   if(quitnow) goto 150

*** PREDICTOR CYCLES ***
SFLAG = 1

two, binary component phases
fug_frac(3) = indpnd(simcount)
fug_frac(1) = depend(simcount)
fug_frac(2) = 1.0d+0 - fug_frac(1) - fug_frac(3)

c zero accumulators and averages
update=0
c -----phase_a
tens = INT(simcount/10)
ones = MOD(simcount,10)
infile=input//'_a.pred'
call mcnpt(pstep_a,infile,outfile,update,SFLAG,1)

c -----phase_b
infile=input//'_b.pred'
call mcnpt(pstep_b,infile,outfile,update,SFLAG,2)
c Calculate integrand of G-D equation based on
c averages from predictor cycles.
call integrnd(F(simcount),depend(simcount),indpnd(simcount))

c *** CORRECTOR CYCLES ***
SFLAG = 2

c apply corrector
if(simcount.eq.1) then
c trapezoid corrector
   depend(simcount) = depend(simcount-1) +
       hh/2. *( F(simcount) + F(simcount-1))
elseif(simcount.eq.2) then
c second corrector
   depend(simcount) = depend(simcount-2) +
       hh/3. *(F(simcount)+4.*F(simcount-1)+
       F(simcount-2))
else
c third corrector and beyond
   depend(simcount) = depend(simcount-1) +
       hh/24. *(9.*F(simcount)+19.*F(simcount-1)+
       -5.*F(simcount-2)+F(simcount-3))
endif

c Loop over corrector iterations
write(37,*) update, depend(simcount)
do 140 update = 1,ncorr
   fug_frac(3) = indpnd(simcount)
fug_frac(1) = depend(simcount)
fug_frac(2) = 1.0d+0 - fug_frac(1) - fug_frac(3)

c -----phase_a
infile=input//'_a.corr'
call mcnpt(cstep_a,infile,outfile,update,SFLAG,1)
c -----phase_b
    infile=input//'_b.corr'
    call mcnpt(cstep_b,infile,outfile,update,SFLAG,2)

c Calculate integrand of G-D equation based on averages from corrector cycles (including all previous iterations).
    call integrnd(F(simcount),depend(simcount),indpnd(simcount))

c apply corrector
   if(simcount.eq.1) then
      c trapezoid corrector
      depend(simcount) = depend(simcount-1) +
                      hh/2. *( F(simcount) + F(simcount-1))
   elseif(simcount.eq.2) then
      c second corrector
      depend(simcount) = depend(simcount-2) +
                      hh/3. *(F(simcount)+4.*F(simcount-1)+
                           F(simcount-2))
   else
      c third corrector and beyond
      depend(simcount) = depend(simcount-1) +
                      hh/24. *(9.*F(simcount)+19.*F(simcount-1)
                        -5.*F(simcount-2)+F(simcount-3))
   endif

   write(37,*) update, depend(simcount)
   call flush(37)

   140 continue
   write(37,*)
   write(37,*)
   write(37,*) simcount
   write(37,'(3F16.7,2F9.6)')
   call flush(37)

   c *** PRODUCTION CYCLES ***
    SFLAG = 3

   fug_frac(3) = indpnd(simcount)
   fug_frac(1) = depend(simcount)
   fug_frac(2) = 1.0d0 - fug_frac(1) - fug_frac(3)

   update=0

   c -----phase_a
    infile=input//'_a.prod'
    call mcnpt(fstep_a,infile,outfile,update,SFLAG,1)

   c -----phase_b
    infile=input//'_b.prod'
    call mcnpt(fstep_b,infile,outfile,update,SFLAG,2)

c Write output to file.

   WRITE(7,'(I2,6(1X,F9.6),2(1X,F9.5))')
     simcount,indpnd(simcount),depend(simcount),avx(1,1),
     avx(2,1),avx(1,2),avx(2,2),h(1),h(2)

call flush(7)
c output file for XMGR
  write(17,*) 0.5*(1.0+avx(1,1)-avx(2,1)),sqrt(3.0)/2.0*avx(3,1)
  write(18,*) 0.5*(1.0+avx(1,2)-avx(2,2)),sqrt(3.0)/2.0*avx(3,2)

c output file for sigmaplt
  write(19,*) avx(1,1), avx(2,1), avx(3,1)
  write(20,*) avx(1,2), avx(2,2), avx(3,2)

c Write positions to file to record frames.
  cnfile=run//CHAR(tens+48)//CHAR(ones+48)//'_a.xyz'
  call writcn(cnfile,1)
  cnfile=run//CHAR(tens+48)//CHAR(ones+48)//'_b.xyz'
  call writcn(cnfile,2)

c Calculate integrand of G-D equation based on
  c averages from production cycles.
  call integrnd(F(simcount),depend(simcount),indpnd(simcount))

c Write integrand to file (for keeping track of step size)
  write(27,*) indpnd(simcount),F(simcount),hh

c Step to next indpnd
  indpnd(simcount+1) = indpnd(simcount) + hh

  if ( simcount.ne.npoints.and.indpnd(simcount+1) .ge. 1.0) then
   write(?,*) "Fugacity fraction is greater than 1",
   $ indpnd(simcount+1)
  C*** Put this statement again at the end of what you want to time
  DELTA = DTIME(TARRAY)
  C*** DELTA is in seconds - change to hours (or minutes)
  EXTIME = DELTA/3600
  WRITE(7,'('' EXECUTION TIME (CPU HOURS) '',F15.4)') EXTIME
  STOP
endif

  if ( simcount.ne.npoints.and.indpnd(simcount+1) .le. 0.0) then
   write(7,*) "Fugacity fraction is less than 0",indpnd(simcount+1)
  C*** Put this statement again at the end of what you want to time
  DELTA = DTIME(TARRAY)
  C*** DELTA is in seconds - change to hours (or minutes)
  EXTIME = DELTA/3600
  WRITE(7,'('' EXECUTION TIME (CPU HOURS) '',F15.4)') EXTIME
  STOP
endif

  if(simcount.le.2) then
    c ------second,third predictor
    depend(simcount+1) = depend(simcount-1) + 2.*hh*F(simcount)
    else
      depend(simcount+1) = depend(simcount)
      : +hh/24.*(55.*F(simcount)-59.*F(simcount-1)+
      : 37.*F(simcount-2)-9.*F(simcount-3))
  endif

  call flush(7)
call flush(17)
call flush(18)
call flush(19)
call flush(20)
call flush(27)
call flush(37)

