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Molecular Modeling of Shape and Polydispersity Effects on Polymer Solution Phase Behavior

by

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ABSTRACT

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This thesis extends and applies statistical associating fluid theory (SAFT) to model phase behavior in polydisperse polymer solutions. SAFT is a molecular based equation of state, used for modeling thermodynamic properties of chain molecules. Knowledge of phase behavior in polymeric systems is important at all stages of polymer processing and manufacturing and is essential for controlling the properties of the polymer, optimizing separation conditions and choosing operating conditions to mitigate fouling due to phase splitting. In particular this thesis has four main contributions.

First, we evaluate the ability of the SAFT formalism to model the effect of solvent shape on phase behavior. We develop a model for the incipient agglomeration temperature in a slurry polymerization reactor by correlating agglomeration to the solid-liquid phase transition in the reactor. We demonstrate that the model can predict the effect on agglomeration of cyclic, linear or branched carriers.

Secondly, we evaluate the ability of the Perturbed-Chain extension to SAFT (PC-SAFT) to model gas solubility in long chain fluids at conditions of high pressure and high temperature. PC-SAFT, unlike conventional approaches, is shown to correctly account
for the dependence of phase behavior as a function of *chain length asymmetry* between the solute and solvent.

Thirdly, we develop robust and efficient algorithms that allow stability analysis and phase equilibrium calculations in molecular weight polydisperse polymer as well as copolymer solutions using a methodology where the size of the system of equations specifying equilibrium is *independent* of the number of pseudocomponents used to represent the polymer molecular weight distribution.

Finally, we present a novel approach to account for the effect of compositional polydispersity in dipolar copolymer solutions where the size of the system of equations specifying equilibrium is *independent* of the number of pseudocomponents used to represent the compositional distribution. Compositional polydispersity refers to the fact that there is a distribution with respect to the comonomer incorporation in the various pseudocomponents of a copolymer. We then use this algorithm to elucidate the effect of pressure, molecular weight, average comonomer concentration and compatibilization on the phase behavior of compositionally polydisperse dipolar copolymer solutions.
To my parents, sister and late grandfather.
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Chapter 1

Introduction

Polymers, long repeated chains built up from small sub-units called monomers, are useful materials because they provide a range of favorable mechanical, thermal, chemical and optical properties. The ease of processability and the range of physical properties exhibited by polymers make them an ideal candidate for a range of applications. Polymers can be naturally occurring (proteins and cellulose) or synthetic e.g. Polyethylene which is a homopolymer made from ethylene, and Poly (ethylene-co-methyl acrylate) which is copolymer formed by polymerizing ethylene and methyl acrylate. The ubiquity of polymers can be appreciated from the fact that in 1996 polymers accounted for $8.2 billion or more than 45% of the chemical trade surplus in the U.S. Manufacturing these complex materials requires detailed knowledge of their phase behavior in solution.

Polymers are frequently manufactured in solutions which consist of the polymer, monomer, carrier for the catalyst and other additives. Because of highly non-ideal behavior, such solutions are prone to splitting into multiple phases as the temperature, pressure or the composition of the reaction mixture changes. Deciding on the optimum processing condition for such solution requires knowledge of the phase behavior and how the phase behavior is affected by molecular characteristics like shape, size, branching, polarity and polydispersity of the polymer. Also for polymer synthesis reactions that are carried out in multi-phase conditions, the thermodynamics determines the equilibrium
composition of the various constituents in the reactor, which in turn determines the final properties of the polymer produced.

Experimental determination of phase behavior is very expensive because of the often extreme processing conditions of pressure and temperature in the reactor. Also limited experimental data cannot be confidently extrapolated outside of the range that such data is measured at. This has created the need for accurate theories such as the Statistical Associating Fluid Theory\(^1\)\(^-\)\(^4\) (SAFT) that can predict polymer solution phase behavior by modeling polymer characteristics at a molecular level. In this thesis we validate the ability of the SAFT formalism to account for the effect of molecular shape on phase behavior and develop methodologies that can be used to efficiently predict the effect of polydispersity in molecular weight and polydispersity in comonomer content, on phase behavior in polydisperse copolymer solutions. In the next section we present a description of the contributions of this thesis.

1.1 Contribution of this research

This thesis has four major contributions, each of which is summarized below:

- We develop a model to predict agglomeration in polymer slurry reactors – Agglomeration in polymer slurry reactors leads to fouling, difficulty in carrier (solvent) separation and deterioration in the properties of the formed polymer. We present a model in Chapter 2 that correlates the agglomeration temperature in the reactor with the solid-liquid transition temperature. This model is successfully able to predict the increase in agglomeration temperature on going from cyclic to
linear to branched carriers. This validates the ability of SAFT, which is the thermodynamic model used for the liquid state, to account for the effect of carrier shape on phase behavior, when the carrier SAFT parameters are fitted to pure component vapor pressure and liquid density.

- We validate the accuracy of the Perturbed Chain extension to SAFT (PC-SAFT\textsuperscript{5,6}) equation of state for modeling highly size asymmetric mixtures and in the process develop a predictive model for hydrogen. PC-SAFT is a modification to SAFT that accounts for the effect of chain length on dispersion interactions. This should make PC-SAFT a better model for long chain molecules. In Chapter 3 we test this assertion by modeling phase equilibrium in highly asymmetric systems (gas solubility in hydrocarbons). PC-SAFT is shown to quantitatively model gas solubility over a range of temperature, pressure and asymmetry where conventional methodologies fail. The hydrogen PC-SAFT parameters that we present in Chapter 3 are seen to predict hydrogen solubility in a range of hydrocarbons without the need for any binary interaction parameter fitted to experimental data.

- The success of the SAFT based formalism to model chain length asymmetry provides the impetus to model chain length polydispersity in polymer solutions. Chain length polydispersity refers to the fact that a polymer does not exist as an entity with a single molecular weight (or chain length) but has a distribution of molecular weights. For chain length polydisperse polymer and copolymer solutions we develop robust and efficient algorithms for thermodynamic stability analysis and phase equilibrium calculations characterized by the invariance of the
size of system of equations specifying the problem with increasing number of polymer pseudocomponents used to represent the polymer molecular weight distribution.

- The next level of complexity in copolymers is compositional polydispersity, i.e. the presence of comonomer distribution in the copolymer. We develop a computationally efficient algorithm to model compositional polydispersity in dipolar copolymer solutions. Subsequently we use this algorithm to elucidate the effect of pressure, molecular weight, average comonomer content and compatibilization on the phase behavior of compositionally polydisperse dipolar copolymer solutions.

We perform the above developments within the SAFT framework. Since a number of equations of state have been used to model polymer solution phase behavior over the last sixty years, in the next section we briefly review the evolution of equations of state for polymer solutions.

1.2 Thermodynamic models for polymer solutions and melts

More than Sixty years ago Flory\textsuperscript{7}, Huggins\textsuperscript{8} and Staverman-Santen\textsuperscript{9} first proposed a thermodynamic model for polymer solutions. Since then polymer equation of states have evolved significantly starting with lattice models to the more sophisticated continuum tangent sphere models which are increasingly being applied for modeling phase behavior in polymer systems. Lambert et al.\textsuperscript{10} provide a comprehensive survey on the evolution of
equations of state for polymer melts and solutions. Curro provides a more detailed review on the fundamental statistical mechanical basis of compressible lattice models\textsuperscript{11}.

Primarily equations of state for chain molecules can be classified into lattice models or continuum models. Figure 1.1 shows the difference between a lattice and continuum model of a liquid. In the lattice model the molecules in the fluid are constrained to be present on the lattice sites as shown while the continuum model makes no such assumption. Lattice based approaches have been extensively used by the polymer community but have limited predictive capability. However the approximation in lattice models that the fluid adopts a discrete solid like structure in space allows for simple analytical solutions. Recent advances in statistical mechanics have led to the development of accurate continuum models which provide a better representation of the fluid state. Continuum models which follow from advances in statistical mechanical theories of integral equations or perturbation theory provide a more realistic structure of the polymeric fluid and can be used over the whole density range unlike lattice theories. The improved physical basis of continuum models comes at the expense of simplicity. Continuum theories are in general more complicated than lattice theories and may require numerical solution at some point. In this section we briefly review developments in modeling polymer solution using both the lattice and continuum approaches. This also serves to motivate our choice of the SAFT\textsuperscript{1-4} formalism for the developments proposed in this thesis. Figure 1.2 depicts the evolution of equations of state for polymer solutions.
1.2.1 Lattice Models

In the Flory-Huggins theory the Gibbs energy of mixing is determined as the sum of the enthalpic and entropic contribution. The enthalpy of mixing is determined by assigning energy of interactions to each kind of segment interaction (polymer-solvent, polymer-polymer and solvent-solvent) and summing the interaction between nearest neighbors. The change in entropy is related to the fraction of sites occupied by the polymer and

Figure 1.1: Representation of a polymer (filled spheres) in a solvent (hollow spheres) in a lattice model (top) and continuum model (bottom).
solvent segments on the lattice. The main drawback of the Flory-Huggins theory is that the lattice is incompressible which precludes the effect of pressure on phase behavior. Thus it is unable to model the lower critical solution temperature (LCST) phase transition in polymer solutions which is caused due to the difference in the compressibility of the solvent and the polymer near the critical temperature of the solvent. Also the fact that the theory treats the liquid state as a solid like structure, and accounts only for nearest neighbor interactions further limits the applicability of the theory to provide fundamental understanding of phase behavior.

The incompressible lattice can be modified in three ways to yield the cell, lattice fluid and lattice hole models, which can account for the effect of pressure variation on the
phase behavior. In the cell model the segments forming the chain molecule can move and vibrate about their equilibrium position within their cell; in the lattice fluid model the lattice is partially filled and the unfilled sites are treated as a different component; and combining both the above methods for incorporating volume change provides the lattice hole model.

**Cell Models** - The compressibility in Prigogine’s cell model (PCM)\(^{12}\) is accounted for by using a partition function (which includes volume dependence) with a lattice which is essentially the same as that for the Flory-Huggins model. The partition function in this case is described in terms of the molecule’s internal degrees of freedom (\(c\)). \(c\) is an empirical parameter and is not clearly related to any molecular characteristic of the chain. The Flory-Orwoll-Vrij (FOV)\(^{13}\) EOS simplifies Prigogine’s cell model by replacing the face-centered cubic geometry for the lattice with a simple cubic geometry. The Perturbed-Hard-Chain (PHC) theory\(^{14}\) modifies PCM to account for some important boundary limits. The PHC theory obeys the ideal gas limit, the external degrees of freedom go to zero at closest packing and the potential energy depends additionally on temperature compared to PCM and FOV where the potential energy only depends on volume. Kim et al.\(^{15}\) simplified the PHC theory equations and obtained the SPHC theory which tended to be preferentially used over PHCT.

**Lattice Fluid Models** - The Lattice Fluid equation of state of Sanchez–Lacombe (SL)\(^{16,17}\) for chain molecules incorporates compressibility in the incompressible lattice by including vacant lattices. The Sanchez-Lacombe equation as originally developed did not obey the ideal gas limit and it has since been modified by Neau\(^{18}\) to what is called the Modified Sanchez-Lacombe (MSL). The SL model assumes random mixing of mers and
vacancies while Costas and Sanctuary\textsuperscript{19,20} EOS assumes random mixing of m-mer and vacancy contact sites. Panayiotou and Vera\textsuperscript{21} use the quasi-chemical approximation\textsuperscript{22} to obtain non-random mixing of vacancies and mers.

\textit{Hole Models} - The Hole model accounts for compressibility by incorporating both lattice vacancies and varying the cell volume. Hence the free volume and lattice energy are functions of the lattice site volume ($\omega$) and the fraction of occupied sites ($\gamma$). This requires the dependence of the free volume and lattice energy on $\gamma$ and $\omega$ to be specified. The Simha-Somcynsky\textsuperscript{23} model was one of the earlier hole models. Nies and Stroeks modify the hole model by using Guggenheim’s expression\textsuperscript{24} and subsequently the quasi-chemical approximation\textsuperscript{25} for the combinatorial factor and the number of mer-mer nearest neighbours. All the lattice based models suffer from the shortcomings mentioned earlier and hence are limited in their ability to predictively model phase behavior in polymer solutions. This has led to the development of continuum based models for polymer solutions.

\subsection*{1.2.2 Continuum Models}

Since the 1980’s a lot of progress has been made in developing continuum models for describing chain molecules like polymers. Most of this work has been on a simple model which represents a chain fluid as freely jointed tangent spheres. Despite the simplicity of this model it captures important properties of polymers like chain connectivity and excluded volume. The hard chain (formed by tangentially bonding hard spheres) can be used as a reference system for perturbation theories. This is an improvement over
conventional equations of state which use hard spheres as the reference fluid. The attractive term in most hard chain based equations of state is incorporated as a perturbation using statistical mechanical perturbation theory. Continuum models for polymers can be characterized as being based on extension of lattice model, integral equation theory or thermodynamic perturbation theory. We review each of these methods next.

1.2.2.1 Generalized Flory Theory

Dickman and Hall\textsuperscript{26} proposed the first equation of state for a freely joined hard sphere chain by replacing the site occupation fraction of chains on a lattice with the packing fraction of hard sphere chains. The key variable in this approach is the insertion probability \((pr)\), which is the probability of inserting an \(m\)-mer into a random configuration of \(m\)-mers without creating any overlap. Dickman and Hall\textsuperscript{26} approximated \(pr\) as the probability of randomly inserting \(m\) monomers into a fluid of monomers following the original Flory and Flory-Huggins lattice theories\textsuperscript{27,28}. The comparison of this theory with molecular simulation was not very encouraging because their approach didn't account for chain connectivity properly. Honnell and Hall\textsuperscript{29} addressed this deficiency by developing the Generalised Flory Dimer Theory which incorporated information about both monomer and dimer insertion probability into a fluid of monomers and dimers respectively. This modification of the GF theory has been shown to be in good agreement for up to 192 mers\textsuperscript{30}. The GF and GFD chains for purely repulsive fluids has been extended to square well attractive chains by Yethiraj and Hall\textsuperscript{31}. 
The GFD theory has also been extended\textsuperscript{32,33} for heterosegmented chains i.e. the segments comprising the chain are not all of the same size.

1.2.2.2 Integral equation based theories

Integral equations can be used to determine the correlations between the segments forming the chain which can be used to obtain the thermodynamic properties of the fluid. Schweizer and Curro\textsuperscript{34} provide a review of advances in integral equation theory. The reference interaction site model for polymeric liquids (PRISM) developed by Schweizer and Curro\textsuperscript{34,36} by extending the RISM integral-equation theory\textsuperscript{37,38} to oligomers and polymers represents the local structure in the polymeric fluid well. However this theory requires considerable numerical computation and does not provide an analytical equation of state for polymers, thus it has not been used for phase equilibria calculations in chain molecules. Also the thermodynamic properties predicted by PRISM have been shown to be poor\textsuperscript{39}.

The solution of the Percus-Yevick (PY) integral equation for the structure of a chain fluid provides a good description of the thermodynamics and phase behavior in chain molecules. Chiew\textsuperscript{40} by using the PY closure and Change and Sandler\textsuperscript{41} by using Wertheim’s Integral equation theory\textsuperscript{42,43} derived an accurate equation of state for hard sphere chains. The reference part of the Perturbed hard sphere chain theory (PHSCT) developed by Song et al.\textsuperscript{44,45} is based on a generalized form of the PY integral equation theory for hard sphere chains determined by Chiew\textsuperscript{40}. A van der Waals attraction term is added as perturbation to the repulsive term in the PHSCT.
1.2.2.3 Thermodynamic Perturbation Theory – (TPT) based theories

Wertheim developed the thermodynamic perturbation theory of polymerization (TPT) \(^{46}\) for hard sphere chains by expanding the Helmholtz energy in a series of integrals of molecular distribution functions and the association potential. Wertheim’s first order theory (TPT1) is applicable to flexible chain molecule while the second order theory (TPT2) accounts for chain branching but requires detailed triplet distribution function\(^{47}\). Wertheim\(^{42,43,48,49}\) for a polydisperse mixture of chain aggregates and Chapman et al.\(^{50}\) for a monodisperse mixture derived the change in enthalpy on chain formation by considering a mixture of associating hard spheres in the limit of complete association. This is the key to the SAFT formalism and has led to the developments of equations of state for chains formed from monomeric segments. The statistical mechanical basis of SAFT makes it possible to extend the equation of state by systematically including more physics in the theory.

Ghonasgi et al.\(^{51}\) have extended the theory to include the effect of intramolecular association. The TPT1 approach has been extended for attractive segments like Square-Well\(^{52}\), Lennard-Jones (LJ)\(^{53,54}\) and Yukawa. Chapman\(^{54}\) extended Wertheim’s theory to associating LJ spheres and chains. Ghonasgi and Chapman\(^{55}\) tested TPT1 for associating LJ chains. Banaszak et al.\(^{53}\) and Johnson et al.\(^{56}\) tested the extensions of Wertheim’s theory for pure LJ chains, and Ghonasgi et al.\(^{57,58}\) demonstrated the theory for mixtures of LJ chains. Perez\(^{59}\), Kraska and Gubbins\(^{60}\) and Blas and Vega\(^{61}\) applied SAFT-LJ to real systems\(^{62}\). These and other development in the TPT1 formalism are reviewed by Müller and Gubbins\(^{63}\). Other improvements have been made by deriving better chain term by
bonding dimers\textsuperscript{64} or trimers\textsuperscript{65} to form long chains. These chain equations of state are in better agreement with simulation data for long chains.

All the above incarnations of SAFT account for the attractive dispersion attraction at the segment level. Gross and Sadowski\textsuperscript{15,6}, by incorporating the dispersion contribution as a perturbation to a hard chain (named as the Perturbed Chain SAFT or PC-SAFT), included the effect of chain connectivity on the dispersion term. This approach in many cases has provided a better prediction of phase behavior in mixtures of long chain molecules as well as polymer solutions\textsuperscript{6,66,67}. Although the SAFT formalism correctly captures the effect of chain length on thermophysical properties a major challenge remained of accurately including dipolar interactions in the chain equation of state. Jog and Chapman\textsuperscript{68} provide a solution to this problem with the Polar-SAFT approach. In this approach they account for dipolar interactions at the segment level using U-expansion perturbation theory\textsuperscript{69} and form the dipolar chain molecule by bonding polar and non-polar chains. This approach is seen to have predictive capability in modeling dipolar interactions from small molecules to polar copolymers with multiple dipolar groups\textsuperscript{70,71}.

SAFT offers several advantages being a statistical mechanics based equation of state. SAFT parameters can be related to physical attributes of model molecules and follow predictable trends in a given homologous series. These parameters are transferable hence parameters fitted for one fluid do not change as other components in the mixture change. Since the equation of state has a theoretical basis, the parameters regressed from a limited set of data can be used to extrapolate the data outside the range of fit. This feature is important for engineers who lack sufficient thermodynamic data for product and process design and limitations on time and money make it impractical for them to
measure additional data. The SAFT formalism has proved successful in modeling a range of mixtures from gases to small molecules to copolymers with associating and dipolar interactions, a review of which can be found elsewhere\textsuperscript{72,73}. In this thesis we verify the capability of the SAFT formalism to accurately model shape and chain length effects in highly size asymmetric mixtures and present algorithms to harness the potential of this physically based equation of state to account for polydispersity in polymeric mixtures. In the next section we present a detailed explanation of the SAFT equation of state.