150 continue

C*** Put this statement again at the end of what you want to time
DELTA = DTIME(TARRAY)

C*** DELTA is in seconds - change to hours (or minutes)
EXTIME = DELTA/3600
WRITE(7,('' EXECUTION TIME (CPU HOURS) '',F15.4)) EXTIME
stop
end

#include"rd_data.f"
#include"readcn.f"
#include"writcn.f"
#include"mcnpt.f"
#include"sumup.f"
#include"energy.f"
#include"termprog.f"
#include"integrand.f"
ifdef CELL_LIST
#include"new_clist.f"
endif
integer i, j, ii
integer simcount, update, npoints, index, k
integer pstep_a, cstep_a, ncorr, fstep_a
integer pstep_b, cstep_b, fstep_b
integer SFLAG
integer tens, ones
real hh
integer cnunit, IPRINT, IBLOCK, IRATIO, IRATB, auto

CHARACTER TITLE*80

integer species (NOP, NPHASE), N(0:NCOMP, NPHASE), phase
real hen (NCOMP, NPHASE)
real x (NCOMP, NPHASE), avx (NCOMP, NPHASE)
real sigmas (NCOMP, NCOMP), eps (NCOMP, NCOMP)
real sig2 (NCOMP, NCOMP), sig3 (NCOMP, NCOMP)
real eps_4 (NCOMP, NCOMP)
real stdx (NCOMP, NPHASE)
real P, TEMP, h (NPHASE), vol (NPHASE), fug_frac (NCOMP)
real box (NPHASE), fug (NCOMP)
real depend (0:200), indpnd (0:200), F (0:200)

logical quitnow

character cnfile*30
character infile*30
character outfile*30
character input*6
character run*6
character xfilea*30, pfilea*30, dfilea*30, posfilea*30
character xfileb*30, pfileb*30, dfileb*30, posfileb*30

common / block4 / update, simcount
common / block6 / infile, outfile, run, cnfile
common / parblock / TITLE, IPRINT, IBLOCK, IRATIO, IRATB
common / block11 / pstep_a, cstep_a, ncorr, fstep_a
common / block11 / pstep_b, cstep_b, fstep_b

common / syspar / TEMP, P
common / fugacity / fug_frac
common / block13 / vol, box, h
common / bina1 / sigmas, eps
common / bina2 / sig2, sig3, eps_4
common / block2 / species, N
common / block9 / x, avx, stdx
common / block10 / xfilea, pfilea, dfilea
C*** Define these at the beginning (the names can be different except DTIME)

REAL TARRAY(2), DELTA, EXTIME, DTIME

EXTERNAL DTIME
subroutine term_fil()
c  open a file and write a zero in it
c  if you want to exit the program gracefully, edit the file
c  and change the 0 to a 1 or F and the program will exit at
c  the next loop
logical quitnow
quitnow=.false.
open(unit=13,file="STOPNOW",status="unknown")
write(13,*) quitnow
close(unit=13)
return
end

subroutine chk_term(quitnow)
c  open above file and read in the value of quitnow
logical quitnow
open(unit=13,file="STOPNOW",status="old")
read(13,*) quitnow
close(unit=13)
return
end
subroutine rd_data(input,npoints,hen,hh)

#include "mainhead4.f"

c ****************************************************************
c Input parameters to define the system.
cnunit=10

open (unit = cnunit, file = 'system.inp', status = 'unknown',
  : form='formatted')

c Title of run.
read (cnunit, '(A6,1x,I1)') run, auto

c Number of data points
read(cnunit, '(/I7)') npoints

c MC steps in predictor
  **phase_a
read(cnunit, '(/I9)') pstep_a
  **phase_b
read(cnunit, '(/I9)') pstep_b

c MC steps in corrector
  **phase_a
read(cnunit, '(/I9)') cstep_a
  **phase_b
read(cnunit, '(/I9)') cstep_b

c Iterations in corrector
  ** phase_a
read(cnunit, '(/I7)') ncorr

c MC steps in production runs
  **phase_a
read(cnunit, '(/I9)') fstep_a
  **phase_b
read(cnunit, '(/I9)') fstep_b
read(cnunit, ')

c Lennard-Jones parameters for the species.
c **phase_a
do I=1,NCOMP
  read(cnunit, '(3F6.3)') (sigmas(I,J),J=1,NCOMP)
  enddo
  read(cnunit,')
do I=1,NCOMP
  read(cnunit, '(3F6.3)') (eps(I,J),J=1,NCOMP)
  enddo

c Reduced temperature and pressure.
read(cnunit, '(/2F9.4)') TEMP,P

c Fugacity fraction of component 2.
read(cnunit, '(/2G10.8)') fug_frac(1), fug_frac(2)
fug_frac(3) = 1.0d0 - fug_frac(1) - fug_frac(2)
if (auto.eq.0) then

  read mole fraction of component 2 in phase 1
  read(cnunit, '(/2F6.4)') avx(1,1), avx(2,1)
  avx(3,1) = 1.0d0 - avx(1,1) - avx(2,1)

c Henry's law constant for dilute component
c **phase_a
  read(cnunit, '(/2E12.5)') hen(1,1), hen(2,1)

c read mole fraction of component 2 in phase 2
  read(cnunit, '(/2F6.4)') avx(1,2), avx(2,2)
  avx(3,2) = 1.0d0 - avx(1,2) - avx(2,2) - avx(1,2)

c Henry's law constant for dilute component.
**phase_b**

```fortran
read(cnunit, '(/2E12.5)') hen(1,2), hen(2,2)
```

Enthalpy of each phase.

```fortran
read(cnunit, '(/2F9.4)') h(1), h(2)
```

Integration stepsize.

```fortran
read(cnunit,'(/G10.8)') hh
```

```fortran
close (unit = cnunit)
```

```fortran
else
```

```fortran
close(unit= cnunit)
```

```fortran
open(unit = cnunit, file='phase1_auto',status='old')
```

```fortran
read(cnunit,*) avx(1,1), hen(1,1), hen(2,1), h(1)
```

```fortran
avx(2,1) = 1.0d+0 - avx(1,1)
```

```fortran
avx(3,1) = 0.0
```

```fortran
close(unit=cnunit)
```

```fortran
open(unit = cnunit, file='phase2_auto',status='old')
```

```fortran
read(cnunit,*) avx(1,2), hen(1,2), hen(2,2), h(2)
```

```fortran
avx(2,2) = 1.0d+0 - avx(1,2)
```

```fortran
avx(3,1) = 0.0
```

```fortran
close(unit=cnunit)
```

```fortran
hh = (((hen(1,1)+hen(2,1))-(hen(1,2)+hen(2,2)))*
```

```fortran
(1-fug_frac(1))*fug_frac(1)+(avx(1,1)-avx(1,2))*
```

```fortran
fug_frac(1))/(avx(1,1)-avx(1,2))
```

```fortran
hh = 0.02/hh
```

```fortran
if (hh.gt.0.02) hh=0.02
```

```fortran
endif
```

```fortran
input='indata'
```

```fortran
return
```

```fortran
end
```
subroutine readcn ( cnfile, phase )