### 1.3 The SAFT Equation of State

SAFT is based on Wertheim’s theory for associating fluids\textsuperscript{42,43,48,49}. Association is a short ranged anisotropic and highly directional interaction that leads to the formation of relatively long-lived clusters as in hydrogen bonding. Chapman et al.\textsuperscript{2,50,74,75} extended Wertheim’s theory of associating fluids to mixtures and covalently bonded linear chains of fixed length by considering the limit of complete association. In SAFT the fluid of interest is initially considered to be a mixture of unconnected segments. SAFT then includes a chain connectivity term to account for the bonding of various groups to form a chain molecule and then explicitly accounts for intermolecular hydrogen bonding. Expressions for the chain formation term and the association term come from extensions of Wertheim's first order perturbation theory. A mean field dispersion term is added to this perturbation expansion. The residual Helmholtz energy (residual to an ideal gas at the same temperature and density) of a fluid of chains is written as a sum of contributions from unbonded segments, chain formation and association. The SAFT equation of state
thus captures the effects of non-spherical shape and association explicitly. This characterizes all versions of SAFT, though different versions may differ in the approach to incorporate mean field attractive interactions. This thesis uses two flavors of the mean field dispersion term. The first is similar to the one proposed by Alder et al. \(^{76}\) and used by Chen and Kreglewski \(^{77}\) in the BACK equation of state. Huang and Radosz first proposed this dispersion term for SAFT and fitted parameters for a variety of pure compounds \(^4\) and generalized it to mixtures \(^3\). This is referred to as the CK-Dispersion term. The other dispersion term is the PC-Dispersion term proposed by Gross and Sadowski \(^5,6\) which accounts for the effect of chain connectivity on the dispersion term and is hence a better model representation of the dispersion interaction.

SAFT views a molecule as a chain of tangentially connected segments. The general form of the SAFT equation can be expressed as:

\[
a^{res} = a^{mg} + a^{chain} + a^{assoc}
\]  

(1.1)

where \(a^{res}\) is the residual Helmholtz energy, residual with respect to an ideal gas at the same temperature and density. The terms on the right hand side of equation (1.1) represent the contributions from the spherical segments, chain formation and intermolecular association respectively. Figure 1.3 illustrates the way SAFT accounts for different contributions to the energy of the mixture of chains as a perturbation to the mixture of the spherical segments forming the chain.

For a pure non-associating fluid, SAFT has three parameters; segment volume \(v^{00}\) (PC-SAFT uses the segment diameter \((\sigma)\) as an equivalent parameter), number of segments per chain \(m\) and the dispersion energy between like segments \(u^0/k\). For self-associating pure fluids, SAFT has two additional pure component parameters, \(c^{AA}\) and
\( \kappa^{AA} \) which are the energy and volume of association interaction respectively. Also SAFT has a binary interaction parameter \( (k_{ij}) \) for the dispersion term which is fitted to mixture data. We now explain the various terms in the SAFT equation of state for a mixture of associating chains.

\[
a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}}
\]

Figure 1.3: Contributions to the SAFT equation of state for an associating chain molecule.

### 1.3.1 The hard sphere contribution

In CK-SAFT (also called SAFT) the segment term consists of contributions due to hard sphere repulsion and dispersion attraction. The latter is a perturbation to the hard sphere reference fluid.

\[
a^{\text{seg}} = m(a^{\text{HS}} + a^{\text{disp}})
\]  

(1.2)

where the factor \( m \) (average chain length of the mixture) converts the terms from per mole of segment basis to per mole of molecules basis. In PC-SAFT the dispersion contribution is a perturbation to the hard chain reference fluid. The hard sphere term is an idealization of the repulsion between segment cores which accounts for the excluded volume between the segments. In real molecules this arises from the overlap of electron clouds. However the repulsion is soft core for real molecules, this is achieved by making
the effective hard sphere diameter temperature dependent. The temperature dependence of the hard sphere diameter is related to the dispersion term and is explained later in this section. Since the reference fluid is a mixture of hard spheres of different sizes, the Helmholtz energy is given by the Mansoori-Carnahan-Starling-Leland expression

$$a_0^{hs} = \frac{6}{\rho} \left[ \frac{\zeta_2^3 + 3\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1^2 \zeta_2 \zeta_3 + \left( \zeta_0 - \frac{\zeta_2}{\zeta_3} \right) \ln(1 - \zeta_3)}{\zeta_3 (1 - \zeta_3)^2} \right]$$

(1.3)

where $\zeta_{k=0-3}$ for chain fluid is given by

$$\zeta_k = \frac{N_{AV}}{6} \rho \sum_i x_i m_i (d_{i})^k$$

(1.4)

where $\rho$ is the molar density of molecules, $N_{AV}$ is the Avogadro’s number, $x_i$ is the mole fraction of component $i$, $m_i$ is the chain length of component $i$ and $d_{i}$ is the temperature dependent segment diameter of component $i$ given in equation (1.5).

1.3.2 The CK-Dispersion contribution

The CK-dispersion term is based on a power series initially fitted by Alder et al. to molecular dynamics data for a square well fluid. Alder’s series was modified by Chen and Kreglewski by making the collision diameter, $d_{ij}$, temperature dependent and considering the two step potential, $u(r)$ shown in Figure 1.4 which is also a function of temperature. Chen and Kreglewski found that the ratio of the width of the soft repulsive step, $S_1$ to the temperature independent segment diameter, $\sigma_{ii}$ is approximately constant ($C = 0.12$) for several gases. Also, they assumed that the height of the repulsive step is about 3 times the depth of the temperature independent attractive step $u_{ii}^0$. Temperature
dependence of the segment diameter $d$ is obtained by solution of the Barker-Henderson integral equation for $d$ based on perturbation theory\textsuperscript{79}. The expression is

$$d_{ii} = \sigma_{ii} \left[ 1 - C \exp \left( -\frac{3u_0^0}{kT} \right) \right]$$

(1.5)

The characteristic volume ($v_{ii}^{00}$) is related to the characteristic segment diameter ($\sigma_{ii}$) by:

$$v_{ii}^{00} = \frac{\pi N}{6 \tau} \sigma_{ii}^3$$

(1.6)

where $\tau = 0.7408$. The temperature dependent segment volume $v_{ii}^0$ is given by:

$$v_{ii}^0 = v_{ii}^{00} \left[ 1 - C \exp \left( -\frac{3u_0}{kT} \right) \right]$$

(1.7)

The temperature dependence of the energy parameter is given by\textsuperscript{80}:

$$u_{ii} = u_{ii}^0 \left[ 1 + \frac{e_{ii}}{kT} \right]$$

(1.8)

The parameter $e_{ii} / k$ is a constant which is difficult to determine from PVT data alone. This parameter is held constant for most molecules ($e_{ii} / k = 10$) and adjusted for a few small molecules\textsuperscript{4}.

The dispersion contribution to Helmholtz free energy is given by:

$$a_{disp} = m \sum_i \sum_j D_{ij} \left[ \frac{u}{kT} \right] \left[ \frac{\xi_3}{\tau} \right]^j$$

(1.9)

The constants $D_{ij}$ are universal constants proposed by Chen and Kreglewski\textsuperscript{77}. The following mixing rules are used for the CK dispersion term. The average chain length is given by:
Figure 1.4: Chen and Kreglewski two step potential model.

\[ m = \sum \limits_i x_i m_i \]  \hspace{1cm} (1.10)

The mixture dispersion energy is given by:
\[
\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j [u_{ij}/kT] v_{ij}^0}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0}
\]  \hspace{1cm} (1.11)

where

\[
v_{ij}^0 = \left[ \frac{1}{2} \left( v_{ii}^0 \right)^{1/3} + \left( v_{jj}^0 \right)^{1/3} \right]^3
\]  \hspace{1cm} (1.12)

and

\[
u_{ij} = (1-k_{ij})(u_{ii}u_{jj})^{1/2}
\]  \hspace{1cm} (1.13)

\(k_{ij}\), the binary interaction parameter between components i and j, accounts for the deviation between the geometric mean mixing rule predicted and actual cross-interaction energy \((u_{ij})\).

### 1.3.3 The Chain Term

SAFT explicitly accounts for the chain effects which constrain the segments of a chain to be connected to each other. The contribution due to chain formation is derived by considering Wertheim’s associating fluid theory in the limit of complete association\(^2\). The chain contribution to the Helmholtz energy for homosegmented (all the segments in a chain are identical) chain is given below. The equations for heterosegmented chains, i.e. chains made up of different kinds of segments are presented in Chapter 6 where heterosegmented (or copolymer) SAFT is used to model copolymers.

\[
a_{\text{chain}} = \sum_i X_i (1 - m_i) \ln y_{ii}^{\text{ref}}(d_{ii})
\]  \hspace{1cm} (1.14)
where $y_{ij}^{ref}$ is the cavity correlation function of spheres making up the chain of component $i$. For hard spheres at contact, the cavity correlation function is the same as the radial distribution function. The expression for radial distribution function at contact is given by Mansoori et al. 78

$$g_y(d_{ij})^{reg} = g_y(d_{ij})^{hs} = y_{ij}^{hs}$$

$$= \frac{1}{1 - \zeta_3} + \frac{3d_{ii}d_{jj}}{d_{ii} + d_{jj}} \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left( \frac{d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right)^2 \frac{\zeta_2^2}{(1 - \zeta_3)^2}$$

(1.15)

For like segments this equation becomes:

$$g_{ii}(d_{ii})^{reg} = g_{ii}(d_{ii})^{hs} = y_{ii}^{hs}$$

$$= \frac{1}{1 - \zeta_3} + \frac{3d_{ii}}{2} \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left( \frac{d_{ii}}{2} \right)^2 \frac{\zeta_2^2}{(1 - \zeta_3)^2}$$

(1.16)

The $\zeta_{k=0-3}$ factors are defined in equation (1.4).

1.3.4 The PC-Dispersion contribution

The PC-Dispersion term which incorporates the effect of chain length on dispersion interactions is an alternative to the CK-Dispersion term. PC-SAFT was initially developed for alkanes by treating the dispersion contribution to the Helmholtz energy as a perturbation to a hard chain fluid. With PC-SAFT, the dispersion contribution becomes:

$$\frac{A_{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT}$$

(1.17)

$$\frac{A_1}{RT} = -2\pi p l_1(\eta, m) \sum_i \sum_j x_i x_j m_i m_j \left( \frac{\epsilon_y}{kT} \right) \sigma_y^3$$

(1.18)
\[ \frac{A_2}{RT} = -\rho \omega m I_2(\eta, m) W^{-1} \sum \sum x, x, m, m_i \left( \frac{\epsilon_{ij}}{kT} \right)^2 \sigma_{ij} \]  

\[ W = 1 + m \frac{8\eta - 2\eta^2}{(1 - \eta)^3} + (1 - m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2} \]  

\[ \epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} \]  

\[ \sigma_{ij} = 0.5(\sigma_i + \sigma_j) \]  

Expressions for \( I_1 \) and \( I_2 \) which are functions of the system packing fraction and average segment number \( (m) \), are given in Gross and Sadowski\(^6\). Equation (1.17) is derived in the spirit of Barker-Henderson perturbation theory and \( A_1 \) and \( A_2 \) correspond to the first and second order contributions respectively to \( A_0^{exp} \).

**1.3.5 The Association Term**

The association term in SAFT is based on Wertheim’s first order thermodynamic perturbation theory (TPT1) \(^{42,43,48,49}\). The association interaction is modeled by a short ranged square well potential whose center is on the association site of the molecule. This model takes into account the short ranged, anisotropic nature of the association interactions. The two parameters that characterize the association between association site of type \( A \) on component \( i \) and association site of type \( B \) on component \( j \) are the association energy or well depth \( \epsilon^{A,B} \) and the association volume \( \kappa^{A,B} \) which corresponds to the range of association interaction (or the well width of the square well potential representing association interaction). The association contribution to Helmholtz energy is given by:
\[ a_{\text{assoc}} = \sum_i X_i \left( \sum_{d'} \left( \ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{M_i}{2} \right) \] (1.23)

where \( M_i \) is the number of association sites on each molecule \( i \), \( X^{A_i} \) is the mole fraction of molecules \( i \) not bonded at site \( A \), \( \sum_{d'} \) represents the sum over all associating sites on molecule \( i \) and \( \sum_i \) is the summation over all components. The fraction of molecules not bonded at site \( A \) is given by:

\[ X^{A_i} = \left( 1 + \rho \sum_j \sum_{B_j} X_j X^{B_j} \Delta^{A,B_j} \right)^{-1} \] (1.24)

where the association strength \( \Delta^{A,B_j} \) is given by

\[ \Delta^{A,B_j} = \sigma^{3}_{ij} K^{A,B_j} g_{ij}(d_{ij}) \left[ \exp \left( \frac{e^{A,B_j}}{kT} \right) - 1 \right] \] (1.25)

\( g_{ij}(d_{ij}) \) represents the hard sphere radial distribution function at contact given by equation (1.15). This concludes the description of the SAFT equation of state. We present the dipolar contribution to the equation of state in Chapter 5. In the next section we present an overview of this thesis.

### 1.4 Overview of thesis

In polymer solutions the two geometric factors of importance are the shape of the solvent and the shape of the polymer. At a coarse level the shape of the polymer is dominated by its size (chain length); further contributions to the polymer’s shape arise due to the presence of comonomers and chain branching. In the following chapters we first evaluate
the validity of SAFT to accurately account for these geometric factors and then propose methodologies to efficiently incorporate the effect of polydispersity on phase equilibrium calculations in polydisperse polymer solutions.

In Chapter 2 we propose and validate a model for agglomeration in polymer slurry reactors. The effectiveness of the model lies in SAFT’s ability to distinguish between linear, cyclic and branched solvents on solid-liquid equilibrium. Even though SAFT is a first order perturbation theory which models molecules as linear chains; by parametrizing the solvent by fitting to saturated vapor pressure and saturated liquid density the effect of the shape of the solvent on thermodynamic properties can be modeled. Thus SAFT is shown to capture the effect of the shape of the solvent on thermodynamic properties.

In Chapter 3 we evaluate the ability of the perturbed chain modification to SAFT (PC-SAFT) to model gas solubility in asymmetric hydrocarbon mixtures over a range of temperature, pressure and chain length asymmetry. The agreement of theory with experimental date of solubility trends with increasing chain length validates the ability of PC-SAFT to capture chain length effects and provides the impetus to model chain length polydispersity in polymer solutions in subsequent chapters. The algorithmic developments for polydispersity that we present in chapters 4-7 are applicable to SAFT in general for any dispersion term (viz. CK-Dispersion or PC-Dispersion).

In Chapter 4 we present robust and efficient algorithms for performing thermodynamic stability analysis and phase equilibrium calculations in molecular weight polydisperse polymer solutions. These algorithms are characterized by the invariance of
the size of the system of equations specifying phase equilibrium with increasing number of pseudocomponents used to represent the polymer molecular weight distribution.

In the next two chapters we present the derivation of the equations which makes the size of the system of equations specifying phase equilibrium invariant to the number of pseudocomponents used to represent the copolymer molecular weight distribution, for a homosegmented model of a dipolar copolymer (Chapter 5) and for a heterosegmented model of a copolymer (Chapter 6). We apply these algorithms for calculating phase equilibrium in polydisperse copolymer solutions.

The next level of complexity in copolymers is compositional polydispersity; that is the pseudocomponents have a distribution with respect to the comonomer content. In Chapter 7 we derive an equation for dipolar copolymers which leads to invariance of the size of system of equations specifying equilibrium, with the number of pseudocomponents used to represent the copolymer comonomer distribution. This enables us to use modifications of the algorithms presented in Chapter 4 to efficiently model phase equilibrium in compositionally polydisperse dipolar copolymer solutions and blends. We then apply the developed algorithm to a compositionally polydisperse dipolar copolymer solution to elucidate the effect of compositional polydispersity on phase behavior with varying pressure, molecular weight and average comonomer composition.

Finally we summarize our contributions in Chapter 8 and also present some directions for future research.
Chapter 2

Solvent Shape Effects: SAFT Modeling of the Effect of Various Carriers on the Operating Range of Slurry Reactors

In this chapter we propose a model for agglomeration in a polyethylene slurry reactor by relating agglomeration to the solid-liquid phase transition of the polymer. The model assumes that the polyethylene dissolution temperature in the carrier (or the solid-liquid equilibrium (SLE) temperature of the polymer at the reactor conditions) correlates with, and is representative of the onset of agglomeration in slurry reactors. We use SAFT to model the liquid phase to elucidate the effect of carriers (solvents), polymer molecular weight, polymer crystallinity, and the effect of excess monomer, on the solid-liquid equilibrium behavior of polyethylene. The carriers considered are non-polar hydrocarbons with differing shapes viz. linear, branched and cyclic molecules. Since SAFT is a first order perturbation theory, the equation of state (EOS) does not distinguish between linear, branched and cyclic molecules. However since the EOS parameters are fitted to pure component data, model predicted thermodynamic properties of different shaped solvents will differ. One goal of this chapter is to test how well SAFT phase equilibria predictions reflect the effect of the shape of the solvent molecule and whether the EOS can be used to screen cyclic, linear and branched solvents to identify a solvent that mitigates agglomeration in the slurry polymer reactor. The effectiveness of SAFT to distinguish between different shaped solvents enables us to propose a model for
agglomeration in polymer slurry reactors based on the observation that the polyethylene-carrier solid-liquid equilibrium temperature correlates well with the onset of agglomeration.

2.1 Introduction

In slurry processes, high-density polyethylene is produced as a solid. The liquid phase acts as a carrier for the catalyst and the solid polymer. The density of the polymer that is produced depends in part on the carrier. For example, if low-density polyethylene were produced using hexane as a carrier, the solid polymer particles would be soft and sticky due to polymer solubility in the hexane carrier. This leads to agglomeration and solid handling problems. Also, any polymer that is dissolved in the carrier can precipitate out in later carrier recovery operations causing fouling of the equipment.

To extend the range of polymers that can be produced in a slurry reactor, it is useful to study how various carriers can affect the operating temperature range of the reactor. The operating temperature of the reactor decides the melt index of the formed polymer. The melt index of a polymer corresponds to its average molecular weight and is a measure of the viscosity of the polymer in the melt state. Polyethylene with an average molecular weight of 150,000 g/mole would have a melt index near 0.3 g/10 minutes. Melt indices above 15 g/10 minutes are desirable for final products where ease of processing is important. Melt indices below 1 g/10 minutes are favored when mechanical properties are important. As the melt index increases the tensile strength and creep
resistance increase but the impact strength falls. Since the melt index of the polymer increases with increasing reactor temperature as shown in Figure 2.1, a higher operating temperature allows production of polymers with a wide range of physical properties. Even a small increase in the temperature has a significant effect on the polymer melt index. The maximum reactor operating temperature is limited by the fact that at a certain temperature the polymer starts getting sticky and agglomerating leading to the problems mentioned earlier.

Thus there is a need to identify the best carrier for the slurry polymerization process. The best carrier will allow the reactor to operate to the highest temperature without agglomeration. Here we use the SAFT EOS to model the effect of different carriers on the maximum operating temperature of the slurry reactor. This will enable identification of the best carrier for slurry polymerization.

Figure 2.1: Polymer melt index dependence on reaction temperature of polymerization.
Agglomeration in polyethylene slurry reactors is a complex process involving many factors including, solvent dissolution in the solid polymer, solid dissolution in the solvent and possibly surface melting of the polymer. Our hypothesis is that the agglomeration temperature correlates with the polymer dissolution temperature (the solid-liquid equilibrium temperature at the given pressure and composition of the liquid phase). As the temperature in the slurry reactor is increased, at a certain temperature the solid polymer will start dissolving in the carrier leading to stickiness and subsequent agglomeration.

This chapter is organized as follows: First the thermodynamic model used for the solid-liquid equilibrium is presented. Next the modeling methodology is discussed followed by results for solid-liquid equilibrium in hydrocarbon and polyethylene systems. Once the effectiveness of the thermodynamic model is tested for representing solid-liquid equilibrium, predictions are made for the polyethylene SLE temperature in different carriers. These predictions are compared with literature data on agglomeration temperature to validate our hypothesis that solid-liquid equilibrium is representative of the onset of agglomeration in polyethylene reactors.

2.2 Theory

Modeling of solid-liquid equilibrium requires a thermodynamic model for each of the solid phase and liquid phase. Traditionally the form of the solid model has not changed much. The predominant solid model used, is one in which the solid phase is a pure crystalline phase as discussed in Prausnitz et al. A variant for the case of
multicomponent phase equilibria is when the solid phase is a solid solution, in this case the solid solution is often assumed to be ideal. The liquid phase on the other hand has been modeled by a variety of models ranging from the ideal solution model (which works very well for a number of systems including n-alkanes with chain length less than 20) to activity coefficient models to statistical mechanics based models like SAFT, which is a commonly used equation of state for modeling liquid phases containing polymers and other complex chain molecules. A review on various applications and extensions to SAFT is provided in Chapter 1.

We have used the SAFT EOS for the liquid phase and a partially crystalline solid model for the solid phase, to model solid-liquid phase equilibrium in polyethylene systems. Calculations using the same approximations for the solid phase have also been reported by others. For a qualitative discussion on the solid-liquid equilibrium in polymer systems refer to Richards.

For solid-liquid equilibrium of a crystalline solute in a solvent, the fugacity of the solute in the solid phase (S) and liquid phase (L) are equal:

\[ f^S = f^L \]  

(2.1)

The fugacity in the liquid phase is given by:

\[ f^L = \phi^L x^L P \]  

(2.2)

where \( \phi^L \) is the fugacity coefficient of the polymer in the liquid phase, \( x^L \) is the mole fraction of polymer in the liquid, and \( P \) is the pressure. Since the solid phase is pure crystalline, the fugacity of the solid is equal to the fugacity of the pure solid at the system temperature and pressure

\[ f^S = f^S_0 \]  

(2.3)
On equating (2.1) and (2.2) above and dividing by the fugacity of the solute as a pure sub-cooled liquid at the temperature and pressure of the system gives:

$$\frac{f_0^S}{f_0^L} = \frac{\phi^L x^L P}{\phi^L_0 P}$$  \hspace{1cm} (2.4)

A thermodynamic cycle\textsuperscript{86,82} relates the fugacity of the pure sub-cooled liquid to that of the pure crystalline solid. In the absence of any solid-solid phase transition this relation is given by:

$$\ln \left( \frac{f_0^L}{f_0^S} \right) = \left( \frac{\Delta H_m}{RT_m} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta v(P - P_{ref})}{RT} + \frac{\Delta C_p}{R} \left( 1 - \frac{T_m}{T} \right) - \frac{\Delta C_p}{R} \ln \left( \frac{T}{T_m} \right) \right)$$  \hspace{1cm} (2.5)

where \(P_{ref}\) is the pressure at which the melting temperature has been measured, \(T_m\) is the melting temperature of the pure solid solute, \(\Delta H_m\) is the molar enthalpy of melting (\(\Delta H_m\) is specified at \(T_m, P_{ref}\)), \(\Delta v\) is the difference in the volume of the liquid and crystalline solute given by \(\Delta v = v^L - v^S\) and \(\Delta C_p\) is the difference in the specific heat of the liquid and crystalline solute given by \(\Delta C_p = C_p^L - C_p^S\). The last two terms in the above equation are small and are of opposite sign and hence are commonly neglected, this gives us the following equation for solid-liquid phase equilibrium of the solute.

$$\ln \left( \frac{\phi^L}{\phi^L_0} \right) = - \left( \frac{\Delta H_m}{RT_m} \left( \frac{T_m}{T} - 1 \right) + \frac{\Delta v(P - P_{ref})}{RT} \right)$$  \hspace{1cm} (2.6)

The above analysis can be generalized to semi-crystallisable polymers as mentioned in the references\textsuperscript{84,86}. Only the crystalline fraction of the polymer is considered to contribute to the fugacity of the solid polymer. The amorphous fraction is treated equivalent to the liquid polymer. Amorphous polymers have 0% crystallinity. The saturated vapor pressure for polymers is very low and hence \(P_{ref}\) is set to zero. Hence the working equation for polymer solutes where \(c\) is the crystalline fraction in the polymer, \(u\) is the number of
repeat units in the polymer and the enthalpy of melting \((\Delta H_u)\) is per crystalline unit in the polymer (as reported by Van Krevelen\(^8^9\)), is given by:

\[
\ln\left(\frac{\phi^L x^L}{\phi_0^L}\right) = -\frac{\Delta H_u}{RT_m} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta vP}{RT} \epsilon u
\]  \hspace{1cm} (2.7)

We calculate the liquid state fugacity coefficients \((\phi)\) above by using SAFT.

### 2.3 Modeling

In this chapter the modeling involves the following two stages. First, we compare the SLE model discussed above with experimental data to test the effectiveness of the model to represent solid-liquid equilibria (or solubility of the solid polymer in the liquid carrier) as a function of polymer concentration.

Next, having verified the effectiveness of the SLE model (using SAFT for the liquid phase) to represent solid-liquid equilibria, we calculate the solid-liquid transition temperature for polyethylene in various carriers. The SLE temperature is then compared to experimentally determined agglomeration temperatures for polyethylene in various carriers to test our hypothesis.

Agglomeration in polyethylene probably has various causes such as the carrier dissolving and penetrating into the polymer and surface melting of the polymer among others. Here we assume that the agglomeration in polyethylene is related to the dissolution of the solid polymer in the carrier and therefore the solid-liquid transition temperature of the polymer is related to the agglomeration temperature. The SAFT
parameters for some of the carriers were previously unavailable. We fit these parameters (listed in Table 2.1) to pure component data.

<table>
<thead>
<tr>
<th>Component</th>
<th>$MW$ (gm/mol)</th>
<th>$m$</th>
<th>$v^0$ (cc/mol)</th>
<th>$u^0/k$ (K)</th>
<th>T range (K)</th>
<th>%AAD ($P^{sat}$)</th>
<th>%AAD ($\rho_L$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-pentene</td>
<td>70.14</td>
<td>3.9135</td>
<td>12.492</td>
<td>202.07</td>
<td>323-373</td>
<td>0.20</td>
<td>0.81</td>
</tr>
<tr>
<td>2,4-dimethylpentane</td>
<td>100.21</td>
<td>5.0199</td>
<td>13.012</td>
<td>201.83</td>
<td>373-473</td>
<td>0.64</td>
<td>1.80</td>
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<tr>
<td>2,2,4-trimethylpentane</td>
<td>114.23</td>
<td>5.1860</td>
<td>13.889</td>
<td>208.05</td>
<td>403-523</td>
<td>0.89</td>
<td>1.93</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
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<td>4.3687</td>
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<td>373-473</td>
<td>0.46</td>
<td>1.57</td>
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<tr>
<td>2,3-dimethylbutane</td>
<td>86.18</td>
<td>4.3511</td>
<td>13.116</td>
<td>206.53</td>
<td>373-473</td>
<td>0.66</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Table 2.1: SAFT parameters for carriers fitted to pure component vapor pressure and saturated liquid density data.

### 2.4 Results

#### 2.4.1 Testing the solid-liquid equilibria model

To demonstrate the effectiveness of the thermodynamic model used to represent solid-liquid equilibrium we perform test calculations for the solubility of polyethylene in alkanes and compare with experimental data. In previous calculations by Pan and Radosz, SAFT calculated solubility in alkane-alkane solid-liquid systems are seen to give good agreement with the experimental data of Hoerr and Harwood and Madsen and Boistelle, even with a $k_{ij}$ of zero. These systems essentially behave as ideal solutions and assuming the liquid phase to be an ideal solution gives similar results.
There is a scarcity of literature data on the solubility of polyethylene in different solvents. SAFT has been used elsewhere\textsuperscript{85-87} to model SLE in polyethylene systems including copolymers. In this work we want to see how good SAFT is in \textit{capturing the effect of solvents of different shapes} on the solid-liquid transition temperature in polyethylene systems.

Richards\textsuperscript{88} gives a qualitative description of the solid-liquid equilibria in polyethylene systems as well as some experimental data. Figure 2.2 shows a representative polyethylene SLE curve in a good solvent. Pan and Radosz\textsuperscript{86} have shown that SAFT calculation for SLE of polyethylene in m-xylene and amyl acetate is in good agreement with experimental data. Since polyethylene is semi-crystalline the crystalline fraction has to be specified. Richards\textsuperscript{88} proposed the following heuristic based on heat capacity and X-ray measurements for the variation of the crystalline fraction with increasing temperature. The crystalline fraction is about 0.75 till 70 °C ($T_0$), thereafter decreasing at an increasing rate to zero at the melting point. We propose the functional form of equation (2.8) to model this behavior.

\[
c = -0.436 \left( 1 - \exp \left[ \frac{T_m - T}{T_m - T_0} \right] \right)
\] (2.8)

Figure 2.3 shows our results for predictive SAFT calculations (k$_i$=0) for solubility variation of a 13600 molecular weight polyethylene in four linear hydrocarbon solvents of increasing molecular weight. The SAFT parameters used are from the correlation by Huang and Radosz\textsuperscript{4} for polyethylene based on regressing parameters for linear alkanes. The crystalline fraction is modeled using equation (2.8).
Figure 2.2: SAFT calculated Solid-Liquid transition curve for Polyethylene (50 K)/hexane system.

Figure 2.3: Comparison of SAFT based SLE model (curves) calculated solubility of Polyethylene(13.6K) in linear hydrocarbons of different chain length with experimental data\textsuperscript{88} (symbols).
Figure 2.4: SAFT calculated variation of SLE transition temperature with crystalline fraction in the polyethylene and the molecular weight of the polyethylene. The system is a PE-heptane-ethylene mixture with 0.1 mass fraction of PE in the liquid phase. The curves are optical guides.

2.4.2 Sensitivity of solid-liquid equilibria curve to polymer molecular weight and crystalline fraction

In Figures 2.4 we show the SAFT predicted variation of the solid-liquid transition temperature with increasing crystalline fraction and polymer molecular weight. The shape of the SLE curve is insensitive to the molecular weight of the polymer. The primary effect of the molecular weight on the SLE curve is through the molecular weight dependence of the melting temperature of the pure polymer. For the melting temperature
of pure polyethylene we use a correlation due to Kim et al.\textsuperscript{92}, \( T_m = T_\infty - A/M_w \) where \( T_\infty \) (417.55 K) is the melting temperature of an infinitely long polyethylene, \( A \) (2.302 \times 10^5 kelvin.gm/mole) is a constant and \( M_w \) is the molecular weight of the polyethylene under consideration. As the molecular weight increases the SLE temperature increases at a fixed composition, but this increase levels off at higher molecular weight just as the melting temperature levels off for higher molecular weight polyethylene.

The dependence of the SLE temperature on crystalline fraction is almost linear with a slight leveling off at higher values of crystalline fraction. The linear behavior is expected since a higher crystalline fraction means that the polymer has a higher content of solid crystalline matter and hence it will take a correspondingly higher temperature to dissolve the polymer.

2.4.3 Prediction of agglomeration temperature

Hogan et al.\textsuperscript{81} studied how different carriers affected the operating temperature of a small batch reactor charged with polyethylene, carrier and ethylene. They found a correlation of the maximum operating temperature of the reactor with the ratio of the number of terminal carbons to the total carbon atoms in the carrier. The maximum operating temperature corresponds to agglomeration and fouling in the reactor. Hogan et al.\textsuperscript{81} do not give any information concerning the polymer molecular weight or crystalline fraction, in their experiments.

Our approach is to calculate the temperature at which the polymer begins to dissolve to an appreciable extent in the carrier. Our hypothesis is that this dissolution temperature will be qualitatively related to the agglomeration temperature. If we perform
the calculation in a consistent way for various carriers, we should be able to predict the relative effect of the carrier on the dissolution temperature and therefore on the agglomeration temperature. To calculate a dissolution temperature, we must choose a representative solubility of the polymer in the carrier. Since, as seen in Figure 2.2, the $T_x$ curve for solid-liquid equilibrium in polyethylene is quite flat at low concentrations of polymer, we choose 10% as a representative low solubility of polymer in the carrier.

Our methodology is to solve for phase equilibrium of three phases (solid, liquid and vapor) and three components (polyethylene, carrier and ethylene which is the monomer) to obtain the three-phase equilibrium temperature for the system. Given our hypothesis, as long as the temperature in the reactor is below this temperature the polymer will remain solid and not start to dissolve and agglomerate.

We include ethylene in our calculation so as to model the conditions in a slurry polymerization reactor accurately. The phase equilibria calculations are performed for polyethylene of molecular weight 500000 and a crystalline fraction of 0.89 (fitted to one data point) at a pressure of 30 bar with the polymer composition in the liquid phase set to 10% by weight. The $k_{ij}$ parameter is set to zero for all these calculations since we want to see the qualitative trend in agglomeration temperature with different carriers.

Figure 2.5 and Table 2.2 compare the results of Hogan et al.\(^8\) with predictions from our proposed model. There is qualitative agreement between the two. Agglomeration and dissolution occur in the cyclic alkanes (cyclopentane and cyclohexane) at the lowest temperatures, the linear alkanes are effective as carriers till higher temperatures and the branched alkanes enable operation of the slurry reactor at
even higher temperatures but the increase in operating temperature levels off with the branched alkanes.

Figure 2.5: Comparison of SLE model predicted \((k_{ij}=0)\) phase transition temperature with experimentally determined agglomeration temperature. The system is modeled as a mixture of carrier, ethylene and polyethylene of molecular weight 500000 and crystalline fraction of 0.89 at a pressure of 30 bar with 10% by mass polymer composition in the liquid phase.
<table>
<thead>
<tr>
<th>Carrier</th>
<th>Carbon Ratio (CH₃ / Total)</th>
<th>Experimental Agglomeration Temperature (°C)</th>
<th>Predicted Agglomeration Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopentane</td>
<td>0.000</td>
<td>85</td>
<td>92.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.000</td>
<td>88</td>
<td>92.6</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.285</td>
<td>103</td>
<td>102.8</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.330</td>
<td>104</td>
<td>103.1</td>
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<tr>
<td>n-pentane</td>
<td>0.400</td>
<td>105</td>
<td>103.6</td>
</tr>
<tr>
<td>1-pentene</td>
<td>0.400</td>
<td>105</td>
<td>102.3</td>
</tr>
<tr>
<td>2,4-dimethylpentane</td>
<td>0.570</td>
<td>107</td>
<td>104.3</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane</td>
<td>0.625</td>
<td>107</td>
<td>103.0</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>0.670</td>
<td>106</td>
<td>104.2</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td>0.670</td>
<td>105</td>
<td>102.1</td>
</tr>
</tbody>
</table>

Table 2.2: Comparison of experimentally determined and SLE calculated agglomeration temperature. The system is modeled as a mixture of carrier, ethylene and polyethylene of molecular weight 500000 and crystalline fraction of 0.89 at a pressure of 30 bar with 10% by mass polymer composition in the liquid phase.

2.5 Conclusions

Agglomeration in polymer solutions can be attributed to many factors including, carrier dissolution in the solid polymer, solid dissolution in the carrier and possibly surface melting of the polymer. To our knowledge the extent of influence of these factors has not been previously quantified. Here we use a simplified model and relate agglomeration to
the solid-liquid phase transition of the polymer. Even though the model is simple, we demonstrate that the polymer solid-liquid transition temperature qualitatively correlates well with the onset of agglomeration for the carriers for which there is experimentally documented agglomeration temperature.

The methodology used in this work can be used to identify the best carrier for the slurry polymerization of polyethylene. From the results presented, it is seen that there is a slight increase in the operating temperature as the carrier goes from cyclic alkanes to linear alkanes to branched alkanes. Thus phase equilibria calculations using SAFT to model the liquid phase can be used to screen solvents based on their shape. Even though the branched alkanes allow only somewhat higher operating temperature than the cyclic alkanes and a marginally higher temperature than the linear alkanes, the small difference in temperature is important since it has a significant effect on the melt index of the polymer and its physical properties.
Chapter 3

Chain Length Effects - Gas Solubility in Hydrocarbons

Long-chain hydrocarbons bridge the gap between simple molecules and polymers. Unlike polymers, mixtures of long-chain alkanes are well-defined in terms of being monodisperse and having quantifiable vapor pressures to which equation of state (EOS) parameters can be fit. However the considerable solvent-solute size asymmetry they exhibit makes them akin to polymers. The ability to quantitatively predict phase behavior in asymmetric mixtures with long chain molecules provides the basis for applying the equation of state for modeling more complex chain length polydisperse polymer systems. The goal of this chapter is to determine the extent to which PC-SAFT is applicable to highly asymmetric mixtures. The applicability of PC-SAFT for modeling phase behavior in asymmetric mixtures will lay the foundation for chapters 4-6, where chain length polydispersity is explicitly included for modeling phase behavior in polymer solutions.

Here we consider asymmetric mixtures of gases and hydrocarbons. We model the solubility of methane, ethane, carbon monoxide and hydrogen in the linear alkane and 1-alkene homologous series using the PC-SAFT equation of state. We obtain the pure component PC-SAFT parameters for the hydrocarbons by correlating vapor pressure and liquid density data, and for hydrogen by fitting to mixture data at high temperatures and pressures. PC-SAFT is seen to correctly model solubility trends with temperature, pressure and increasing carbon number of the solvent. We demonstrate that a single
binary interaction parameter \((k_{ij})\) that is independent of solvent carbon number and in many cases temperature applies to each gas/homologous series pair.

### 3.1 Introduction

Gas solubility is of considerable interest, not only for the theoretical understanding of the liquid state but also due to its varied applications ranging from solubility of gases in human tissues to gas solubility in the Fisher-Tropsch synthesis. Solubility of hydrogen and carbon monoxide in particular and ethane and methane in general, in alkanes and alkenes of varying carbon number up to high temperature and pressure are important for processes involving syngas (mixture of hydrogen and carbon monoxide) reactions.

The available literature data for gas solubility under relevant conditions (especially at high temperature, high pressure and high carbon numbers) is scarce and often inconsistent \(^9\). Also current models used in industry (like group contribution based models, Predictive Soave Redlich Kwong (PSRK), Soave Redlich Kwong (SRK), Peng Robinson and semi-empirical approaches based on regular solution theory) are not reliable for extrapolation to high carbon numbers or over wide temperature and pressure ranges. Extrapolating ability is further reduced due to the lack of a firm experimental database to correlate parameters.

Thus, there is a need to have a physically sound thermodynamic model, which can be used with confidence to predict gas solubility over a wide range of temperature and pressure conditions, for different systems including those with considerable size asymmetry. Gas-hydrocarbon mixtures are highly size asymmetric systems and hence
provide a test for chain equations of state to correctly model the dependence of phase behavior on increasing size asymmetry in the system.

A detailed account of gas solubility can be found in Prausnitz et al.\textsuperscript{82} and comprehensive references to gas solubility data are given in Poling et al.\textsuperscript{94}. The IUPAC series on gas solubility\textsuperscript{93} is a critically evaluated compendium of solubility data available in literature. The IUPAC series editors have noted that there is a plethora of information on gas solubility in literature, many of which are inaccurate and inconsistent, and there is a need for vigilance whenever literature data is used. All references to experimental data in this work are from the IUPAC solubility series\textsuperscript{93} unless otherwise noted.