C *******************************************************************
C ** SUBROUTINE TO READ IN THE CONFIGURATION FROM UNIT 10 **
C *******************************************************************

CHARACTER cnfile*30
REAL RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)
REAL vol(NPHASE), box(NPHASE), h(NPHASE)
REAL rrbox
integer N(NCOMP,NPHASE), species(NOP,NPHASE)

INTEGER CNUNIT, i
PARAMETER ( CNUNIT = 10 )
INTEGER NN, phase

COMMON / config / RX, RY, RZ
common / block13 / vol, box, h
common / block2 / species, N

C ********************************************************************

OPEN ( UNIT = CNUNIT, FILE = cnfile, STATUS = 'OLD')
READ (CNUNIT,* ) NN, box(phase)
DO i=1,NOP
   READ (CNUNIT,* ) RX(i,phase), RY(i,phase), RZ(i,phase),
   & species(i,phase)
ENDDO
CLOSE ( UNIT = CNUNIT )

RETURN
END
subroutine integrnde(F, depend, indpnd)

real F, depend, indpnd
real x(NCOMP,NPHASE), avx(NCOMP,NPHASE), stdx(NCOMP,NPHASE)
common / block9 / x, avx, stdx

F = -((avx(3,1)-avx(3,2))*(1-depend)*depend+(avx(1,1)-avx(1,2))*depend*indpnd)/((avx(1,1)-avx(1,2))*(1-depend)*indpnd+(avx(3,1)-avx(3,2))*depend*indpnd)

return
end
subroutine mcnpt(nstep, infile, outfile, bfile, update, SFLAG, phase)

REAL RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)

INTEGER STEP, NSTEP, IPRINT, IBLOCK, IRATIO, IRATB, I, K, L
INTEGER rnd_num
integer dcount, vcount
integer ACM, ACATMA, ACBOXA
double precision ACV, ACP, ACD, NORM
double precision ach, ACVSQ, ACPSQ
double precision ACDSQ

double precision AVV, AVP, AVD
REAL DENS, TEMP, RCUT, RMIN, PRESUR, VOL, PRES, VN
REAL BOXINV, BOXNEW, RATBOX, RAT12, RAT6, DVOL, DPV
real terme9, DRMXX, DBXX, BETA, DUMMY, RATIO
REAL RRBOX, RATIO, DELTVB, RCUT
REAL RXIOLD, RYIOLD, RZIOLD, RXINEW, RYINEW, RZINEW
real RXINEW2, RYINEW2, RZINEW2

double precision V12OLD, V6OLD, V12NEW, V6NEW

double precision W12OLD, W6OLD, W12NEW, W6NEW

double precision DELV12, DELV6, DELW12, DELW6, DELTV

double precision V6, W6, V12, W12

double precision VLRC, VLRCN, WLRC, WLRCN, VS, WS, PS

donble precision SR3, SR9, VLRC6, WLRC6, VLRC12, WLRC12, PI

real h

real avVOL(NPHASE), BOX(NPHASE), avh(NPHASE)

integer j, ii, jj, update
INTEGE IMOVE, NMOVE

CHARACTER TITLE*80, CNFILE*30

character infile*30, outfile*30

LOGICAL OVRLAP

real NOBS

real SQX2
real SQX2_SUM

real avx2_SUM, AVV_SUM, AVP_SUM, AVD_SUM, avh_SUM, avVOL_SUM
real STDV, STDP, STDD, STDH, STDX (NCOMP, NPHASE)

integer species(NOP, NPHASE), phase
integer N(0:NCOMP, NPHASE), Ntry (NCOMP)
real sigmas(NCOMP, NCOMP)
real eps(NCOMP, NCOMP)
real sig2(NCOMP, NCOMP)
real sig3(NCOMP, NCOMP)
real eps_4 (NCOMP, NCOMP)
real RCUT3
real term3u
real term3w
real term9u
real term9w
integer ACSWAP, scount, tryiden

double precision acx(NCOMP)
real x (NCOMP, NPHASE), avx (NCOMP, NPHASE)
real sratio, fug(NCOMP)
real xnew(NCOMP)

integer NSWAP, SFLAG

integer LIST(NOP), UPLIST(0:NOP), CELLLIST(NOP), HEAD(512), MAP(13312), M

COMMON / cell_vars / LIST, UPLIST, CELLLIST, HEAD, MAP, M
COMMON / config / RX, RY, RZ
common / syspar / TEMP, PRESUR

common / block13 / avVOL, BOX, avh
PARAMETER ( PI = 3.1415927 )

external time,drandm,srand,rand
double precision drandm
integer iseed
integer time

C ** SET DEPENDENT PARAMETERS **

open ( unit = 8, file = infile, status = 'old')
c RUN TITLE
READ (8,('(A7)') ) TITLE
c INTERVAL BETWEEN PRINTS IN CYCLES
READ (8,'(/I7)') IPRINT
c INTERVAL FOR BLOCK AVERAGES
READ (8,'(/I7)') IBLOCK
c INTERVAL FOR UPDATE OF MAXIMUM DISPLACEMENT OF ATOMS IN CYCLES
READ (8,'(/I7)') IRATIO
c INTERVAL FOR UPDATE OF MAXIMUM DISPLACEMENT OF THE BOX IN CYCLES
READ (8,'(/I7)') IRATB

VOL = BOX(phase)*BOX(phase)*BOX(phase)
BOXINV = 1.0 / BOX(phase)
DENS = NOP / VOL
RCUT = 2.5

IF ( RCUT .GT. ( 0.5 * BOX(phase) ) ) then
   print*, 'rcut', rcut, 'box', box(phase)
   STOP 'CUT-OFF TOO LARGE'
endif

DBOXMX = BOX(phase) / 15.0
DRMAX = 0.15

RMIN = 0.70
BETA = 1.0 / TEMP

C ** CALCULATE LONG-RANGE CORRECTIONS FOR LJ POTENTIAL. **
C ** 6 IS FOR ATTRACTIVE CONTRIBUTIONS 12 IS FOR REPULSIVE **

term3u = 0.0
term9u = 0.0
term3w = 0.0
term9w = 0.0
VLRC12 = 0.0
VLRC6 = 0.0
WLRC12 = 0.0
WLRC6 = 0.0
RCUT3  = RCUT*RCUT*RCUT

do  ii=1,NCOMP
  do  jj=1,NCOMP
    SR3  = sig3(ii,jj)/RCUT3
    SR9  = SR3*SR3*SR3
    term9w  = -eps(ii,jj)* sig3(ii,jj)* SR9*4./3.
    term3w  = eps(ii,jj)* sig3(ii,jj)* 2.*SR3
    VLRC12 = term9u * x(ii,phase)* x(jj,phase) + VLRC12
    VLRC6  = term3u * x(ii,phase)* x(jj,phase) + VLRC6
    WLRC12 = term9w * x(ii,phase)* x(jj,phase) + WLRC12
    WLRC6  = term3w * x(ii,phase)* x(jj,phase) + WLRC6
  enddo
enddo

VLRC12  = 8.* PI* DENS* NOP* VLRC12
VLRC6   = 8.* PI* DENS* NOP* VLRC6
WLRC12  = -8.* PI* DENS* NOP* WLRC12/3.
WLRC6   = -8.* PI* DENS* NOP* WLRC6/3.

VLRC  = VLRC12 + VLRC6
WLRC  = WLRC12 + WLRC6

C  ** ZERO ACCUMULATORS **

ratio = 0.0
sratio = 0.0
bratio = 0.0

ACM = 0
ACATMA = 0
ACBOXA = 0

ACV = 0.0
ACP = 0.0
ACD = 0.0
ach = 0.0

ACVSQ = 0.0
ACPSQ = 0.0
ACDSQ = 0.0

dcount = 0
vcount = 0

ACSWAP = 0

do  k=1,NCOMP
  acx(k) = 0.0
enddo

scount = 0

AVV_SUM  = 0.0
AVP_SUM  = 0.0
AVD_SUM  = 0.0
avh_SUM  = 0.0
avx2_SUM = 0.0
avVOL_SUM = 0.0
SQX2_SUM = 0.0

C ** CALCULATE INITIAL ENERGY AND VIRIAL **
call sumup ( RCUT, RMIN, OVRLAP, V12, V6, W12, W6,phase )

#ifdef CELL_LIST
   call LINKS(RCUT,phase)
#endif

C IF ( OVRLAP ) STOP 'OVERLAP IN INITIAL CONFIGURATION'

C ** CALCULATE THE INITIAL ENERGY AND VIRIAL **
VS = ( V12 + V6 + VLRC ) / NOP
WS = ( W12 + W6 + WLRC ) / NOP
PS = DENS * TEMP + ( W12 + W6 + WLRC ) / VOL

C ** ADD LONG RANGE CORRECTIONS **
C ** INTO THE ENERGY AND VIRIAL **
V12 = V12 + VLRC12
V6 = V6 + VLRC6
W12 = W12 + WLRC12
W6 = W6 + WLRC6

NSWAP = NOP
NMOVE = NOP + NSWAP + NOP/10

C ***************************************************************
C ** MAIN LOOP STARTS **
C ***************************************************************
DO 100 STEP = 1, NSTEP
   DO 50 IMOVE = 1,NMOVE
      rnd_num=INT( drandm(0)*NMOVE ) + 1
      if(rnd_num.le.NOP) then
         c ** trial particle displacement **
         dcount = dcount + 1
         c ** select atom to move **
         I =INT( drandm(0)*(NOP-1) ) + 1
         RXIOLD = RX(I,phase)
         RYIOLD = RY(I,phase)
         RZIOLD = RZ(I,phase)
         c ** CALCULATE V FOR AN ATOM IN OLD STATE **
         call energy ( RXIOLD, RYIOLD, RZIOLD, I, RCUT, :
                        V12OLD, V6OLD, W12OLD, W6OLD, SPECIES(I,phase),phase,0)
         c ** MOVE ATOM I **
         c leave new positions in uncorrected form
         RXINEW = RXIOLD + ( 2.0 * drandm(0) - 1.0 ) * DRMAX
         RYINEW = RYIOLD + ( 2.0 * drandm(0) - 1.0 ) * DRMAX
         RZINEW = RZIOLD + ( 2.0 * drandm(0) - 1.0 ) * DRMAX
         c correct positions to stay in central box
         RXIOLD = RXINEW
         RYIOLD = RYINEW
         RZIOLD = RZINEW
      endif
   50 continue
100 continue

C ***************************************************************
RXINEW = RXINEW - ANINT ( RXINEW * BOXINV ) * BOX(phase)
RYINEW = RYINEW - ANINT ( RYINEW * BOXINV ) * BOX(phase)
RZINEW = RZINEW - ANINT ( RZINEW * BOXINV ) * BOX(phase)

** CALCULATE V FOR ATOM IN NEW STATE **

call energy( RXINEW, RYINEW, RZINEW, I, RCUT,
: V12NEW, V6NEW, W12NEW, W6NEW,species(I,phase), phase,1)

** CHECK FOR ACCEPTANCE **

DELV12 = V12NEW - V12OLD
DELV6 = V6NEW - V6OLD
DElw12 = W12NEW - W12OLD
DELW6 = W6NEW - W6OLD
DELTv = DELV12 + DELV6
DELTvb = BETA * DELTv

IF ( DELTB .LT. 75.0 ) THEN
  IF ( DELT .LE. 0.0 ) THEN
    V12 = V12 + DELV12
    V6 = V6 + DELV6
    W12 = W12 + DELW12
    W6 = W6 + DELW6
    RX(I,phase) = RXINEW
    RY(I,phase) = RYINEW
    RZ(I,phase) = RZINEW
    ACATMA = ACATMA + 1
  ENDIF
ENDIF