PSRK is a group contribution equation of state based on the SRK equation and uses the UNIFAC method to calculate mixture parameters\textsuperscript{95-97}. The downside of this method is that of any cubic equation of state, which represents behavior in small molecules well but is unable or requires a large $k_{ij}$ to model phase behavior in mixtures with significant size asymmetry. Group contribution based methods\textsuperscript{98} have also been used in predicting gas solubility in pure and mixed solvents. These methods are unable to predict gas solubility as the size asymmetry between the mixture components increase.

Here we evaluate the capability of PC-SAFT to correlate and predict gas solubility in hydrocarbons over a range of conditions. PC-SAFT as discussed in Chapter 1 is an equation of state for chain molecules based on Wertheim’s first order perturbation theory\textsuperscript{42,43,48,49}. Chapman et al.\textsuperscript{1,2} derived the SAFT equation of state by applying and extending Wertheim’s theory to mixtures of chains. Gross and Sadowski introduced the Perturbed-Chain dispersion term to SAFT by extending Barker and Henderson
perturbation theory\textsuperscript{79,99} to chains. PC-SAFT thus accounts for chain connectivity on the dispersion term.

One advantage of the SAFT based equations of state (such as PC-SAFT) is its ability to predict chain length dependence of the pure component parameters. For chain molecules, the segment volume and segment energy are nearly constant with increasing molecular weight, while the segment number increases almost linearly with molecular weight. In this chapter we analyze trends in gas solubility with increasing chain length of the solvent and test the predictive capability of PC-SAFT to model asymmetric gas/solvent systems and capture the solubility dependency on chain length.

3.2 Pure component parameters

The pure component PC-SAFT parameters used for the alkanes, carbon monoxide and the smaller alkenes are from Gross and Sadowski\textsuperscript{6}. For the longer alkenes we fit the PC-SAFT parameters to reproduce the pure component vapor pressure and the saturated liquid density. We obtain the hydrogen PC-SAFT parameters by fitting to mixture data; the motivation for this is discussed in the section on hydrogen solubility.

It was shown by Gross and Sadowski\textsuperscript{6} that functions of the form given below are useful for correlating pure-component parameters with varying segment number. The suitability of these functions arise from the fact that these functions allow variation in parameters for short chains but converge to constant values for high segment numbers.

The relation for the segment diameter as a function of molecular weight ($M_i$) is given by:

\[
\sigma_i = q_{01} + \frac{M_i - M_{CH4}}{M_i} q_{11} + \frac{M_i - M_{CH4}}{M_i} \frac{M_i - 2M_{CH4}}{M_i} q_{21}
\]  

(3.1)
The ratio of the chain length parameter to the molecular weight \((M_i)\) is correlated as:

\[
\frac{m_i}{M_i} = q_{02} + \frac{M_i - M_{CH4}}{M_i} q_{12} + \frac{M_i - M_{CH4}}{M_i} \frac{M_i - 2M_{CH4}}{M_i} q_{22}
\]  

(3.2)

For the dispersion energy parameter the variation with molecular weight \((M_i)\) is:

\[
\frac{\varepsilon_{ii}}{k} = q_{03} + \frac{M_i - M_{CH4}}{M_i} q_{13} + \frac{M_i - M_{CH4}}{M_i} \frac{M_i - 2M_{CH4}}{M_i} q_{23}
\]  

(3.3)

Where \(M_{CH4}\) is the molecular weight of methane and \(q_{ik}\) are constants fitted to the pure component parameters for the 1-alkene series. These constants are regressed by fitting to the pure component parameters for the 1-alkene homologous series and are listed in Table 3.1. The PC-SAFT parameters of the 1-alkenes and hydrogen as well as the temperature range over which they have been fit and the % deviations are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Constants</th>
<th>units</th>
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<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_{j1})</td>
<td>(^{\circ})C</td>
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<tr>
<td>(q_{j2})</td>
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<td>(q_{j3})</td>
<td>K</td>
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<td>133.62</td>
<td>15.648</td>
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</table>

Table 3.1: Correlation coefficients for 1-alkene PC-SAFT parameters.
<table>
<thead>
<tr>
<th>Component</th>
<th>( M ) (gm/mol)</th>
<th>( M )</th>
<th>( \sigma ) (Å)</th>
<th>( \varepsilon/k ) (K)</th>
<th>T range (K)</th>
<th>%AAD (P&lt;sub&gt;at&lt;/sub&gt;)</th>
<th>%AAD (P&lt;sub&gt;c&lt;/sub&gt;)</th>
<th>ref&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>28.05</td>
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<td>3.4450</td>
<td>176.47</td>
<td>104-400</td>
<td>1.16</td>
<td>2.61</td>
<td>1</td>
</tr>
<tr>
<td>Propene</td>
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</table>

Table 3.2: PC-SAFT parameters.

3.3 Results and discussions

In this section we present comparison of PC-SAFT predictions for gas solubility with experimental data and list the recommended \( k_{ij} \) in Table 3.2 for each system. For each of the gases (methane, ethane, hydrogen and carbon monoxide), we identify accurate solubility literature data in the homologous series of n-alkanes and 1-alkenes. Then, we fit \( k_{ij} \) for each gas/homologous series pair to this literature data. Once the \( k_{ij} \) has been identified by fitting to limited mixture data for a gas/homologous series pair we use the same \( k_{ij} \) to predict solubility in other members of the homologous series and at different temperatures (and compare these results to literature data at these conditions where such data exists). The ability of PC-SAFT with a single binary parameter to model solubility data for a gas/homologous series pair and over a wide temperature range confirms the predictive/extrapolative capability of the equation of state.

3.3.1 Gas solubility in alkanes

Methane

In Figure 3.1 we present results for the solubility of methane in alkanes of carbon number 6-15 from the models mentioned in section 3.1 and experiment at atmospheric pressure and 25°C. Since we are interested in the predictive ability of these models, we set \( k_{ij} \) to zero for calculations with the equations of state. As can be seen, PC-SAFT predicts the effect of solvent chain length on the solubility of methane better than CK-SAFT; this
Figure 3.1: Variation of methane solubility with increasing carbon number of the alkane solvent. Comparison between PC-SAFT (k_{ij}=0) (●), CK-SAFT (k_{ij}=0) (×), group contribution method \(^{98}\) (curve) and experimental data \(^{103, 93}\) (▲, □) at 1.013 bar and 298.15 K.

Figure 3.2: Comparison of PC-SAFT predicted (k_{ij}=0.02, 0.03) methane solubility in dodecane with IUPAC \(^{93}\) correlated experimental data (□) at 1.013 bar.
motivates our choice of PC-SAFT to model gas solubility. The better behavior of PC-SAFT compared to CK-SAFT is due in part to the fact that PC-SAFT is better at correlating liquid densities and vapor pressures for the alkanes than is CK-SAFT as shown by Gross and Sadowski\textsuperscript{6}. The solubility predicted by the group contribution method\textsuperscript{98} of methane in alkane is in reasonably good agreement with the experimental data over the carbon number range of 6-15 in the alkanes, but the trend with increasing carbon number appears to be too flat. The experimental and PC-SAFT results show a continually increasing solubility with increasing carbon number of the solvent alkane, but the group contribution method predicts that the trend in solubility levels off at higher (~hexadecane) alkanes as shown in Figure 3.1.

The PC-SAFT prediction ($k_{ij} = 0$) qualitatively agrees with the experimental data and shows the correct trend for methane solubility with increasing solvent carbon number but over-predicts the solubility. As shown in Figure 3.2, the PC-SAFT $k_{ij}$ parameter for the methane-dodecane system shows temperature dependence and increases from 0.02 to 0.03 over the temperature range 250 K – 350K.

Ethane

Multiple experimental data sets on the solubility of ethane in alkanes at 1.013 bar and 298.15 K are inconsistent amongst themselves. The optimized $k_{ij}$ for the ethane-octane (refer to Figure 3.3 and Figure 3.4) and ethane-dodecane system (refer to Figure 3.5) is 0.02. Based on this limited comparison we use a temperature and chain length independent $k_{ij}$ of 0.02 to model ethane solubility in alkane systems. The resulting PC-SAFT calculated solubility is around the same range but lower than the results of the
Figure 3.3: Comparison of PC-SAFT (curve) predicted \((k_{ij}=0.02)\) ethane solubility in octane with IUPAC\textsuperscript{93} experimental data (□) at 4.05 bar.

Figure 3.4: Comparison of PC-SAFT (curve) predicted \((k_{ij}=0.02)\) ethane solubility in octane with IUPAC\textsuperscript{93} experimental data (□) at 298.15 K.
Figure 3.5: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0.02$) ethane solubility in dodecane with IUPAC\textsuperscript{93} experimental data (□) at 4.05 bar.

Figure 3.6: Comparison of PC-SAFT (△) predicted ($k_{ij}=0.02$) ethane solubility trend with increasing carbon number of the solvent alkane with solubility values from tentative IUPAC\textsuperscript{93} correlation (□) at 1.013 bar and 298.15 K.
prediction from the tentative correlation given by the IUPAC series as seen in Figure 3.6. Because of the lack of consistent data sets on which the IUPAC correlation is based, the IUPAC correlation is considered by the editors to be of doubtful reliability and can only be expected to give predictions in the correct ballpark. Assuming that the data used to test the PC-SAFT model (see Figures 3.3-3.5) is accurate, the IUPAC correlation over predicts the solubility of ethane in alkanes at 1.013 bar and 298.15 K by about 10%.

**Carbon Monoxide**

We fit $k_{ij}$ for the carbon monoxide-alkane system to reproduce carbon monoxide solubility in dodecane and in octane as shown in Figure 3.7 and Figure 3.8, respectively. The above calculations show that a temperature independent $k_{ij}$ of 0.125 accurately predicts carbon monoxide solubility with increasing carbon number of the alkane solvent.

**Hydrogen**

The PC-SAFT parameters for hydrogen were previously unavailable. A challenge to determining PC-SAFT parameters for hydrogen is that PC-SAFT parameters have conventionally been fitted to pure component vapor pressure and saturated liquid density data. However the vapor-liquid coexistence for pure hydrogen occurs at very low temperatures (4K-15K) where quantum effects predominate. Such parameters are not expected to be applicable at temperatures of industrial interest (~298.15 K and higher).

We fit the PC-SAFT parameters for hydrogen to hydrogen/decane mixture vapor-liquid equilibria data over a pressure range of 1.5 – 247 bar and a temperature range of 462.5 – 583.5 K. Hydrogen parameters thus fitted accurately predict phase behavior in
Figure 3.7: Comparison of PC-SAFT (×) predicted (kij=0.125) Carbon Monoxide solubility in dodecane with experimental data from Gao104 (□).

Figure 3.8: Comparison of PC-SAFT (×) predicted (kij=0.125) Carbon Monoxide solubility in octane with experimental data from IUPAC93 (□).
hydrogen systems other than with decane e.g. with higher alkanes as shown in Figure 3.9-3.13 and alkenes (refer section 3.3.2), over a wide range of temperature and pressure. All PC-SAFT solubility predictions using the hydrogen parameters agree with experimental data with a $k_{ij}$ of zero. In Figures 3.10-3.13 we compare experimental data$^{100}$ and PC-SAFT predicted solubility of hydrogen in C16, C28, C36 and C46 alkanes respectively. Each curve is for a given mole fraction of hydrogen (specified in the legend) in the liquid phase. We obtain the EOS parameters for the higher alkanes (C36 and C46) from correlation for alkane parameters$^{101}$ due to the absence of available vapor pressure for these fluids. The excellent agreement between theory and experiment verifies the accuracy of the regressed hydrogen parameters.

We use PC-SAFT to predict the trend in hydrogen solubility as a function of the solvent (n-alkane) carbon number. The results including that for the group contribution method are compared in Figure 3.14. Reported experimental data at 298.15 K and 1 bar for the solubility of hydrogen in n-alkanes has an inconsistency at decane as seen in Figure 3.10. If the experimental data for the decane/hydrogen system is correct then the experimental data for the other alkane/hydrogen system has a scatter of 10% while if the experimental data for the decane/hydrogen system is incorrect PC-SAFT predictions are off by 10%. In either case, PC-SAFT predicts ($k_{ij} = 0$) solubility in alkanes within 10% of experimental data with the correct qualitative trend.

**Mass Fraction solubility trend with increasing chain length**

In Figure 3.15 we present results for the PC-SAFT predicted variation in hydrogen solubility on a mass fraction basis with increasing chain length of the solvent.
Figure 3.9: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0$) hydrogen solubility in hexadecane with experimental data (□) from IUPAC$^{93}$.

Figure 3.10: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0$) hydrogen solubility in hexadecane with experimental data$^{100}$ (symbols).
Figure 3.11: Comparison of PC-SAFT (curve) predicted ($k_j=0$) hydrogen solubility in octacosane with experimental data$^{100}$ (symbols).
Figure 3.12: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0$) hydrogen solubility in hexatriacontane with experimental data\textsuperscript{100} (symbols).
Figure 3.13: Comparison of PC-SAFT (curve) predicted \((k_{ij}=0)\) hydrogen solubility in hexatetracontane with experimental data\(^{100}\) (symbols).

Figure 3.14: Comparison of PC-SAFT \((\Delta)\) predicted \((k_{ij}=0)\) hydrogen solubility trend with increasing carbon number of the solvent alkane with experimental data \((\Box)\) from IUPAC\(^{93}\) and group contribution method\(^{98}\) (curve).
We have observed similar trends for the solubility of the other gases. Even though there is an increasing molar solubility of the gas with increasing chain length of the solvent, this increase is offset by the increase in molecular weight of the solvent when comparing on a mass basis and hence the mass solubility along a homologous series decreases. The solubility decreases with increasing chain length and reaches a limiting value for very high carbon number. The limiting behavior of the solute mass fraction with increasing carbon number of the solvent occurs because for large enough solvent size, the hydrogen cannot detect the size of the solvent molecule.

3.3.2 Gas solubility in 1-alkenes

We generate PC-SAFT parameters for alkenes from 1-nonene to 1-hexadecene by fitting to saturated vapor pressure and liquid density data. We supplement these parameters with the parameters for lower alkenes from Gross and Sadowski\(^6\) to generate correlations for PC-SAFT parameters varying with molecular weight for 1-alkenes. Such correlations considerably simplify parameter identification for all members of a homologous series, even ones for which there is not sufficient or accurate pure component vapor pressure and liquid density data. This is particularly helpful in parameter characterization of higher ends (high molecular weight components) and hydrocarbon mixtures.

As the alkene chain length increases, the effect of the single double bond is diluted and we expect the gas solubility in alkenes to converge to gas solubility in the corresponding alkane for higher carbon numbers. PC-SAFT predicts this trend. For all the
gases considered here the solubility predictions using PC-SAFT in corresponding alkanes and 1-alkenes overlap for carbon number greater than eight.

**Hydrogen**

The only solvents for which we found reliable experimental data for hydrogen solubility in alkenes are 1-octene and 1-heptene by Sokolov and Polyakov\textsuperscript{102}. Figure 3.16 and Figure 3.17 compare reported and PC-SAFT predicted hydrogen solubility. The experimental and predicted values ($k_{ij}=0$) are in excellent agreement over a temperature range of 320K - 460K and a pressure range of 40 bar – 304 bar. This indicates that the hydrogen PC-SAFT parameters regressed as mentioned earlier are accurate and can predict phase equilibria in systems outside the conditions of the original fit.

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>SOLUTE</th>
<th>$k_{ij}$</th>
<th>Fitted to system with solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane/Alkene</td>
<td>Methane</td>
<td>0.025</td>
<td>Dodecane</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>0.020</td>
<td>Octane, Dodecane</td>
</tr>
<tr>
<td></td>
<td>Carbon monoxide</td>
<td>0.125</td>
<td>Octane, Dodecane</td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td>0.000</td>
<td>Hexadecane, Hexene, Octene</td>
</tr>
</tbody>
</table>

Table 3.3: Recommended $k_{ij}$ for gas/hydrocarbon pairs and the systems to which they were fitted.
Figure 3.15: PC-SAFT predicted ($k_{ij}=0$) variation of hydrogen solubility (on a mass basis) with increasing carbon number of alkane solvent at 1 bar and 298.15 K.

Figure 3.16: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0$) hydrogen solubility in 1-octene with experimental data (symbols) from Sokolov et al.\textsuperscript{102}. 
Figure 3.17: Comparison of PC-SAFT (curve) predicted ($k_{ij}=0$) hydrogen solubility in 1-heptene with experimental data (symbols) from Sokolov et al.\textsuperscript{102}.

Figure 3.18: Comparison of model predicted solubility of ethane with increasing chain length of the solvent. The solubilities in alkanes and alkenes converge as chain length increases.
Other gases

The gas solubility in 1-alkenes converges to that in the corresponding n-alkanes (Figure 3.18) for carbon numbers greater than eight. This is observed for each of the gases hydrogen, methane, ethane and carbon monoxide. Therefore it is reasonable to assume the same $k_{ij}$ for the gas/1-alkene system as the gas/alkane systems for the higher alkenes.

3.4 Conclusions

We model solubility of hydrogen, carbon monoxide, methane and ethane in the homologous series of alkanes and 1-alkenes using PC-SAFT. The solubility in 1-alkenes converges to the solubility in the corresponding alkane for increasing chain lengths. The predictive capability of the PC-SAFT equation of state is demonstrated by comparing to experimental data over the limited range that such data is available. A constant, temperature and carbon number independent $k_{ij}$ makes it possible to have confidence in PC-SAFT predictions in regions where there is no experimental data. For many of the systems studied a constant (and even zero for hydrogen systems) $k_{ij}$ is able to give quantitative results. PC-SAFT with a fixed or zero $k_{ij}$ gives correct qualitative trends and is hence useful as an extrapolative tool.

Some of the calculations (Figure 3.1 and Figure 3.14) show that predictions using the group contribution method\textsuperscript{98} are acceptable for low carbon numbers but the solubility trend with increasing carbon numbers is inaccurate. The deficiency in this approach is that the solubility on a molar basis levels off as the molecular weight of the solvent is
increased while the actual solubility is an increasing function of the solvent molecular weight.

We use PC-SAFT to model hydrogen which is an industrially important gas. The hydrogen parameters can predict phase equilibria in hydrogen mixtures over a wide range of temperatures with different solvents.

The ability of PC-SAFT to model size asymmetric systems provides the impetus for modeling chain length polydispersity in homopolymer and copolymer solutions in chapters 4-6.
Chapter 4

Polydispersity in Polymer Solutions – Algorithms for Stability

Analysis and Phase Equilibrium

Thermodynamic phase equilibria calculations for systems containing polymers and/or many molecular species are computationally expensive and difficult because the number of equations that need to be solved increases with the number of species present and because of the large size asymmetry that often leads to numerical instability. By taking advantage of the underlying form of recently proposed polymer equations of state (such as SAFT), we propose algorithms that greatly simplify both the calculation of thermodynamic stability and phase equilibria for polydisperse polymer solutions. The proposed algorithms are applicable to polymer solutions including copolymers that may contain any number of pseudocomponents. The stability algorithm consists of the generation of trial compositions of the polymer pseudocomponents from the parameter space of a distribution function rather than from the more conventional composition space of each pseudocomponent. This together with the proposed phase equilibrium calculation algorithms in which the number of equations to be solved is made independent of the number of pseudocomponents used to represent a polymer’s molecular weight distribution (MWD), considerably reduces the complexity and dimensionality of the phase equilibrium problem. Calculations using this approach show promise in the ability to detect thermodynamic instability in a polydisperse polymer
system, even for polymers with multimodal molecular weight distribution (MWD) that are in solution with multiple solvents.