ELSEIF ( EXP ( - DELTB ) .GT. drandm (0) ) THEN
  V12 = V12 + DELV12
  V6 = V6 + DELV6
  W12 = W12 + DELW12
  W6 = W6 + DELW6
  RX(I,phase) = RXINEW
  RY(I,phase) = RYINEW
  RZ(I,phase) = RZINEW
  ACATMA = ACATMA + 1
ENDIF

ENDIF

** ENDS ATOMS DISPLACEMENT STEP **

elseif(rnd_num.gt.NOP.and.rnd_num.le.(NOP+NSWAP))then
  ** attempt particle identity change **
  scount = scount + 1
  ** select particle **
  I = INT( drandm(0)*(NOP-1) ) + 1
  RXIOLD = RX(I,phase)
  RYIOLD = RY(I,phase)
RZIOLD = RZ(I,phase)

** CALCULATE V FOR A particle IN OLD STATE **

call energy ( RXIOLD, RYIOLD, RZIOLD, I, RCUT,
: V12OLD, V6OLD, W12OLD, W6OLD,species(I,phase),phase,0)

** switch identity of particle **

tryiden = INT( drandm(0)*(NCOMP-1) ) + 1 +species(I,phase)
if (tryiden.gt.NCOMP) tryiden = tryiden - NCOMP

do 10 J = 1,NCOMP
if (J.eq.species(I,phase)) then
 Ntry(J) = N(J,phase) - 1
 xnew(J) = REAL(Ntry(J))/REAL(NOP)
elseif(J.eq.tryiden) then
 Ntry(J) = N(J,phase) + 1
 xnew(J) = REAL(Ntry(J))/REAL(NOP)
else
 Ntry(J) = N(J,phase)
 xnew(J) = x(J,phase)
endif
10 continue

** CALCULATE V FOR A particle IN NEW STATE **

call energy ( RXIOLD, RYIOLD, RZIOLD, I, RCUT,
: V12NEW, V6NEW, W12NEW, W6NEW,tryiden, phase,0)

** Calculate difference in long ranges corrections **

term3u = 0.0
term9u = 0.0
term3w = 0.0
term9w = 0.0
VLRC12 = 0.0
VLRC6 = 0.0
WLRC12 = 0.0
WLRC6 = 0.0
RCUT3 = RCUT*RCUT*RCUT

VLRC12=term9u*(xnew(ii)*xnew(jj)-x(ii,phase)*x(jj,phase))+VLRC12
VLRC6 =term3u*(xnew(ii)*xnew(jj)-x(ii,phase)*x(jj,phase))+VLRC6
WLRC12=term9w*(xnew(ii)*xnew(jj)-x(ii,phase)*x(jj,phase))+WLRC12
WLRC6 =term3w*(xnew(ii)*xnew(jj)-x(ii,phase)*x(jj,phase))+WLRC6

** difference between LRC in old and new state **
VLRC12 = 8.* PI* DENS* NOP* VLRC12
VLRC6 = 8.* PI* DENS* NOP* VLRC6
WLRC12 = -8.* PI* DENS* NOP* WLRC12/3.
WLRC6 = -8.* PI* DENS* NOP* WLRC6/3.

C ** CHECK FOR ACCEPTANCE **

DELV12 = V12NEW - V12OLD + VLRC12
DELV6 = V6NEW - V6OLD + VLRC6
DELW12 = W12NEW - W12OLD + WLRC12
DELW6 = W6NEW - W6OLD + WLRC6
DELTV = DELV12 + DELV6
DELTVB = BETA * DELTV - ALOG(fug(tryiden)/fug(species(I,phase)))

IF ( DELTVB .LT. 75.0 ) THEN
  IF ( DELTVB .LE. 0.0 ) THEN
    V12 = V12 + DELV12
    V6 = V6 + DELV6
    W12 = W12 + DELW12
    W6 = W6 + DELW6
    species(I,phase) = tryiden
    do 25 J = 1,NCOMP
      x(J,phase) = xnew(J)
      N(J,phase) = Ntry(J)
    25 continue
    ACSWAP = ACSWAP + 1
  ELSEIF ( EXP ( - DELTVB ) .GT. drandm(0) ) THEN
    V12 = V12 + DELV12
    V6 = V6 + DELV6
    W12 = W12 + DELW12
    W6 = W6 + DELW6
    species(I,phase) = tryiden
    do 30 J = 1,NCOMP
      x(J,phase) = xnew(J)
      N(J,phase) = Ntry(J)
    30 continue
    ACSWAP = ACSWAP + 1
  ENDIF
ENDIF

C ** ENDS particle identity change STEP **

ELSE
  C ** ATTEMPT A BOX MOVE **

  vcount = vcount + 1
  BOXNEW = BOX(phase) + ( 2.0 * drandm (0) - 1.0 ) * DBOXMX
  RATBOX = BOX(phase) / BOXNEW
  RRBOX = 1.0 / RATBOX
  RCUTN = RCUT * RRBOX

  C ** CALCULATE SCALING PARAMETERS **

  RAT6 = RATBOX ** 6
  RAT12 = RAT6 * RAT6
C ** SCALE ENERGY, AND VIRIAL INCLUDING LRC **

\[ V_{12\text{NEW}} = V_{12} \times \text{RAT}_{12} \]
\[ V_{6\text{NEW}} = V_{6} \times \text{RAT}_{6} \]
\[ W_{12\text{NEW}} = W_{12} \times \text{RAT}_{12} \]
\[ W_{6\text{NEW}} = W_{6} \times \text{RAT}_{6} \]

C ** CALCULATE CHANGE IN ENERGY AND VOLUME **

\[ \Delta E = V_{12\text{NEW}} + V_{6\text{NEW}} - V_{12} - V_{6} \]
\[ \Delta P = \text{PRESUR} \times (\text{BOXNEW}^{3} - \text{VOL}) \]
\[ \Delta V = 3.0 \times \text{TEMP} \times \text{NOP} \times \text{ALOG} (\text{RATBOX}) \]
\[ \Delta \text{THB} = \text{BETA} \times (\Delta E + \Delta P + \Delta V) \]

C ** CHECK FOR ACCEPTANCE **

IF ( \Delta \text{THB} .LT. 75.0 ) THEN
  IF ( \Delta \text{THB} .LE. 0.0 ) THEN
    \[ V_{12} = V_{12\text{NEW}} \]
    \[ V_{6} = V_{6\text{NEW}} \]
    \[ W_{12} = W_{12\text{NEW}} \]
    \[ W_{6} = W_{6\text{NEW}} \]
    \[ \text{DO 98 I = 1, NOP} \]
    \[ RX(I,\text{phase}) = RX(I,\text{phase}) \times \text{RRBOX} \]
    \[ RY(I,\text{phase}) = RY(I,\text{phase}) \times \text{RRBOX} \]
    \[ RZ(I,\text{phase}) = RZ(I,\text{phase}) \times \text{RRBOX} \]
  98 CONTINUE
  \[ \text{BOX(\text{phase}) = BOXNEW} \]
  \[ \text{ACBOXA = ACBOXA + 1} \]
  \[ \text{BOXINV} = 1.0 / \text{BOX(\text{phase})} \]
  \[ \text{VOL} = \text{BOX(\text{phase})}^{3} \]
  \[ \text{DENS} = \text{NOP} / \text{VOL} \]
  \[ \text{RCUT} = \text{RCUTN} \]
ELSEIF ( EXP( - \Delta \text{THB} ) .GT. \text{drandm} (0) )THEN
  \[ V_{12} = V_{12\text{NEW}} \]
  \[ V_{6} = V_{6\text{NEW}} \]
  \[ W_{12} = W_{12\text{NEW}} \]
  \[ W_{6} = W_{6\text{NEW}} \]
  \[ \text{DO 99 I = 1, NOP} \]
  \[ RX(I,\text{phase}) = RX(I,\text{phase}) \times \text{RRBOX} \]
  \[ RY(I,\text{phase}) = RY(I,\text{phase}) \times \text{RRBOX} \]
  \[ RZ(I,\text{phase}) = RZ(I,\text{phase}) \times \text{RRBOX} \]
  99 CONTINUE
\[ \text{BOX(\text{phase}) = BOXNEW} \]
\[ \text{ACBOXA = ACBOXA + 1} \]
\[ \text{BOXINV} = 1.0 / \text{BOX(\text{phase})} \]
\[ \text{VOL} = \text{BOX(\text{phase})}^{3} \]
\[ \text{DENS} = \text{NOP} / \text{VOL} \]
\[ \text{RCUT} = \text{RCUTN} \]
ENDIF
ENDIF

ifdef CELL_LIST
if(1.0/REAL(M)*BOX(phase)*1.005.lt.rcut) call LINKS(rcut,phase)
endif

C ** ENDS ATTEMPTED BOX MOVE **
endif
50 CONTINUE

C Calculate properties at the end of the step.
VN = ( V12 + V6 ) / NOP
PRES = DENS * TEMP + ( W12 + W6 ) / VOL
h = VN + PRESUR/DENS

C ** INCREMENT ACCUMULATORS **
ACM = ACM + 1
ACV = ACV + VN
ACP = ACP + PRES
ACD = ACD + DENS
ach = ach + h
acx(1) = acx(1) + x(1,phase)
acx(2) = acx(2) + x(2,phase)
acx(3) = acx(3) + (1.0d+0-x(1,phase) - x(2,phase))
ACVSQ = ACVSQ + VN ** 2
ACPSQ = ACPSQ + PRES ** 2
ACDSQ = ACDSQ + DENS ** 2

C ** PERFORM PERIODIC OPERATIONS **
IF ( MOD ( STEP, IRATIO ) .EQ. 0 ) THEN
C ** ADJUST MAXIMUM DISPLACEMENT FOR ATOMS **
RATIO = REAL(ACATMA) / REAL(dcount)
IF ( RATIO .GT. 0.5 ) THEN
DRMAX = DRMAX * 1.05
ELSE
DRMAX = DRMAX * 0.95
ENDIF
ACATMA = 0
dcount = 0
sratio = REAL(ACSWAP)/REAL(scount)
ACSWAP = 0
scount = 0
ENDIF
IF ( MOD ( STEP, IRATB ) .EQ. 0 ) THEN
C ** ADJUST MAXIMUM DISPLACEMENT FOR THE BOX **
BRATIO = REAL(ACBOXA)/REAL(vcount)
IF ( BRATIO .GT. 0.5 ) THEN
  DBOXMX = DBOXMX * 1.05
ELSE
  DBOXMX = DBOXMX * 0.95
ENDIF

ACBOXA = 0
vcount = 0
ENDIF

c Calculate block averages.

IF ( MOD ( STEP, IBLOCK) .EQ. 0 ) THEN
  NORM = REAL ( ACM )
  AVV = ACV / NORM
  AVP = ACP / NORM
  AVD = ACD / NORM
  avh(phase) = ach / NORM
  do k=1,NCOMP
    avx(k,phase) = acx(k)/NORM
  enddo

c calculate average volume.
  avVOL(phase) = NOP/AVD

c Summations for calculation of mean and std deviation of block average data.
  AVV_SUM = AVV_SUM + AVV
  AVP_SUM = AVP_SUM + AVP
  AVD_SUM = AVD_SUM + AVD
  avh_SUM = avh_SUM + avh(phase)
  avx2_SUM = avx2_SUM + avx(2,phase)
  avVOL_SUM = avVOL_SUM + avVOL(phase)
  SQX2 = avx(2,phase)* avx(2,phase)
  SQX2_SUM = SQX2_SUM + SQX2

c only reset accumulators if not in corrector segment.
if (update.le.1) then
  ACM = 0
  ACATMA = 0
  ACBOXA = 0
  ACV = 0.0
  ACP = 0.0
  ACD = 0.0
  ach = 0.0
  dcount = 0
  vcount = 0
  ACSTRT = 0
  do k=1,NCOMP
    acx(k) = 0.0
  enddo
scount = 0
end if
ENDIF

100 CONTINUE

C *******************************************************************
C ** MAIN LOOP ENDS **
C *******************************************************************

c Calculate final property averages and standard deviations
NOBS = real(nstep)/real(iblock)

IF (NOBS.GT.1.0) THEN
  avx(2,phase) = avx2_SUM/NOBS
  AVV  = AVV_SUM/NOBS
  AVP  = AVP_SUM/NOBS
  AVD  = AVD_SUM/NOBS
  avh(phase)  = avh_SUM/NOBS
  avVOL(phase) = avVOL_SUM/NOBS

  STDOUT(2,phase)=ABS(NOBS*SQX2_SUM-avx2_SUM*avx2_SUM)/(NOBS*(NOBS-1))
  STDOUT(2,phase) = SQRT(STDOUT(2,phase))
ENDIF