4.1 Introduction

Polydisperse materials are those which contain particles that have properties depending continuously on one or several parameters. In this chapter we consider polymers which are polydisperse in molecular weight, and use simplifications resulting from the form of recent polymer equations of state to present robust algorithms to test the thermodynamic stability and perform phase equilibrium (flash) calculations in polydisperse polymer solutions. In particular we apply the algorithms to the Statistical Associating Fluid Theory based (SAFT\textsuperscript{2,4} and PC-SAFT\textsuperscript{6}) equations of state. In this chapter we present robust thermodynamic stability analysis and phase equilibrium calculation algorithms in which the size of the equations specifying either problem is independent of the number of pseudocomponents used to represent the polymer MWD. The development of these computationally efficient and robust algorithms will allow incorporation of polydispersity effects in polymers in process simulation software which is of growing importance given the ubiquity of polymers.

The ability to model and predict phase equilibria in polymer systems is important in all stages of polymer manufacturing and processing and is essential for controlling the properties of the polymer. For polydisperse polymers the partitioning of the pseudocomponents between various phases dictates the MWD in each phase and therefore the properties of the polymer in any phase. An example is the high pressure
synthesis of low density polyethylene. A simplified flow diagram of the process is reproduced in Figure 4.1. Ethylene compressed to high pressure is mixed with initiator and enters the reactor where polymerization occurs. Polyethylene is obtained as the solute in supercritical ethylene. To precipitate the polymer the pressure is reduced somewhat causing phase separation. In the high pressure separator the phase separation leads to the formation of a polymer-lean and a polymer-rich phase. The low molecular weight polyethylene (wax) in the polymer lean phase is precipitated by cooling while the high pressure ethylene is recycled. The polymer rich phase enters the low-pressure separator where the polyethylene precipitates. Particularly in the high pressure separator the choice of temperature and pressure is important for the quality of the polyethylene produced and the production costs. If the pressure is too low then phase separation is high but then it’s difficult to recover the pressure required for polymerization while if the pressure is too high then the phase separation is not adequate. Therefore calculation of phase equilibria while accounting for the presence of polydispersity is important to optimize high pressure polymerization of ethylene.

Recent developments in molecular modeling of long chain molecules exemplified by the SAFT\textsuperscript{1-4,6} based equations of state has led to widespread interest in predicting phase behavior using such developments in polymer solutions while further advances allow SAFT to account explicitly for the presence of polar groups, comonomers and polydispersity\textsuperscript{70,85,87,105-113}.
Figure 4.1: High Pressure synthesis of low-density polyethylene

For polymer systems, advances in computational techniques and numerical methods (i.e. stability and flash calculations) have not kept up with advances in theoretical model development. This is due to a combination of factors, including the extreme asymmetry in the molar masses of the polymer and solvent and the polydisperse nature of the polymers. The former leads to extremely small fugacities and mole fractions for the polymer (especially in the polymer lean phase), which may pass the underflow limit of the computer in some cases. The latter adds additional complexity to the already difficult problem by considerably increasing the dimensionality of the variable space over which the problem is solved. Current flash algorithms when applied to polymer solutions are difficult to converge and the convergence is sensitive to the initial guess for the variables\textsuperscript{114}. The principle of congruence as outlined below is one way to make this problem tractable.
The SAFT equation of state and other polymer equations of state\textsuperscript{115} obey the principle of congruence\textsuperscript{116}. This principle states that the residual properties of a mixture of similar components depend on the average properties in the mixture and not on the detailed composition of the various components. For a polydisperse polymer modeled using a number of pseudocomponents, this leads in the aforementioned equations of state to the residual chemical potential of a polymer pseudocomponent being a linear function of the pseudocomponent’s molecular weight. The linear relation between the residual chemical potential of a chain molecule and its chain length (or molecular weight) has also been shown using molecular simulation by Spyriouni et al.\textsuperscript{117}. For phase behavior, one finds that the logarithm of the partition coefficient of a polymer pseudocomponent between two phases $\alpha$ and $\beta$ is a linear function of the pseudocomponent’s molecular weight both in homopolymer\textsuperscript{101,112,113,115} and copolymer solutions\textsuperscript{118}.

\[
\ln(K_i) = \ln\left(\frac{x_i^\alpha}{x_i^\beta}\right) = A + M_i B \tag{4.1}
\]

where $K_i$ is the partition coefficient, $x_i^\alpha$ is the mole fraction of the polymer pseudocomponent in phase $\alpha$ and $M_i$ is the molecular weight of the polymer pseudocomponent. $A$ and $B$ are only functions of the average molecular weight of the polymer in the two phases, of the temperature, and of the density in the two phases. Phase equilibria calculation can be greatly simplified using equation (4.1), since solving for $A$ and $B$ satisfies the equilibrium condition for all the polymer pseudocomponents. In this chapter we use the simplification made possible due to the principle of congruence to construct algorithms for thermodynamic stability analysis and phase equilibrium.
calculations (Pressure-Temperature (PT) flash and cloud point calculation) for polydisperse polymer solutions. The methodologies that we propose for phase equilibrium calculation in polydisperse polymer solutions are independent of the specific thermodynamic model used and only depend on the validity of equation (4.1).

The approach developed in this chapter is preferable to conventional approaches, a brief review of which follows. Excellent reviews on approaches to phase equilibria calculations in polydisperse systems have been published by Cotterman and Prausnitz\textsuperscript{119} and more recently by Browzik and Kehlen\textsuperscript{120} and Sollich\textsuperscript{121}. Previous approaches can be classified primarily into pseudocomponent based or continuous thermodynamics based.

The earliest approach accounting for polydispersity was by representing the molecular weight distribution using pseudocomponents\textsuperscript{122-127}. Pseudocomponents are discrete components that are generated by dividing the continuous distribution into k arbitrary intervals of fixed length. The molecular weight of the pseudocomponent is the average molecular weight in the interval and the mass fraction is the area under the distribution curve in the interval as shown in Figure 4.2. If the pseudocomponents are suitably chosen then they can give reasonable results. Often it is not clear what a suitable choice is and randomly chosen pseudocomponents may give results that depend on the pseudocomponents chosen. Also in this case the equations specifying phase equilibrium increase with the number of pseudocomponents and so there is a tradeoff between computational expense and accurate description of the MWD using enough pseudocomponents.
Cotterman and Prausnitz\textsuperscript{128}, Chou and Prausnitz\textsuperscript{129} and Shibata et al.\textsuperscript{130} used quadrature to determine pseudocomponents. Quadrature is a very efficient method to generate pseudocomponents. Quadrature formulas determine the best pseudocomponents that represent the distribution function on replacing integration with summation. Quadrature formulas are related to limits of integration with different quadrature used for different MWD and variable range of the distribution function. The disadvantage of this method as used earlier was that since it's essentially a pseudocomponent method the computational expense increased with the number of quadrature points (pseudocomponents). However, the advantage of the quadrature method is that convergence to the actual solution can be achieved with the use of only a few pseudocomponents (under 10). However on retaining only a few pseudocomponents information about the shape of the distribution function is lost. The size of the system of equations in the algorithms presented in this chapter do not change with the number of pseudocomponents, this allows for retaining as many pseudocomponents (so information of the shape of the distribution function is not lost) as required without compromising on computational expense, thus we address the major problem with pseudocomponent based methods.

Continuous thermodynamics\textsuperscript{128} involves using the experimental or analytical distribution function to represent the MWD. This leads to the thermodynamic properties of the system being functionals of the distribution function. The convenience of continuous thermodynamics is reduction in computation time since the system of equations to be solved is fixed and the fact that it gives analytical solutions for simple cases. But for practical cases the integrals appearing in the phase equilibrium problem
need to be estimated numerically which reduces the elegance of working with a continuous distribution function.

Figure 4.2: A Gaussian distribution (weight fraction vs. molecular weight) discretised into pseudocomponents. Only alternate pseudocomponents (in black) have been displayed for clarity.

Also while it maybe straightforward to perform cloud point calculation; flash calculations are complicated to perform with continuous thermodynamics\textsuperscript{131}. Flash calculations either require numerical integration or assumption that the form of the distribution function in various phases is the same. The latter assumption is not correct in the general case. Hendriks\textsuperscript{132} performed the numerical integration using Gaussian quadrature while Cheluget and Vera\textsuperscript{133} performed numerical integration using the Legendre-Gauss quadrature. The quadrature method here is different from that mentioned
earlier. In this\textsuperscript{132,133} approach quadrature is used to for numerical integration and the size of the system of equations is not affected by the number of quadrature points. In the earlier method\textsuperscript{128,130}, quadrature is used to generate pseudocomponents and the size of the system of equations increases with the number of pseudocomponents (and hence the number of quadrature points). Cotterman and Prausnitz\textsuperscript{134} proposed the method of moments that involves satisfying the mass balance for the first and second moment of the distribution function. This approximation can lead to large errors in wide distributions. Also distribution functions can only represent simple unimodal distributions analytically. Polymers often have multimodal distribution which cannot be easily described using distribution functions and hence continuous thermodynamics. The moment method separately developed by Sollich and Cates\textsuperscript{135} and Warren\textsuperscript{136} is an alternate method to calculate phase equilibria in polydisperse solutions, but can only be applied with continuous distribution functions. This method gives accurate results for cloud and shadow curves but only approximate results for multi-phase flash calculations\textsuperscript{137}. In the algorithms proposed in this chapter since the size of the system of equations to be solved is independent of the no. of pseudocomponents it is possible to use enough pseudocomponents to completely reproduce the shape of the distribution function. This allows for accurate representation of the shape of the distribution function even for multimodal distribution functions. The formulation of the algorithms we present allows accurate solutions for cloud point calculation as well as flash unlike continuous thermodynamics based methods.

Methodologies for cloud point calculations in polydisperse polymer solutions using molecular based equations of state have been well developed in the last few
years\textsuperscript{101,112,131,138}. This is understandable since the primary source of literature data on polymer solution phase behavior is cloud point data and hence to compare theory developments against experimental data requires the ability to perform cloud point calculations effectively. Less effort has been spent on developing robust methodologies for flash calculations in these systems. However from an industrial standpoint the ability to perform flash calculations is the key to modeling various separation equipments in the polymer manufacturing process. This has led to considerable recent activity in developing flash algorithms for polymer solutions as evidenced by the interest shown in this field by various groups\textsuperscript{113,139,140}.

Green et al.\textsuperscript{141} observed that the presence of fractal behavior with respect to the point of initiation of the flash makes the initialization a key ingredient for any flash algorithm. Based on their study Green et al.\textsuperscript{141} conclude that reliable initialization is very difficult to achieve and serious consideration must be given to initialization for any flash algorithm to be successful even for simple mixtures. A PT-flash incorporating the principle of congruence has been recently proposed by Behme et al.\textsuperscript{113} but it does not mention the initialization method for the flash. In this chapter we propose ways to make the PT-flash for polydisperse polymer solutions relatively insensitive to initialization. The Interval Newton method applied to phase equilibria\textsuperscript{140} guarantees convergence to the global optimum but at the cost of high computational expense. The advent of new methodologies for example in Stadtherr’s group\textsuperscript{142,143} to make such global optimization faster will provide a way to solve non linear equations accurately and quickly.

The other aspect of polydisperse solutions that we address in this chapter is the determination of thermodynamic stability. The stability algorithm determines whether a
solution is thermodynamically stable as a single phase at any given condition (pressure, temperature and composition). The conditions for phase equilibria are necessary not sufficient conditions. Even metastable states that may not physically exist may satisfy phase equilibrium conditions. Thus checking for phase stability is an important reality check to any phase equilibria calculation. Running a thermodynamic stability check on a feed solution is useful for two reasons. 1) If the feed is stable then there is no need to do time consuming phase equilibria calculation. 2) In case the stability check shows that the feed phase is thermodynamically unstable then the stability test implicitly generates the composition of a trial phase which can be used as a guess for the subsequent flash calculation. To test for stability, a tangent hyper plane is drawn at the composition of the mixture \(( \bar{x} )\) under consideration (Figure 4.3). For the mixture to be thermodynamically stable no portion of this tangent plane should intersect the Gibbs energy surface. The stability test involves minimizing the tangent plane distance (distance between the tangent plane and the Gibbs energy surface at \( \bar{x} \)). A negative tangent plane distance means that the feed is unstable. Derivation of the stability criterion for monodisperse systems and further details on doing stability calculations can be found in Michelsen\(^{144}\). We develop and use simplifications in the form of polymer equations of state to make the checking of thermodynamic stability easy for polydisperse polymer solutions which may contains hundreds of pseudocomponents.

The aim of this chapter is to present algorithms to perform thermodynamic stability analysis and phase equilibrium calculations for polydisperse polymer solutions.
Figure 4.3: Excess Gibbs energy of mixing versus mole fraction in a binary mixture. \( z \) is the feed composition. \( x^a \) and \( x^b \) are the equilibrium phase compositions once the feed phase splits. \( 
abla \text{PD}(x, z) \) is the tangent plane distance between the tangent at \( z \) to the Gibbs energy surface at \( x \).

The methodologies developed in this chapter are used in chapter 5, 6 and 7 to investigate the effect of polydispersity on copolymer solutions. The rest of the chapter is organized as follows. In section 4.2 we present the methodology for performing thermodynamic stability analysis in polydisperse polymer solutions. In section 4.3 we present the equations for a robust PT-flash for polydisperse solutions and the methodology used to make the solution of the system of equations tractable. In Section 4.3.1 we detail the initiation methodology for the flash algorithm. Being able to converge the flash robustly without user intervention is a key achievement of this work and is enabled by the ability of the initiation methodology to provide accurate initial guesses for the flash variables. Next, in section 4.4 we present a robust cloud point calculation algorithm for polydisperse polymers in multiple solvents to trace phase boundaries. Finally in section
4.5 we present the results of the stability and flash calculation for select polydisperse polymer solutions.

4.2 Thermodynamic Stability Analysis: Algorithm and Methodology

Consider a feed mixture at a pressure $P$ and temperature $T$, consisting of $n$ components of which $p$ components are polymer pseudocomponents (of single polymer specie) and $s$ are solvents ($n = p + s$). In other words there are $k$ real components in the system, $s$ solvents and 1 polymer ($k = s + 1$). The polymer contains $p$ pseudocomponents. The thermodynamic stability of the feed mixture can be determined using the tangent plane distance method$^{144}$. The tangent plane distance (TPD) for a feed of composition $\bar{z}$ and a trial phase with composition $\bar{x}$ is given by:

$$TPD = \sum_{i=1}^{n} x_i \left[ \frac{\mu_i^f}{RT}(T, P, \bar{x}) - \frac{\mu_i^f}{RT}(T, P, \bar{z}) \right]$$  \hspace{1cm} (4.2)

If the feed is stable then the TPD is non-negative for any trial compositions $\bar{x}$. A negative TPD means that the feed will phase split into two or more phases.

Let $\rho_1$ and $\rho_2$ be the densities of feed and the trial phase respectively at $P$ and $T$, then the chemical potential can be written as a sum of the residual and ideal contribution as:

$$TPD = \sum_{i=1}^{n} x_i \left[ \frac{\mu_i^{\text{res}}}{RT}(T, \rho_2, \bar{x}) + \ln(\rho_2 x_i) - \frac{\mu_i^{\text{res}}}{RT}(T, \rho_1, \bar{z}) + \ln(\rho_1 z_i) \right]$$  \hspace{1cm} (4.3)
In equation (4.3) the chemical potential is residual to that of an ideal gas at the same temperature and density. The residual chemical potential of component $i$ is related to its fugacity coefficient $\phi_i$ by:

$$\ln(\phi_i) = \frac{\mu_i^{res}(T, \rho, x)}{RT} - \ln(Z)$$  
(4.4)

where $Z$ is the compressibility factor of the mixture. Combining equations (4.2) and (4.4) we get:

$$TPD = \sum_{i=1}^{n} x_i \left[ \ln(\phi_i Z_i) + \ln(\rho_i x_i) - \ln(\phi_i Z_i) - \ln(\rho_i z_i) \right]$$  
(4.5)

Since $Z = \frac{P}{\rho RT}$, at constant $P$ and $T$ we get:

$$TPD = \sum_{i=1}^{n} x_i \left[ \ln(\phi_i(T, \rho, x)) + \ln(x_i) - \ln(\phi_i(T, \rho, z)) - \ln(z_i) \right]$$  
(4.6)

It follows from the principle of congruence that the residual chemical potential and hence the log of the fugacity coefficient of different polymer pseudocomponents in a mixture vary linearly with the molecular weight of the pseudocomponent. This has been demonstrated for the SAFT (and PC-SAFT) equation of state in solutions of polydisperse homopolymers$^{101,112,113,115}$ and polydisperse copolymers$^{118}$.

$$\ln(\phi_i) = K_A + M_i K_B$$  
(4.7)

where $K_A$ and $K_B$ are only functions of the temperature, density, number average molecular weight of the polymer, total polymer composition and the solvent compositions i.e. $K_A, K_B = f(T, \rho, M_n, x_p, \{x_s\})$. They do not depend on the detailed molecular weight distribution of the polymer but only on the average properties of the polymer.
\[ TPD = \sum_{i \rightarrow \text{polymer}} x_i \left[ \ln(x_i) + K_{A2} + M_i K_{B2} - K_{A1} - M_i K_{B1} - \ln(z_i) \right] + \]
\[ \sum_{i \rightarrow \text{solvents}} x_i \left[ \ln(\phi_i(T, \rho_2, z)) + \ln(x_i) - \ln(\phi_i(T, \rho_1, z)) - \ln(z_i) \right] \]

where the subscript 1 and 2 on \( K_A \) and \( K_B \) refers to the feed and trial phase respectively. The first summation is over all polymer pseudocomponents while the second summation is over all solvents.

Since the composition of each pseudocomponent occurs in equation (4.8), it follows that determining the stability of the solution requires the detailed molecular weight distribution of the polymer in the feed (\( z \)) and the trial (\( x \)) phases. The pseudocomponents representing the feed can be generated by direct numerical integration of the MWD curve resulting from the size exclusion chromatography (SEC) analysis. Industrially produced polymers are now routinely characterized using such analyses\(^{145}\). The thermodynamic stability of the system is determined by minimizing the TPD for different values of the trial phase composition (\( x \)). If the TPD is non-negative for any trial composition the feed solution is stable. Thus the problem is setup as a minimization problem with \( x \) as the vector of independent variables. As the number of pseudocomponents used to represent the polymer molecular weight distribution increases, the dimensionality of the optimization problem also increases. To accurately model multimodal distributions it is often necessary to have hundreds of pseudocomponents and an optimization problem with hundreds of variables would become difficult in terms of locating the global minimum in TPD.

We reduce the complexity of the above problem by searching over the parameter space of a distribution function instead of searching over the composition space of the
pseudocomponents. We have found that in general different distribution functions (Schulz-Flory, Schulz-Zimm, Log-Normal etc.) can be used to represent the pseudocomponent distribution in the trial phase and hence be used in stability determination. A disadvantage of these functions is that they represent unimodal distributions. A better choice is to use the equilibrium distribution function to represent the trial phase distribution. The equilibrium distribution function is the EOS predicted distribution of the phase at equilibrium with the feed and can be obtained by re-arranging equation (4.1):

\[ x_i = z_i \exp(A + M_i * B) \]  

(4.9)

This function has the advantage that it can represent multimodal molecular weight distributions depending on the feed distribution. This choice of distribution is especially appropriate for a feed near a phase boundary since the stability algorithm will find a trial phase that approaches the corresponding equilibrium composition. Thus the stability routine can provide an initialization for the subsequent flash.