C ** WRITE OUT FINAL CONFIGURATION AND BOXLENGTH **
CNFILE = 'a_phase.xyz'
CALL writcn ( CNFILE,phase )
END
C *******************************************************************
C ** CALCULATES THE TOTAL POTENTIAL ENERGY FOR A CONFIGURATION. **
C **
C ** THE SUBROUTINE RETURNS THE TOTAL POTENTIAL ENERGY AT THE **
C ** BEGINNING AND END OF THE RUN. **
C *******************************************************************

INTEGER phase
REAL RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)
double precision V12, V6, W12, W6
REAL rcut, rmin
REAL avVOL(NPHASE),BOX(NPHASE),avh, BOXL
LOGICAL OVRLAP
REAL RCUTSQ, RMINSQ, VIJ12, VIJ6
REAL RXI, RYI, RZI, RXIJ, RYIJ, RZIJ
REAL SR2, SR6, RIJSQ, BOXINV
integer species(NOP,NPHASE),N(NCOMP,NPHASE)
real sig2(NCOMP,NCOMP)
real sig3(NCOMP,NCOMP)
real eps_4(NCOMP,NCOMP)
INTEGER I, J
COMMON / config / RX, RY, RZ
common / block13 / avVOL,BOX,avh
common / bina2 / sig2,sig3,eps_4
common / block2 / species,N

C *******************************************************************

BOXL= BOX(phase)
OVRLAP = .FALSE.
RCUTSQ = RCUT * RCUT
RMINSQ = RMIN * RMIN
BOXINV = 1.0 / BOXL

V12 = 0.0
V6 = 0.0
W12 = 0.0
W6 = 0.0

C ** LOOP OVER ALL THE PAIRS IN THE LIQUID **

DO 100 I = 1, NOP - 1
   RXI = RX(I,phase)
   RYI = RY(I,phase)
   RZI = RZ(I,phase)

   DO 99 J = I + 1, NOP
      RXIJ = RXI - RX(J,phase)
RYIJ = RYI - RY(J,phase)
RZIJ = RZI - RZ(J,phase)
c ** minimum image **
RXIJ = RXIJ - ANINT ( RXIJ * BOXINV ) * BOXL
RYIJ = RYIJ - ANINT ( RYIJ * BOXINV ) * BOXL
RZIJ = RZIJ - ANINT ( RZIJ * BOXINV ) * BOXL
RIJSQ = RXIJ * RXIJ + RYIJ * RYIJ + RZIJ * RZIJ

IF ( RIJSQ .LT. RMINSQ ) THEN
  OVRLAP = .TRUE.
  RETURN
ELSEIF ( RIJSQ .LT. RCUTSQ ) THEN
  SR2 = sig2(species(i,phase),species(j,phase)) / RIJSQ
  SR6 = SR2 * SR2 * SR2
  V12 = IK12 + SR6 * eps_4(species(i,phase),species(j,phase))
  V6 = V6 + V12
  W12 = W12 + V12
  W6 = W6 + V12 * 0.5
ENDIF
99 CONTINUE
100 CONTINUE

W12 = 12.0 * W12 / 3.0
W6 = 12.0 * W6 / 3.0
RETURN
END
SUBROUTINE LINKS ( RCUT, phase )

C *******************************************************************
C ** ROUTINE TO SET UP LINKED LIST AND THE HEAD OF CHAIN ARRAYS **
C ** **
C ** EACH ATOM IS SORTED INTO ONE OF THE M**3 SMALL CELLS. **
C ** THE FIRST ATOM IN EACH CELL IS PLACED IN THE HEAD ARRAY. **
C ** SUBSEQUENT ATOMS ARE PLACED IN THE LINKED LIST ARRAY. **
C ** ATOM COORDINATES ARE ASSUMED TO BE BETWEEN -0.5 AND +0.5. **
C ** THE ROUTINE IS CALLED EVERY TIMESTEP BEFORE THE FORCE ROUTINE.**
C *******************************************************************

INTEGER M, phase

REAL RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)
INTEGER HEAD(512), LIST(NOP), UPLIST(0:NOP), MAP(13312)
INTEGER CELLIST(NOP)

REAL CELLI, RCUT, CELL, BOX(NPHASE), avvol(NPHASE), avh(NPHASE)
INTEGER ICELL, I, NCELL

COMMON / config / RX, RY, RZ
common / block13 / avVOL, BOX, avh
COMMON / cell_vars / LIST, UPLIST, CELLIST, HEAD, MAP, M

C *******************************************************************
C ** ZERO HEAD OF CHAIN ARRAY **
C
M = int(box(phase)/(rcut*1.01))
if (M.gt.8) M=8

DO 10 ICELL = 1, M**3
    HEAD(ICELL) = 0
10 CONTINUE

CELLI = REAL ( M )/ BOX(phase) / 1.005
CELL = 1.0 / CELLI

IF ( CELL .LT. RCUT ) THEN
    STOP ' CELL SIZE TOO SMALL FOR CUTOFF '
ENDIF

C *******************************************************************
C ** SORT ALL ATOMS **
C
DO 20 I = 1, NOP
    ICELL = 1 + INT ( RX(I,phase) * CELLI + real(M)*0.5 )
    : + INT ( RY(I,phase) * CELLI + real(M)*0.5 ) * M
    : + INT ( RZ(I,phase) * CELLI + real(M)*0.5 ) * M * M
    UPLIST(I) = 0
    UPLIST(HEAD(ICELL)) = I
    LIST(I) = HEAD(ICELL)
    HEAD(ICELL) = I
    CELLIST(I)=ICELL
20 CONTINUE
call maps
RETURN
END
SUBROUTINE updtlist ( I,phase,rcut )

C *******************************************************************
C ** ROUTINE TO SET UP LINKED LIST AND THE HEAD OF CHAIN ARRAYS  **
C **
C ** Linked lists are updated when an atom is moved from one cell **
C ** to another  **
C *******************************************************************

INTEGER   M, phase
REAL       RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)
REAL       RXIOLD, RYIOLD, RZIOLD
INTEGER   HEAD(512), LIST(NOP), UPLIST(0:NOP), MAP(13312)
REAL       CELLI, RCUT, CELL, BOX(NPHASE),avvol(NPHASE),avh(NPHASE)
INTEGER   ICELL, I, ICELLOLD, CELLLIST(NOP)
COMMON / config / RX, RY, RZ
common / block13 / avVOL,BOX,avh