Even though the MWD of the trial phase represented by the above distribution function should detect instability best when the feed composition is close to the cloud point composition at the given pressure and temperature, the algorithm is able to correctly detect instability in feed away from the cloud point curve and with multimodal MWD. Thus the composition of the various pseudocomponents in the trial phase is given by the MWD function and the parameters of the distribution function \((A \text{ and } B)\) become the optimizing variables. This simplifies and considerably reduces the dimensionality of the problem, since the variable set now consists only of the solvent composition and two parameters of the distribution function. The size of the optimization problem for
determining thermodynamic stability in this case becomes independent of the number of pseudocomponents used to represent the polymer MWD.

Note that the MWD function used to represent the trial phase is only used as a simplification to search the composition space of the pseudocomponents for instability. The flash calculation is independent of the particular MWD of the pseudocomponents in the trial phase used for stability analysis.

If the stability algorithm cannot find a negative TPD, either the feed is stable or the minimization has failed to locate a negative TPD minimum. Ideally a global minimization should be done to ensure that the feed is stable. Since global searches are computationally very expensive, we use local minimization techniques using a quasi-Newton method. In particular we use the DONLP2 software\textsuperscript{146} which uses the BFGS updating scheme to perform the minimization. The pseudo-code for the stability algorithm is shown below along with the initialization for the variables:

\[ \text{do } i = 1, k \]

\[ A = 1e - 2 \]

\[ B = 1e - 5 \]

\[ x_i = x_{\text{guess}} \]

\[ x_{jzi} = \frac{(1 - x_{\text{guess}})}{k-1} \]

\[ \text{minimize(TPD)} \]

\[ \text{end do} \]

where

\[ x_{\text{guess}} \in \{0.999, 0.99, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7\} \]
The code cycles over all values of \( x_{\text{guess}} \), unless it locates a negative TPD, in which case it exits the loop. This method correctly identifies stability/instability in all cases considered here.

### 4.3 Pressure-Temperature Flash: Algorithm and Methodology

A PT-flash calculation involves determining the phase amounts and compositions of the equilibrium phases (here we consider vapor-liquid or liquid-liquid equilibrium) that an unstable feed at a given composition, pressure and temperature will phase split into. The equations specifying equilibrium in a PT-flash involve the isofugacity equation with mass balance and the constraints that the mole fractions and phase fractions should sum to unity. As outlined by Behme et al.\(^{113} \), we write the equations specifying a PT-flash for a \( k \) component solution with \( 1 \) polydisperse polymer and \( k-I \) monodisperse solvents.

Mass balance for each solvent, where \( \alpha \) is the phase fraction in moles and \( F \) refers to the feed phase while \( I \) and \( II \) are the resulting equilibrium phases formed, is given by:

\[
x_i^F = \alpha^I x_i^I + \alpha^{II} x_i^{II} \quad \quad i = 1,2,...s
\]  

Since the mole fraction in each phase and the phase fractions should sum to unity, it follows that:

\[
\sum_{i=1}^{K} x_i^I - \sum_{i=1}^{K} x_i^{II} = 0 \quad (4.11)
\]

\[
\alpha^I + \alpha^{II} = 1 \quad (4.12)
\]

Mass balance for the polymer, where \( M_n \) refers to the number average molecular weight in the phase and \( x_p \) the overall polymer composition in the phase is given by:
\[ x_p^F M_n^F = \alpha^I x_p^I M_n^I + \alpha^II x_p^II M_n^II \] (4.13)

The isofugacity condition for the solvent in the 2 phases is given by:

\[ 1 - \frac{x_i^I \varphi_i^I}{x_i^II \varphi_i^II} = 0 \quad i = 1,2,...s \] (4.14)

The composition of the pseudocomponents should sum to give the overall polymer composition in the phase. This condition in phase I and II is respectively given by the following equations (4.15) and (4.16).

\[ 1 - \frac{x_p^F}{x_p^I} \sum_{j=1}^{p} X_j^F \left[ \frac{\alpha^I + \alpha^II \varphi_{p,j}^I}{\varphi_{p,j}^II} \right]^{-1} = 0 \] (4.15)

\[ 1 - \frac{x_p^F}{x_p^II} \sum_{j=1}^{p} X_j^F \left[ \frac{\alpha^II + \alpha^I \varphi_{p,j}^II}{\varphi_{p,j}^I} \right]^{-1} = 0 \] (4.16)

where \( X_j^F \) is the mole fraction of the \( j \)th polymer pseudocomponent in the feed, on a solvent free basis. Equations (4.15) and (4.16) can be combined to give the following equation:

\[ \frac{x_p^F}{x_p^I} \sum_{j=1}^{p} X_j^F \left[ \frac{\alpha^I + \alpha^II \varphi_{p,j}^I}{\varphi_{p,j}^II} \right]^{-1} - \frac{x_p^F}{x_p^II} \sum_{j=1}^{p} X_j^F \left[ \frac{\alpha^II + \alpha^I \varphi_{p,j}^II}{\varphi_{p,j}^I} \right]^{-1} = 0 \] (4.17)

The equation for the number average molecular weight of the polymer in phase II is obtained by multiplying the molecular weight of the pseudocomponent with the mole fraction:

\[ M_n^II - \frac{x_p^F}{x_p^II} \sum_{j=1}^{p} X_j^F M_{p,j} \left[ \frac{\alpha^II + \alpha^I \varphi_{p,j}^II}{\varphi_{p,j}^I} \right]^{-1} = 0 \] (4.18)

The equation of state calculates the log of the fugacity coefficient from the chemical potential. Since the fugacity coefficients for the polymer pseudocomponents can be very
small (even up to the order of $10^{-1000}$) explicitly evaluating the fugacity coefficients can give numbers below the underflow limit of the computer and $\frac{\varphi^H_{p,j}}{\varphi^I_{p,j}}$ cannot be evaluated. Neglecting $\frac{\varphi^H_{p,j}}{\varphi^I_{p,j}}$ for a small value of the fugacity coefficient may not be reasonable because even though $\varphi^H_{p,j}$ and $\varphi^I_{p,j}$ are individually small numbers, the quotient can be numerically significant. To rigorously account for the quotient for each pseudocomponent we performed the following algebraic manipulation, which leads to all numerically significant contributions being accounted for in the mass balance:

$$\frac{\varphi^H_{p,j}}{\varphi^I_{p,j}} = \exp\left[\ln(\varphi^H_{p,j}) - \ln(\varphi^I_{p,j})\right] \tag{4.19}$$

On convergence the composition of the pseudocomponents (on a solvent free basis) in each phase are calculated by the following equations:

$$X^I_j = \frac{x^F_p X^F_j}{x^I_p \left[ \alpha^I \frac{\varphi^I_{p,j}}{\varphi^H_{p,j}} + \alpha^I \right]} \quad j = 1,2,...,P \tag{4.20}$$

$$X^H_j = \frac{x^F_p X^F_j}{x^H_p \left[ \alpha^H + \alpha^I \frac{\varphi^H_{p,j}}{\varphi^I_{p,j}} \right]} \quad j = 1,2,...,P \tag{4.21}$$

Equations 10 (k-1 equations), 12 (1 equation), 14 (k-1 equations), 17(1 equation) and 18(1 equation) are the equations that define the PT-flash. This gives a total of 2k+1 non-linear equations.

The variables being solved for are:

(k-1) compositions for each phase: $x^I, x^H$
Number average molecular weight in phase 1: $M_n^I$

Number average molecular weight in phase 2: $M_n^{II}$

Phase fraction of phase 2: $\alpha^{II}$

The total number of variables is $2(k-1)+3 = 2k+1$

This is a set of $2k+1$ non-linear equations in $2k+1$ variables which is solved using the Newton-Raphson approach. Once this system of equations has been solved, $K_A$ and $K_B$ can be determined from analytical expressions derived elsewhere$^{101,112,113,115}$. The molecular weight distribution in the two phases can now be calculated by substituting equation (4.7) in equations (4.20) and (4.21).

There are physical upper and lower bounds on all the variables (the compositions and phase fraction lie between 0 and 1, while the number average molecular weight ($M_n$) must lie between the minimum ($MW_{min}$) and maximum ($MW_{max}$) molecular weight of the pseudocomponent in the feed). The presence of variables of widely differing order of magnitude can lead to highly ill-conditioned matrices used in the process of solving the non-linear equations. Hence $M_n$ in both the phases is scaled as follows, so that all variables lie in the range 0-1.

$$SM_n = \frac{M_n - MW_{min}}{MW_{max} - MW_{min}} \quad (4.22)$$

$SM_n$ (scaled $M_n$), along with the compositions and the phase fraction are the variables of the non-linear equations.

The Newton’s step generated in an iteration of the non-linear equation solver can lead to unphysical values of the variables lying outside the bounds 0 and 1. This issue can be addressed in an adhoc fashion by including barrier functions such that if the variable is
outside the bounds then the objective functions return with a very high value. Since the variables have no physical significance outside their bounds, the above equations (4.10-4.19) are not defined in that case and hence discontinuous and non-differentiable outside the bounds. This absence of derivative information prevents the solver from accounting for the bounds and it can spend a lot of time searching in the unphysical variable space and not be able to solve the system of equations. An additional constraint on having composition as variables is that the compositions should sum to unity.

In this chapter we have addressed both these issues by a change of variables. We have introduced the following change of variables\textsuperscript{147} to generalized cylindrical polar coordinates that satisfies both the criteria $1 \geq x_i \geq 0$, $\sum_i x_i = 1$ and converts the problem to an unconstrained problem.

$$x_i = \cos^2 \theta_i \prod_{j=1}^{i-1} \sin^2 \theta_j, \quad i < k$$

$$x_k = \prod_{j=1}^{k-1} \sin^2 \theta_j$$

$$SM_n = \cos^2 \theta_m$$

$$\alpha^\| = \cos^2 \theta_i$$

The variables are now $\theta^I_j$ and $\theta^\|_j$ $j = 1, 2 \ldots k-1$ $\theta^I_m, \theta^\|_m$ and $\theta_i$.

With the above transformation of variables, for any value of iterates generated for $\bar{\theta}$, the primary variables (compositions, phase fraction and scaled number average molecular weights) lie within the feasible region (between 0 and 1).
The stability of the Newton-Raphson procedure can be affected by the accuracy of the Jacobian matrix. In this work we have generated derivatives using Automatic Differentiation\textsuperscript{148}.

The system of equations is highly non-linear and non-convex and the convergence to a solution critically depends on being able to initialize the variables accurately. The next section explains the initiation method developed in this work that allows for robust convergence without the need for any user intervention.

4.3.1 Initiation

The system of non-linear equations stated above with the transformed variables converges to the equilibrium solution in many cases with user specified initial variable estimates. But it is especially useful to have an alternate initialization methodology that is robust enough to converge without the user having to guess initial estimates for the variables. The initialization method we now propose also has the added usefulness that it can be used to generate the complete Pressure-composition (P-w) coexistence curve for a given feed composition.

Consider a feed at conditions $z$, $P_A$ and $T$. First the stability of the feed is checked; if the feed is stable then it will exist as a single stable phase, if the feed is unstable then the pressure is increased and the feed is checked for instability at each new pressure until a pressure is located where the feed is stable. At the last unstable pressure ($P_B$), the feed composition is close to the cloud point curve and is approximately equal to the equilibrium composition at that pressure and temperature. The trial phase from the
stability calculation for this state point is hence a good initial approximation for the other equilibrium phase at that temperature and pressure. The PT-flash initialized at this condition converges quickly. Next, using zero order homotopy (the converged solution at a given state point is used as the guess for the next state point) the pressure is decreased, with flash calculations at each pressure until the original pressure (P_A) is recovered.

This method traces out the P-w coexistence curve for the polymer solvent system from the pressure of interest (P_A) to the limit of instability pressure (P_B). Using this algorithm the flash calculations take less than a second. The stability calculation can take up to ten seconds for a polydisperse polymer with a single solvent, depending on how far the feed pressure is from the pressure of incipient stability at the feed composition. Figure 4.4 represents the algorithm pictorially on a P-w diagram. If the pressure is fixed and the temperature varied then the above algorithm can be similarly used for generating the T-w coexistence curve at a given feed.

![Figure 4.4: Schematic for the PT-flash algorithm. Starting feed is at pressure P_A. The stability algorithm increases the pressure until it locates the pressure of incipient instability (P_B). A PT-flash at P_B converges easily and the coexistence curve is traced from P_B to P_A using homotopy.](image-url)
4.4 Cloud Point Calculation: Algorithm and Methodology

The cloud point of a polymer solution is the condition at which the solution at a given composition transitions from a single phase to two phases on varying temperature or pressure, the associated cloudiness associated with immiscibility being responsible for the name. The cloud point calculation involves calculating the conditions specifying the phase (composition and pressure or temperature) that is in equilibrium with a solution of specified composition. The algorithm for cloud point calculation that we present follows that proposed by Koak and Heidemann\textsuperscript{138} but generalizes it to the case of a polydisperse polymer with multiple solvents using the simplification afforded by equation (4.1). The composition in the cloud phase (phase I) is given by $z$. The composition in the equilibrium shadow phase (phase II) is calculated from the partition coefficient ($K$) as:

$$Y_i = K_i z_i$$

The $Y_i$ are equal to the mole fraction in the cloud phase on convergence. During the iterative solution process however they are treated as mole numbers and normalized to a unit basis whenever mole fractions are required.

Koak and Heidemann\textsuperscript{138} introduced an elegant way of specifying the cloud phase composition by using a variable $\nu$. $\nu$ is defined such that $\exp(\nu)$ is the mass of polymer per unit mass of solvent. This allows $\nu$ to vary from negative infinity to positive infinity as the cloud phase composition varies from pure solvent to pure polymer. $m_{pi}$ is the mass of the $i^{th}$ polymer pseudocomponent on a solvent-free basis and $m_{sj}$ is the mass of the $j^{th}$ solvent on a polymer-free basis such that for $p$ pseudocomponents and $s$ solvents,
\[
\sum_{i=1}^{p} m_{pi} = 1 \quad \text{and} \quad \sum_{i=1}^{s} m_{si} = 1.
\]

For unit mass of solvent in the cloud phase the no. of moles of polymer pseudocomponent \( i \) is \( n_i = \frac{e^\psi m_i}{M_i}, \quad i = 1, \ldots, p \)

The polymer mole fraction in the cloud phase is given for each pseudocomponent by:

\[
z_i = \frac{e^\psi m_{pi} / M_i}{\sum_{i \rightarrow \text{solvents}} m_{si} / M_i + \sum_{j \rightarrow \text{polymer}} e^\psi m_{pj} / M_j}
\]

(4.27)

and the solvent mole fraction of each solvent in the cloud phase is:

\[
z_i = \frac{m_{si} / M_i}{\sum_{i \rightarrow \text{solvents}} m_{si} / M_i + \sum_{j \rightarrow \text{polymer}} e^\psi m_{pj} / M_j}
\]

(4.28)

Following the suggestion of Michelsen\(^{149}\) and Koak and Heidemann\(^{138}\), the variables of the phase equilibrium problem are transformed to similar orders of magnitude by choosing \( \ln(K_i) \) as the variables and \( \ln T \) or \( \ln P \) depending on whether isobars or isotherms are being calculated. The vector of independent variables (\( \psi \)) that are required to specify the two phase equilibrium depend on the kind of phase boundary of interest. For a cloud point curve at constant pressure the independent variables are:

\[
\psi = \left( \ln K_{pi}, \ln K_{pp}, \ln K_{si}, \ldots, \ln K_{sp}, \ln T, v \right)^T
\]

(4.29)

The first two partition coefficients are for the smallest and largest polymer pseudocomponents, while the following partition coefficients are for each of the solvent. The partition coefficient of the smallest and largest pseudocomponent can be used to determine \( A \) and \( B \) in equation (4.1) and this specifies the partition coefficient for all the pseudocomponents. Thus, using equation (4.1) reduces the polymeric contribution to the
dimensionality of the phase equilibrium problem from \( p \) to 2; a reduction of possibly several orders of magnitude.

At constant temperature the cloud point curve can be calculated by using the following independent variables:

\[
\psi = \left( \ln K_{p1}, \ln K_{pp}, \ln K_{s1}, \ldots, \ln K_{ss}, \ln P, \ln \nu \right)^T
\]  

(4.30)

Finally it is often required to know where the two phase boundary of a polymer solution is in the pressure-temperature space. This calculation can be achieved by fixing \( \nu \) to the composition of the solution of interest and solving for the partition coefficients, pressure and temperature.

\[
\psi = \left( \ln K_{p1}, \ln K_{pp}, \ln K_{s1}, \ldots, \ln K_{ss}, \ln P, \ln T \right)^T
\]

So for each kind of cloud point curve (at constant pressure or constant temperature or constant composition) the number of variables is \( s + 4 \). The equations specifying two phase equilibrium for a polydisperse polymer in solution with multiple \( (s) \) solvents are:

Equality of chemical potential in the cloud and shadow phase for each solvent,

\[
F_i = \left( \frac{\mu_i}{RT} \right)^{ii} - \left( \frac{\mu_i}{RT} \right)^{ij} = 0, \quad i = 1, 2, \ldots s
\]  

(4.31)

The \( Y_i \) should sum to unity on convergence.

\[
F_{s+1} = \sum_{i=1}^{n} Y_i - 1 = \sum_{i=1}^{n} z_i K_i - 1 = 0
\]  

(4.32)

where \( n \) is the number of total components including \( p \) polymer pseudocomponents.

Satisfaction of equation (4.1) by the smallest and largest pseudocomponent ensures that equilibrium condition is met by all the pseudocomponents and this provides the last 2 equations specifying the phase equilibrium criteria:
\[ F_{s+2} = \ln K_{p1} - \left( A + M_{p1} B \right) = 0 \]  \hspace{1cm} (4.33)

\[ F_{s+3} = \ln K_{pp} - \left( A + M_{pp} B \right) = 0 \]

This gives \( s + 3 \) equations in \( s + 4 \) variables. The final equation comes from specifying any one of the variables using an equation of the following form where \( S \) is the value of the specified variable \( (\psi_s) \).

\[ F_{s+4} = \psi_s - S = 0 \]  \hspace{1cm} (4.34)

This completes the system of \( s + 4 \) equations in \( s + 4 \) variables that can be used to generate cloud point curves on P-w, T-w or PT space. For calculating the P-w and T-w phase envelope it is convenient to specify one of the \( K_i \) as being fixed. The above system of equations is solved using the Newton-Raphson procedure. As Koak and Heidemann\textsuperscript{138} mentions fixing the \( K \) value of the heaviest component as the specified variable \( (\psi_s) \) permits convergence of the Newton-Raphson procedure even from poor guesses for the variable \( v \). The cloud point calculation can also be initiated using a converged PT-flash result. Since the stability of the calculations depends on the accuracy of the Jacobian matrix, we use ADIFOR\textsuperscript{148} generated derivatives to stabilize the solution procedure.

**4.4.1 Extrapolation**

Once the system of equations converges for a single point on the cloud point curve the rest of the phase diagram can be traced out by varying any one of the variables. Guesses for subsequent points on the phase diagram are generated by fitting a polynomial to previous points \textsuperscript{144}. The sensitivities of the independent variables along the cloud point
curve to a change in the one specified variable, at a converged point is given by the solution to the following equation:

\[
j \begin{bmatrix} \frac{\partial \psi}{\partial s} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}
\]  

(4.35)

The linear extrapolation for each independent variable is written as:

\[
\psi_{s_2}^0 = \psi_{s_1} + \frac{\partial \psi}{\partial s} (s_2 - s_1)
\]  

(4.36)

Other alternatives are fitting a cubic to the previous two converged solutions and their derivatives or fitting a cubic to the last four convergent points. In the algorithm’s current implementation a linear extrapolation is used to generate guesses for the first few points on the phase diagram and then subsequent guesses are generated by fitting a cubic to previous four converged points. Selecting the variable with the largest sensitivity \( \frac{\partial \psi}{\partial s} \) in magnitude as the specified variable avoids specification that might be infeasible arising due to the variable being at its extremum.

4.5 Results

We have performed stability and PT-flash calculations for polydisperse polyethylene (PE) solutions for both the SAFT and PC-SAFT equations of state using parameters reported in literature\(^{4,6}\). In Figure 4.5, the PT phase envelop is calculated for the PE/ethylene system. The stability algorithm proposed in this work accurately delineates
the region of thermodynamic stability and instability. The polymer in this case has a polydispersity index of about 2 and the feed MWD has been discretized to give 36 pseudocomponents. The PE/ethylene binary interaction parameter \( k_{ij} \) was set to 0.0404. Figure 4.6 maps out the PT phase envelope using stability analysis for a ternary system (PE/ethylene/hexane). The curve is from phase equilibrium calculation while the symbols are the limit of instability using the stability algorithm. Figure 4.7 shows the cloud and shadow point curve for a monodisperse PE and polydisperse PE (MWD in Table 4.1) in hexane from SAFT. The stability algorithm identifies the 2 phase region (filled symbols) and single phase region (unfilled symbols).

The other set of systems studied to test the stability and flash algorithm is a 250 pseudocomponent polymer with unimodal, bimodal and trimodal MWD generated by direct numerical integration of the MWD curve resulting from SEC analysis. The MWD for the PE is shown in Figure 4.8. In the absence of any other information the \( k_{ij} \) between PE and hexane was set to zero. Calculations were performed for a feed with 0.15 mass fraction polymer at 220 °C and 10 bar (VLE) and 250 °C and 65 bar (LLE). Flash calculations were preceded by stability calculation in each case which predicted instability for the cases considered.

Figure 4.9 and Figure 4.10 show the results of the locus of equilibrium compositions with changing pressure on flashing a feed (PE/hexane) with 0.15 polymer mass fraction at 250 °C and 220 °C respectively. Note that these are coexistence curves on flashing a feed of fixed composition and MWD at different pressures. The coexistence curve differs from the cloud and shadow curve for a polydisperse solution. The highest point on the coexistence curve intersects with the cloud and shadow curve since the feed
Figure 4.5: PT envelope for binary polyethylene (M_n = 56K, M_w = 99K) - ethylene mixture (with 0.167 wt% PE in the cloud point mixture). The stability algorithm accurately delineates the stable region (unfilled symbols) from the unstable region (filled symbols).

Figure 4.6: PT envelope for ternary polyethylene (M_n = 56K, M_w = 99K) /ethylene/hexane mixture (with 0.167 wt% PE in the cloud point mixture). The algorithm accurately determines the thermodynamic stability limit.
composition is the cloud phase composition in this case. The coexistence curves terminate at this highest point since above this pressure the feed is stable as a single phase. Note that hexane is sub-critical at the lower temperature and supercritical at the higher temperature. The discontinuity in the slope of the P-w curve in Figure 4.10 indicates the transition from LLE to VLE in the presence of a sub-critical solvent while the absence of any discontinuity in the slope in Figure 4.9 indicates a supercritical solvent, with fluid-fluid equilibrium over the entire composition range.

The polymer rich equilibrium phase has a MWD that mimics the feed MWD. The equilibrium MWD are shown for the two equilibrium liquid phases at 65 bar and 220 °C for each feed distribution (from Figure 4.8) in Figure 4.11.

Figure 4.7: Cloud and shadow point curve (P-w) for a polyethylene (M_n = 33000, M_w = 124093) hexane system. The lower curve is calculation for the monodisperse polymer with a molecular weight of M_n. The curves on the top are polydisperse calculations with 10 pseudocomponents. The curve on the left is the shadow phase and the one on the right is the cloud phase. Symbols denote the feed condition, stability algorithm identifies the stable (unfilled symbols) and unstable feed (filled symbols).
Figure 4.8: 250 pseudocomponents generated from SEC data. Unimodal, bimodal and trimodal feed distribution with the polydispersity index (PI) specified.

<table>
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<tr>
<th>Molecular weight</th>
<th>Mass fraction</th>
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<tr>
<td>1049116</td>
<td>0.0241</td>
</tr>
<tr>
<td>4562825</td>
<td>5.96E-04</td>
</tr>
</tbody>
</table>

Table 4.1: Molecular Weight Distribution for PE in cloud phase for Figure 4.9.
Figure 4.9: P-w coexistence curve for PE/hexane generated by flashing a feed with 0.15 mass fraction PE at 250 °C. The dotted line shows the feed composition.

Figure 4.10: P-w coexistence curve for PE/hexane generated by flashing a feed with 0.15 mass fraction PE at 220 °C. The kink in the curve signifies the transition for VLE to LLE.
Figure 4.11: MWD in equilibrium phases on flashing a ternary feed of PE/ethylene/hexane at 250 °C and 65 bar with 0.15 mass fraction PE and 0.03 mass fraction hexane.

4.6 Conclusions

In this chapter we present robust and efficient algorithms for thermodynamic stability analysis, Pressure-Temperature (PT) flash and cloud point calculation for polydisperse polymer systems. The proposed algorithm simplifies the checking of thermodynamic stability for polydisperse polymer solutions which may contain hundreds of pseudocomponents by limiting the optimizing variables to the parameter space of a distribution function as opposed to the composition space of each pseudocomponent. This considerably reduces the dimensionality of the problem. This chapter also details a robust two-phase, PT flash and cloud point calculation algorithm in which the size of the system
of equations to be solved is independent of the number of pseudocomponents used to represent the polymer MWD. The robustness of the flash results from the initiation methodology presented which allows for fast convergence without the need for user intervention. The proposed algorithms have been used to calculate phase equilibrium in polydisperse polymer solutions including polymers with multimodal molecular weight distribution, in solution with multiple solvents.
Chapter 5

Phase Equilibria in Polydisperse Dipolar Copolymer Solutions

In this chapter we derive the equations which prove the applicability of the algorithms presented in Chapter 4 for molecular weight polydisperse homopolymers, to molecular weight polydisperse dipolar copolymer systems. To minimize the number of parameters that is fitted to mixture data, we model the dipolar copolymer as a homosegmented chain (all segments have the same size and dispersion energy). We determine the dipolar copolymer parameters a-priori by relating these parameters to the parameters for polyethylene and the dipolar comonomer fluid. While this simplification is only expected to provide a first pass model for a dipolar copolymer, we are able to qualitatively model characteristics of dipolar copolymer solutions using this approach. The applicability of the algorithms presented in Chapter 4 for dipolar copolymer solutions leads to the size of the system of equations specifying phase equilibrium in these solutions being independent of the number of pseudocomponents used to represent the copolymer molecular weight distribution (MWD). We perform phase equilibrium calculations using the proposed algorithm, in polydisperse polyethylene-co-vinyl acetate (EVA) solutions to illustrate the effect of polydispersity on the phase behavior of polydisperse dipolar copolymer solutions.
5.1 Introduction

The addition of comonomers to polyethylene extends the range of desirable properties that the resulting polymer exhibits. For instance poly (ethylene-co-vinyl acetate) is used in a wide range of applications because of its better gloss, tensile strength, flexibility and other product properties as compared to low density polyethylene (LDPE). The stronger inter-chain cohesion due to polar interactions is responsible for the improved physical properties of polar copolymers.

Accurate information on the phase behavior of dipolar copolymer solutions is important in the copolymer manufacturing process for the following two reasons. First, in the high pressure polyethylene process (HPPE) that EVA is produced in, it is sometimes desirable to carry out the reaction in a two-phase region as discussed by Folie and Radosz\textsuperscript{150}. The solubility of the monomer, free radical, initiator and chain terminating agent will differ in both the phases. This affects the polymerization kinetics and the final properties of the polymer product formed. Secondly, downstream from the reactor the polymer is separated from the bulk of the unreacted monomer using a low pressure fluid-liquid separator. The polymer with wide molecular weight distribution undergoes fractionation in this separation process with the light ends being extracted in the polymer-lean phase and the majority of the polymer being in the polymer-rich phase.

To optimize the polymerization process and supercritical separation process it is necessary to estimate the equilibrium phase amounts, compositions and physical properties (molecular weight and MWD) of the phases over a range of pressures and temperatures. Folie\textsuperscript{151} has discussed previous efforts to model the phase behavior and
fractionation in EVA systems and the shortcomings of these methods. The two limitations in modeling the above processes was the lack of 1) a physically based equation of state that could explicitly account for multiple dipolar groups in the polymer and 2) the inability to account for polydispersity without compromising on computational expense or accuracy as discussed in Chapter 4. The former limitation was addressed by Jog and Chapman\cite{68} with the development of an equation state (Polar-SAFT) that can simultaneously account for the effect of molecular shape and multiple dipolar sites on thermodynamic properties. The development of this theory is introduced in the next section. In this chapter we solve the latter limitation of the lack of an efficient methodology to handle polydispersity in dipolar copolymers. We accomplish this by showing that the dipolar contribution to the free energy depends only on the first moment of the molecular weight distribution and that the residual chemical potential of a dipolar pseudocomponent varies linearly with the pseudocomponent's molecular weight. This allows the algorithms presented in Chapter 4 to be used for molecular weight polydisperse dipolar copolymer solutions. In the next section we detail the derivation of the equation that simplifies the handling of polydispersity in dipolar copolymer solutions.

5.2 Theory

Jog and Chapman\cite{68,70} developed an approach to model dipolar chain fluids that explicitly accounts for multiple dipolar functional groups and the effect of non-spherical molecular shape. A model of a chain molecule with the dipoles perpendicular to the line joining the center of the spheres is shown in Figure 5.1. In the SAFT formalism the residual
Helmholtz energy to an ideal gas at the same temperature and density is the sum of the hard sphere ($A^{hs}$), chain ($A^{chain}$), dispersion ($A^{dispersion}$), association ($A^{assoc}$) and the polar ($A^{polar}$) contribution.

$$A^{res} = A^{hs} + A^{dispersion} + A^{polar} + A^{chain} + A^{assoc}$$  \hspace{1cm} (5.1)

The hard sphere, chain, dispersion and association contributions to the Helmholtz energy have been explained in Chapter 1. Here we present the dipolar contribution to the Helmholtz energy due to Jog and Chapman$^{68,70}$ and derive the simplifications that allow us to efficiently account for polydispersity. The $u$-expansion$^{69}$ is the most widely applied statistical mechanical perturbation theory developed for spherical polar fluids. Using the

![Dipolar Chain Molecule](image.png)

Figure 5.1: Model of a dipolar chain molecule. The dipole is oriented so that it is perpendicular to the line joining the center of the spheres.

$u$-expansion, the dipolar term can be expanded as an infinite series of terms of second, third and higher order. The second and third order term are calculated explicitly while terms higher than the third order are estimated by the Padé approximant of Rushbrooke et al.$^{152}$. The change in the free energy due to polar interactions can be written using the Padé approximant as:

$$A^{polar} = \frac{A_2}{1 - A_3 / A_2}$$  \hspace{1cm} (5.2)

The terms $A_2$ and $A_3$ are given by
\[
\frac{A_2}{NkT} = \frac{2\pi}{9} \frac{\rho}{(kT)^2} \sum_i \sum_j x_i x_j m_i m_j X_{pi} X_{pj} \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij} \tag{5.3}
\]

\[
\frac{A_3}{NkT} = \frac{5}{162} \pi^2 \frac{\rho^2}{(kT)^3} \sum_i \sum_j \sum_k x_i m_i x_j m_j x_k m_k X_{pi} X_{pj} X_{pk} \frac{\mu_i^2 \mu_j^2 \mu_k^2}{d_{ij} d_{jk} d_{ik}} I_{3,ijk} \tag{5.4}
\]

where \( \rho \) is the number density, \( x_i \) is the mole fraction, \( m_i \) is the chain length parameter which is proportional to the molecular weight of the polymer \( m_i = \alpha M_i \), \( X_{pi} \) is the fraction of polar segments in the chain and \( \mu_i \) is the dipole moment of component \( i \). \( d_{ij} \) is the temperature dependent mean diameter of components \( i \) and \( j \). In the derivation that follows \( \sum_p \) refers to summation over all the polymer pseudocomponents while \( \sum_s \) refers to summation over all the solvents present in the system.

The integrals \( I_{2,ij} \) and \( I_{3,ijk} \) in equations (5.3) and (5.4) are related to the corresponding pure fluid integrals by van der Waals one fluid theory approximation:

\[
I_{2,ij} = I_2(\rho d_s^3) \tag{5.5}
\]

\[
I_{3,ijk} = I_3(\rho d_s^3) \tag{5.6}
\]

where \( I_2 \) and \( I_3 \) are the corresponding pure fluid integrals given by Rushbrooke at al.\cite{152}

The average diameter according to van der Waals one fluid theory is defined as:

\[
d_s^3 = \frac{\sum_i \sum_j x_i m_i x_j m_j d_{ij}^3}{\sum_i \sum_j x_i m_i x_j m_j} \tag{5.7}
\]

From the definition of the number average molecular weight of the polymer \( \bar{M}_n \), it follows that:

\[
\sum_{i=1}^{\rho} x_i m_i = \alpha \sum_{i=1}^{\rho} x_i M_i = \bar{x}_n \alpha \bar{M}_n = \bar{x}_n \bar{m}_n \tag{5.8}
\]
where \( \bar{x}_n = \sum_{p} x_i = 1 - \sum_{s} x_i \) is the total polymer mole fraction in the solution and \( \bar{m}_n \) is the chain length corresponding to the \( \bar{M}_n \) of the polymer.

\[
d_x^3 = \frac{\sum_{p} x_i m_i x_j m_j d_{ij}^3 + 2 \sum_{p} x_i m_i x_j m_j d_{ij}^3 + \sum_{s} x_i m_i x_j m_j d_{ij}^3}{\sum_{p} x_i m_i x_j m_j + 2 \sum_{p} x_i m_i x_j m_j + \sum_{s} x_i m_i x_j m_j} \quad (5.9)
\]

\[
d_x^3 = \frac{(\bar{x}_n \bar{m}_n)^2 d_{pp}^3 + 2 \bar{x}_n \bar{m}_n \sum_{s} x_j m_j d_{ij}^3 + \sum_{s} x_i m_i x_j m_j d_{ij}^3}{(\bar{x}_n \bar{m}_n)^2 + 2 \bar{x}_n \bar{m}_n \sum_{s} x_j m_j + \sum_{s} x_i m_i x_j m_j} \quad (5.10)
\]

The summation in equation (5.3) can be split up and rewritten as:

\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \left( \sum_{p} x_i x_j m_i m_j X_{p, X_{p}} \frac{\mu_i \mu_j}{d_{ij}^3} L_{2,ij} + 2 \sum_{p} x_i x_j m_i m_j X_{p, X_{p}} \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} L_{2,ij} \right) + \sum_{s} x_i x_j m_i m_j X_{p, X_{p}} \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} L_{2,ij} \quad (5.11)
\]

For each summation above, \( L_2 \) is evaluated at \( \rho d_x^3 \) where \( d_x^3 \) is given by (5.10). Thus, \( L_2 \) only depends on the average properties of the polymer and is independent of the detailed polymer distribution. The first term in equation (5.11) evaluates to the following expression, where \( X_{pp} \) is the fraction of polar segments in the polymer.

\[
\sum_{p} x_i x_j m_i m_j \frac{\mu_i \mu_j}{d_{ij}^3} I_2 \sum_{p} x_i x_j m_i m_j \quad (5.12)
\]

\[
\sum_{p} x_i x_j m_i m_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_2 \bar{m}_n^2 \bar{x}_n^2 \quad (5.13)
\]

The second term in equation (5.11) also depends only on the average properties of the polymer and reduces to:
\[ \sum_{p} \sum_{s} (\cdot) = X_{pp} \mu_{p}^{2} \overline{m}_{n} x_{n} \sum_{i=p+1}^{p+s} x_{i} m_{i} X_{pi} \frac{\mu_{i}^{2}}{d_{pi}^{2}} I_{2} \]  

(5.14)

Similarly the third order contribution to the Helmholtz energy is written as:

\[ \frac{A_{3}}{NkT} = \frac{5 \pi^{2} \rho^{2}}{162 (kT)^{3}} \left( \sum_{p} \sum_{p} \sum_{s} x_{m} x_{j} x_{i} m_{j} m_{k} X_{pr} X_{pj} X_{pk} \frac{\mu_{i}^{2} \mu_{j}^{2} \mu_{k}^{2}}{d_{ij} d_{jk} d_{ik}} I_{3,ijk} + \right. 

\[ \left. 3 \sum_{p} \sum_{s} \sum_{s} x_{m} x_{j} x_{i} m_{j} m_{k} X_{pr} X_{pj} X_{pk} \frac{\mu_{i}^{2} \mu_{j}^{2} \mu_{k}^{2}}{d_{ij} d_{jk} d_{ik}} I_{3,ijk} + \right. 

\[ \left. 3 \sum_{p} \sum_{s} \sum_{s} x_{m} x_{j} x_{i} m_{j} m_{k} X_{pr} X_{pj} X_{pk} \frac{\mu_{i}^{2} \mu_{j}^{2} \mu_{k}^{2}}{d_{ij} d_{jk} d_{ik}} I_{3,ijk} + \right. 

\[ \left. \sum_{s} \sum_{s} \sum_{s} x_{m} x_{j} x_{i} m_{j} m_{k} X_{pr} X_{pj} X_{pk} \frac{\mu_{i}^{2} \mu_{j}^{2} \mu_{k}^{2}}{d_{ij} d_{jk} d_{ik}} I_{3,ijk} \right) \]  

(5.15)

\[ \sum_{p} \sum_{p} \sum_{p} (\cdot) = X_{pp}^{3} \frac{\mu_{p}^{6}}{d_{p}^{3}} I_{3,pppp} \overline{m}_{n} x_{n}^{3} \]  

(5.16)

\[ \sum_{p} \sum_{p} \sum_{s} (\cdot) = X_{pp}^{2} \frac{\mu_{p}^{4}}{d_{p}^{2}} \overline{m}_{n} x_{n}^{2} \sum_{i=p+1}^{p+s} x_{i} m_{i} X_{pi} \frac{\mu_{i}^{2}}{d_{pi}^{2}} I_{3,ppi} \]  

(5.17)

\[ \sum_{p} \sum_{s} \sum_{s} (\cdot) = X_{pp} \mu_{p}^{2} \overline{m}_{n} x_{n} \sum_{i=p+1}^{p+s} \sum_{j=p+1}^{j+p+1} x_{i} m_{i} X_{pi} x_{j} m_{j} X_{pj} \frac{\mu_{i}^{2} \mu_{j}^{2}}{d_{pi} d_{pj} d_{ij}} I_{3,ppij} \]  

(5.18)

From equations (5.13) - (5.18) it follows that polar contribution to the Helmholtz energy depends on the temperature, density, number average molecular weight (\( \overline{M}_{n} \)) (or the number average chain length \( \overline{m}_{n} \)) of the polymer, total polymer composition (\( \overline{x}_{n} \)) and the solvent compositions (\( \{x_{s}\} \)).