COMMON / cell_vars / LIST, UPLIST,CELLLIST, HEAD, MAP,M

C*******************************************************************

C Check to see if the atom changed cells

CELLI = REAL ( M )/BOX(phase)/1.005
ICELLOLD =CELLLIST(I)

ICELL = 1 + INT ( RX(I,phase) * CELLI + real(M)*0.5 )
: + INT ( RY(I,phase) * CELLI + real(M)*0.5 ) * M
: + INT ( RZ(I,phase) * CELLI + real(M)*0.5 ) * M * M

If (ICELLOLD.ne.ICELL) then
C Remove atom from the old cell and fix LIST and UPLIST
if(LIST(I).eq.0.and.UPLIST(I).eq.0) then
    HEAD(ICELLOLD)= 0
elseif(LIST(I).eq.0) then
    LIST(UPLIST(I))= 0
elseif(UPLIST(I).eq.0) then
    HEAD(ICELLOLD)=LIST(I)
    UPLIST(LIST(I))= 0
else
    UPLIST(LIST(I)) = UPLIST(I)
    LIST(UPLIST(I)) = LIST(I)
endif
C Add atom to the list at its new location
LIST(I) = HEAD(ICELL)
if(LIST(I).ne.0) UPLIST(LIST(I)) = I
UPLIST(I) = 0
HEAD(ICELL) = I
CELLLIST(I)=ICELL
endif

RETURN
END
subroutine maps

COMMON /cell_vars/ LIST, UPLIST, CELLLIST, HEAD, MAP, M

C *******************************************************************
C ** ROUTINE TO SET UP A LIST OF NEIGHBOURING CELLS **
C ** **
C ** THIS SUBROUTINE SETS UP A LIST OF THE THIRTEEN NEIGHBOURING **
C ** CELLS OF EACH OF THE SMALL CELLS IN THE CENTRAL BOX. THE **
C ** EFFECTS OF THE PERIODIC BOUNDARY CONDITIONS ARE INCLUDED. **
C ** THE SUBROUTINE IS CALLED ONCE AT THE BEGINNING OF THE **
C ** SIMULATION AND THE MAP IS USED IN THE FORCE SUBROUTINE **
C *******************************************************************

INTEGER M
INTEGER LIST(NOP), UPLIST(0:NOP), HEAD (512), MAP (13312)
INTEGER IX, IY, IZ, IMAP, ICELL, CELLLIST(NOP)

C *******************************************************************
C ** STATEMENT FUNCTION TO GIVE CELL INDEX **
ICELL(IX, IY, IZ) = 1 + MOD (IX - 1 + M, M)
: + MOD (IY - 1 + M, M) * M
: + MOD (IZ - 1 + M, M) * M * M

C ** FIND HALF THE NEAREST NEIGHBOURS OF EACH CELL **
DO 50 IZ = 1, M
DO 40 IY = 1, M
DO 30 IX = 1, M
IMAP = (ICELL (IX, IY, IZ) - 1) * 26
MAP (IMAP + 1) = ICELL (IX + 1, IY, IZ)
MAP (IMAP + 2) = ICELL (IX + 1, IY + 1, IZ)
MAP (IMAP + 3) = ICELL (IX, IY + 1, IZ)
MAP (IMAP + 4) = ICELL (IX - 1, IY + 1, IZ)
MAP (IMAP + 5) = ICELL (IX + 1, IY, IZ - 1)
MAP (IMAP + 6) = ICELL (IX + 1, IY + 1, IZ - 1)
MAP (IMAP + 7) = ICELL (IX, IY + 1, IZ - 1)
MAP (IMAP + 8) = ICELL (IX - 1, IY + 1, IZ - 1)
MAP (IMAP + 9) = ICELL (IX + 1, IY, IZ + 1)
MAP (IMAP + 10) = ICELL (IX + 1, IY + 1, IZ + 1)
MAP (IMAP + 11) = ICELL (IX, IY + 1, IZ + 1)
MAP (IMAP + 12) = ICELL (IX - 1, IY + 1, IZ + 1)
MAP (IMAP + 13) = ICELL (IX, IY, IZ + 1)
MAP (IMAP + 14) = ICELL (IX - 1, IY, IZ)
MAP (IMAP + 15) = ICELL (IX - 1, IY - 1, IZ)
MAP (IMAP + 16) = ICELL (IX, IY - 1, IZ)
MAP (IMAP + 17) = ICELL (IX + 1, IY - 1, IZ)
MAP (IMAP + 18) = ICELL (IX - 1, IY, IZ + 1)
MAP (IMAP + 19) = ICELL (IX - 1, IY - 1, IZ + 1)
MAP (IMAP + 20) = ICELL (IX, IY - 1, IZ + 1)
MAP (IMAP + 21) = ICELL (IX + 1, IY - 1, IZ + 1)
MAP (IMAP + 22) = ICELL (IX - 1, IY, IZ - 1)
MAP (IMAP + 23) = ICELL (IX - 1, IY - 1, IZ - 1)
MAP (IMAP + 24) = ICELL (IX, IY - 1, IZ - 1)
MAP( IMAP + 25 ) = ICELL( IX + 1, IY - 1, IZ - 1 )
MAP( IMAP + 26 ) = ICELL( IX , IY , IZ - 1 )

30  CONTINUE
40  CONTINUE
50  CONTINUE

RETURN
END
SUBROUTINE writcn ( cnfile,phase )

C *******************************************************************
C ** SUBROUTINE TO WRITE OUT THE CONFIGURATION TO UNIT 10 **
C *******************************************************************

CHARACTER cnfile*30
REAL RX(NOP,NPHASE), RY(NOP,NPHASE), RZ(NOP,NPHASE)
REAL vol(NPHASE),BOX(NPHASE),h(NPHASE)
integer update, simcount,i,phase

integer species(NOP,NPHASE)
integer N(NCOMP,NPHASE)

INTEGER CNUNIT
PARAMETER ( CNUNIT = 10 )

COMMON / config / RX, RY, RZ
common / block13 / vol,BOX,h
common / block2 / species,N
common / block4 / update,simcount

C ********************************************************************

OPEN ( UNIT = CNUNIT, FILE = cnfile, STATUS = 'UNKNOWN')

WRITE ( CNUNIT,* ) NOP, BOX(phase)

DO i=1,NOP
  WRITE ( CNUNIT,* ) RX(i,phase), RY(i,phase), RZ(i,phase),
     species(i,phase)
ENDDO

CLOSE ( UNIT = CNUNIT )

RETURN
END