\[ \frac{A_{3}}{NkT} = f(\rho, T, \overline{x}_{n}, \overline{M}_{n}, \{x_{s}\}) \]  

(5.19)

\[ \frac{A_{3}}{NkT} = f(\rho, T, \overline{x}_{n}, \overline{M}_{n}, \{x_{s}\}) \]  

(5.20)

The residual chemical potential of a polymer pseudocomponent 'i' is given by:
\[
\mu_{i}^{polar} = \frac{\partial}{\partial n_i} \left( \frac{nA_{i}^{polar}}{NkT} \right)
\]

(5.21)

where \( n \) is the total number of moles in the system.

\[
\frac{\partial \left( n \frac{A_{i}^{polar}}{NkT} \right)}{\partial n_i} = n \left( \frac{A_2}{NkT} - \frac{A_3}{NkT} \right) 2 \frac{A_2}{NkT} \frac{\partial \left( \frac{A_2}{NkT} \right)}{\partial n_i} - n \left( \frac{A_2}{NkT} \right)^2 \frac{\partial \left( \frac{A_2}{NkT} \right)}{\partial n_i} + \frac{A_{i}^{polar}}{NkT}
\]

(5.22)

\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \sum_i \sum_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij}
\]

(5.23)

\[
\frac{n \partial \left( \frac{A_2}{NkT} \right)}{\partial n_i} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \frac{\partial}{\partial n_i} \left( \sum_i \sum_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij} \right) + \frac{A_2}{NkT}
\]

(5.24)

The summation over all components \( i, j \) can be split up as below into summation over polymer and solvents.

\[
\sum_i \sum_j = \sum_p \sum_p + 2 \sum_p \sum_s + \sum_s \sum_s
\]

\[
\frac{\partial}{\partial n_i} \left( \sum_p \sum_t n_i \mu_i \mu_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij} \right) = \frac{2}{n} \left[ \sum_p \sum_t m_p \mu_p^4 \frac{\mu_p^4}{d_p^3} I_{2,pp} - 2\sum_s \sum_t m_s \mu_s^2 X_{pp} \frac{\mu_s^2}{d_p^3} I_{2,sp} \right]
\]

(5.25)

\[
\frac{\partial}{\partial n_i} \left( \sum_s \sum_t n_i \mu_i \mu_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij} \right) = \frac{1}{n} \left[ \sum_s \sum_t m_s \mu_s \mu_p \sum_i \mu_i \mu_j \frac{\mu_j^2}{d_{ij}^3} I_{2,pi} - \right]
\]

(5.26)
\[
\frac{\partial}{\partial n_i} \left( \frac{\sum_s \sum_{n, m, m_j} x_{n, m, m_j} \rho_{n, m, m_j} \mu_i^2 \mu_j^2 \delta_y^{2j}}{n^2} \right) = -2 \left[ \sum_s \sum_s x_i x_j m_i m_j x_{n, m, m_j} \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij} \right]
\]

(5.27)

\[
\frac{n\partial}{\partial n_i} \left( \frac{A_2}{NkT} \right) = \frac{2\pi n}{9} \frac{\rho}{(kT)^2} \frac{\partial}{\partial n_i} \left( \sum_p \sum_p + 2 \sum_s \sum_s + \sum_s \sum_s \right)
\]

(5.28)

\[
\frac{n\partial}{\partial n_i} \left( \frac{A_2}{NkT} \right) = -\frac{4\pi}{9} \left( \frac{\rho}{(kT)^2} \right)
\]

\[
\left\{ \begin{array}{l}
\bar{x}_n \bar{m}_n \frac{\mu_i^4}{d_p^3} I_{2,pp} - \frac{\mu_i^2}{d_p^3} I_{2,pp} \\
2\bar{x}_n \bar{m}_n \frac{\mu_i^4}{d_p^3} I_{2,pp} + \left[ \sum_s \sum_{x_j m_j} x_j m_j x_{n, m, m_j} \frac{\mu_j^2}{d_{ij}^3} I_{2,ij} \right] \\
\sum_s \sum_s x_i x_j m_i m_j x_{n, m, m_j} \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_{2,ij}
\end{array} \right.
\]

(5.29)

\[
\frac{n\partial}{\partial n_i} \left( \frac{A_2}{NkT} \right) = A + BM_i
\]

(5.30)

where \( A, B = f(T, \rho, \bar{x}_n, \bar{m}_n, \{x_i\}) \)

Similarly

\[
\frac{n\partial}{\partial n_i} \left( \frac{A_3}{NkT} \right) = C + DM_i
\]

(5.31)

Substituting equations (5.30) and (5.31) in equation (5.21) gives the linear relation between the polar contribution to the residual chemical potential and molecular weight of the polymer pseudocomponent (\( M_i \)).
\[ \frac{\mu_{i}^{\text{polar}}}{RT} = E + M_i F \] (5.32)

where \( A, B, C, D, E, F = f(T, \rho, \bar{x}_n, \bar{m}_n, \{x_i\}) \) are functions only of the number average molecular weight of the polymer, total polymer composition, density, temperature and solvent compositions. \( K1 \) and \( K2 \) that occur next also have the same functional dependence. The residual chemical potential of a polymer pseudocomponent is given by the summation:

\[ \mu^{\text{res}} = \mu^{\text{hs}} + \mu^{\text{dispersion}} + \mu^{\text{chain}} + \mu^{\text{polar}} \] (5.33)

Jog and Chapman\(^{112}\) have shown that the hard sphere, chain and Chen-Kreglewski dispersion contribution to the residual chemical potential for a polymer pseudocomponent varies linearly with its molecular weight just as equation (5.32). Ting\(^{101}\) has shown the same linear behavior for the perturbed-chain dispersion term. Thus the residual chemical potential for a polymer pseudocomponent \( i \) can be written as:

\[ \frac{\mu_{i}^{\text{res}}}{RT} = K1 + M_i K2 \] (5.34)

The simplification in solving for phase equilibria comes from the fact that the functions \( K1 \) and \( K2 \) are the same for all the polymer pseudocomponents. Given the above simplification for the polar term, phase equilibria calculation in polydisperse dipolar copolymer solutions can be performed using the algorithms presented in Chapter 4 in which the problem size is independent of the number of polymer pseudo-components \( (p) \) used to represent the polymer molecular weight distribution.
5.3 Results

Application to Ethylene-co-vinyl acetate (EVA) copolymer

*Ethylene/vinyl acetate vapor-liquid equilibria (VLE)*

First we model vinyl acetate (VA) using polar PC-SAFT by fitting the pure component parameters, including the fraction of polar segments for vinyl acetate ($x_p\_VA$) to vapor pressure and saturated liquid density. The PC-SAFT parameters for the components are listed in Table 5.1. Figures 5.2-5.4 show comparison of predictive results ($k_{ij}=0$) from the model and experimental data$^{153}$ for VLE in vinyl acetate/ethylene. It is seen that even with a zero $k_{ij}$, polar PC-SAFT accurately models the VLE behavior of this systems by explicitly accounting for the dipolar interactions.

<table>
<thead>
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<th>Component</th>
<th>$M$ (-)</th>
<th>$\sigma$ (Å)</th>
<th>$\mu^0/k$ (K)</th>
<th>Dipole fraction (-)</th>
<th>Dipole moment (Debye)</th>
</tr>
</thead>
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<td>3.4450</td>
<td>176.47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Vinyl Acetate</td>
<td>3.343</td>
<td>3.3000</td>
<td>234.29</td>
<td>0.0931</td>
<td>1.7</td>
</tr>
<tr>
<td>EVA</td>
<td>878.42</td>
<td>4.0217</td>
<td>252.00</td>
<td>0.01676</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5.1: Polar PC-SAFT parameters

*Monodisperse EVA/ethylene liquid-liquid equilibria (LLE)*

EVA is a polar copolymer and the co-polymeric nature is accounted for in our model by having dipole on some of the segments in the polymer. We model EVA as a homo-segmented polymer (all the polymer segments are of the same size and have the same
dispersion energy). We use the same parameters as Polyethylene for the dispersion energy, chain length parameter and the segment size for the copolymer. This is a first pass approximation for modeling a dipolar copolymer. A more sophisticated model for copolymers (which is presented in Chapter 6) will account for the difference in size and dispersion energy between the monomer and co-monomer segments in the copolymer.

The simplified model for dipolar copolymers presented in this chapter can be justified in two ways. 1) This reduces the number of adjustable binary parameters \( k_{ij} \) in the model to one as compared to three in the more sophisticated model. 2) The effect of the dipolar group in EVA should have a stronger effect on the phase behavior than the presence of

![Figure 5.2: Vinyl acetate/Ethylene VLE at 293.15K. Comparison between polar PC-SAFT \( (k_{ij}=0) \) and experimental data\textsuperscript{153} (symbols).]
Figure 5.3: Vinyl acetate/Ethylene VLE at 333.15K. Comparison between polar PC-SAFT ($k_{ij} = 0$) and experimental data \(^{153}\) (symbols).

Figure 5.4: Vinyl acetate/Ethylene VLE at 353.15K. Comparison between polar PC-SAFT ($k_{ij} = 0$) and experimental data \(^{153}\) (symbols).
different segment types in the copolymer. The dipole moment and the fraction of polar
segments for the vinyl acetate comonomer in EVA are fixed to be the same as that of the
vinyl acetate molecule.

We scale the fraction of polar segments in EVA ($x_{p_{EVA}}$) with the mass fraction
of vinyl acetate ($x_{m_{VA}}=0.18$) in the copolymer, where $x_{p_{VA}}$ is the fraction of polar
segments in the vinyl acetate molecule.

$$x_{p_{EVA}} = x_{p_{VA}} \times x_{m_{VA}}$$ (5.35)

In Figure 5.5 we present a LLE isotherm for the EVA (Molecular weight of 33400, 18% 
by mass of vinyl acetate in the copolymer) / ethylene system modeled using polar PC-
SAFT. The model with $k_{ij} = 0.037$ agrees very well with experimental data except at low
polymer compositions at which the P-x,y curve qualitatively differs for monodisperse and
polydisperse polymers. To reproduce the shape of the curve at low polymer compositions
we need to account for the polydisperse nature of the polymer.

**Polydisperse EVA/ethylene LLE**

We model polydisperse EVA (Molecular weight of 33400 and polydispersity index 4.0) 
by setting the polar PC-SAFT parameters to be the same for all the EVA
pseudocomponents and the $k_{ij}$ between the copolymer pseudocomponents to be zero.
Figure 5.6 shows results for EVA/ethylene LLE cloud point calculation with EVA
represented by 24 pseudocomponents. The molecular weight distribution of the cloud
phase is given in Table 5.2. We generate the pseudocomponents for the polar copolymer
using Gauss-Laguerre quadrature.
We demonstrate distinctive features of phase behavior in a polydisperse dipolar copolymer in Figure 5.6. The cloud point curve and the shadow point curve are distinct due to the molecular weight distribution in both the phases being different. The critical point is not at the highest pressure and is shifted to a higher composition compared to the monodisperse EVA. Figure 5.7 shows the distribution in the molecular weight in the cloud and shadow phases for a pre-critical and post-critical pressure. Below the critical pressure the cloud phase is polymer rich and contains the high molecular weight pseudocomponents while the shadow phase is solvent rich and contains the low molecular weight polymer fractions. At the critical point the cloud and the shadow phase have the same composition and molecular weight distribution. Above the critical pressure the cloud phase is polymer lean while the shadow phase is polymer rich.

Figure 5.5: EVA/Ethylene LLE at 373.15K, assuming EVA is monodisperse. Comparison between polar PC-SAFT ($k_{ij} = 0.037$) and experimental data\textsuperscript{153} (symbols).
Figure 5.6: EVA/Ethylene LLE at 373.15K, accounting for polydispersity in EVA. Comparison between polar PC-SAFT ($k_{ij}=0.037$) and experimental data\textsuperscript{153} (symbols).

Figure 5.7: Molecular weight distribution in the cloud phase (blue curve) and shadow phase before the critical point (black curve) and after the critical point (red curve).
<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Mass fraction</th>
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</thead>
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<td>82039</td>
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</tr>
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<td>152539</td>
<td>1.95E-01</td>
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</tr>
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<td>7184194</td>
<td>2.31E-23</td>
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</tbody>
</table>

Table 5.2: Molecular weight distribution in the cloud phase.

5.4 Conclusions

This chapter generalizes the linear dependence of the residual chemical potential of a polymer on its molecular weight to dipolar copolymers. Using this simplification we model dipolar copolymer solution phase behavior using an algorithm wherein the size of the system of equations specifying equilibrium is independent of the number of
pseudocomponents used to represent the dipolar copolymer molecular weight distribution. This is attractive when compared to the approach of equating chemical potential of each pseudocomponent to fulfill the criteria of phase equilibrium where the computational expense increases non-linearly with the number of pseudocomponents. We use the proposed algorithm to model phase behavior in polydisperse EVA in ethylene to illustrate the effect of polydispersity on the phase behavior of polydisperse dipolar copolymer solutions.
Chapter 6

Phase Equilibria in Polydisperse Copolymer Solutions

In this chapter we generalize the simplification for performing phase equilibria calculation in polydisperse homosegmented (all segments in a chain molecule have the same size and dispersion energy) solutions presented in Chapter 4 and 5, to heterosegmented fluids by deriving equation (4.1) for copolymers. In a heterosegmented fluid the chain molecule comprises of segments that differ in size and dispersion energy, thus providing a model for copolymer molecules. The derivation is based on the assumptions that the discrete pseudocomponents have the same segment parameters (segment size, segment dispersion energy and the ratio of chain length to molecular weight) for a particular segment type. The fraction of each segment type in a pseudocomponent is the same in all pseudocomponents. That is, different pseudocomponents differ only in molecular weight and not with respect to any other characteristic.

6.1 Introduction

The demand on polymers to have a variety of properties and perform under a range of conditions has led to the increasing replacement of homopolymers with copolymers which are composed of different types of chemical repeat units (CRU). For example Low
Density Polyethylene (LDPE) is a copolymer of ethylene with alpha olefins (like butene and hexene). Primarily copolymers are made of two different repeat units but more than two repeat units have also been used for synthesizing copolymers. The presence of differing repeat units in the same polymer chain gives rise to random, alternating and blocks copolymers depending on the arrangement of CRUs. Depending on the requirements of the application, copolymer chains may differ in the composition of the comonomer. Thus an equation of state that can quantify the behavior of the copolymer solution as a function of the comonomer composition (over the entire composition range), arrangement of the comonomer and type of comonomer functional group is of importance. Copolymer PC-SAFT\textsuperscript{6,154} is a segment based equation of state that provides this functionality. It allows segments in the same chain to have different size and energy characteristics thus providing a model for a copolymer.

In this chapter we develop a method to efficiently account for molecular weight polydispersity using Copolymer PC-SAFT. The effect of polydispersity on phase behavior is very important in polymer solutions, especially at low polymer composition. LDPE produced in a two phase system exhibits superior film properties because of narrower molecular weight distribution and less long chain branches\textsuperscript{150}. The methodology that we propose in this chapter allows for robust calculation of the molecular weight distribution in equilibrium phases for copolymer solutions and hence better process optimization for instance of the LDPE manufacturing process. In the next section we present details of the Copolymer PC-SAFT equation of state and derive the equation allowing simplification of phase equilibrium calculations for polydisperse copolymer solutions.
6.2 Copolymer PC-SAFT - Simplification for polydisperse copolymer solutions

Copolymer PC-SAFT$^{6,154}$ is an equation of state in the form of a thermodynamic perturbation theory based on Wertheim's theory$^{42,43,48,49}$. As discussed in Chapter 1, PC-SAFT views a molecule as a chain of tangentially connected spheres (segments) with hardcore repulsion and a mean field attractive dispersion interaction between the chains. Copolymer PC-SAFT generalizes PC-SAFT to heterosegmented chains (segments having different size and dispersion energies can bond to form a chain). This makes Copolymer PC-SAFT a segment based equation of state (EOS) i.e. the EOS parameters are for segments and the molecules are formed by bonding the different segment types appropriately. Each segment type ($i$) has three copolymer PC-SAFT parameters, namely segment diameter ($\sigma_i (\AA)$), segment dispersion energy parameter ($\varepsilon_i/k (K)$) and the ratio of chain length to molecular weight ($\alpha_i$). Figure 6.1 exhibits a model of a copolymer chain.

Consider a mixture of $p$ copolymer pseudocomponents and $s$ solvents. There are $n_{seg}$ segment types in the system. The derivation of the equations below is completely general in that the copolymer and the solvents can be made of any combination of the segment types. The copolymer pseudocomponents are subject to following assumptions:

1. All the pseudocomponents are made of the same type of segments; hence the segment parameters (segment diameter ($\sigma_i$), dispersion energy parameter ($\varepsilon_i/k$) and ratio of chain length to molecular weight ($\alpha_i$)) for a given segment type are the same for all the pseudocomponents.

2. The fraction by mass of co-monomer is the same in each pseudocomponent.
This mixture is treated as a \((p+s)\) component system.

For a non-associating fluid the compressibility factor and residual chemical potential can be written as \(^2\)

\[
Z = 1 + Z^{hs} + Z^{chain} + Z^{\text{dispersion}}
\]  

\[
\frac{\mu_i}{kT} = \frac{\mu_i^{id}}{kT} + \frac{\mu_i^{\text{res}}}{kT} = \ln(\rho x, \Lambda^3) + \frac{\mu_i^{hs}}{kT} + \frac{\mu_i^{\text{chain}}}{kT} + \frac{\mu_i^{\text{dispersion}}}{kT}
\]

Figure 6.1: Model of a heterosegmented chain molecule.

Here the residual chemical potential is residual to an ideal gas at the same temperature, density and composition as the solution under consideration. \(\Lambda^3\) includes only temperature dependent contributions to the chemical potential. We will show that the phase equilibrium conditions for copolymer/solvent system simplify because the mixture properties depend only on the number average molecular weight of the copolymer and not on the detailed copolymer molecular weight distribution.

The copolymer consists of at least 2 segment types and the solvents are usually made of a single segment type but to keep the derivation general each solvent can consist
of up to \( n_{seg} \) segment types. The compressibility factor and chemical potential depend on certain reduced densities that are defined by:

\[
\zeta_k = \frac{\pi}{6} \rho \sum_{i=1}^{p+p_{seg}} \sum_{j=1}^{n_{seg}} x_i m_{seg_{ij}} d_{ij}^k
\]

\[
= \frac{\pi}{6} \rho \left[ \sum_{i=1}^{p} \sum_{j=1}^{n_{seg}} x_i (\alpha_j f_j M_j) d_{ij}^k + \sum_{i=p+1}^{p+p_{seg}} \sum_{j=1}^{n_{seg}} x_i m_{seg_{ij}} d_{ij}^k \right]
\]

\[
= \frac{\pi}{6} \rho \left[ \sum_{i=1}^{p} x_i M_i \sum_{j=1}^{n_{seg}} (\alpha_j f_j) d_{ij}^k + \sum_{i=p+1}^{p+p_{seg}} \sum_{j=1}^{n_{seg}} x_i m_{seg_{ij}} d_{ij}^k \right]
\]

\[
= \frac{\pi}{6} \rho \left[ x_p \bar{M}_n \sum_{j=1}^{n_{seg}} (\alpha_j f_j) d_{ij}^k + \sum_{i=p+1}^{p+p_{seg}} \sum_{j=1}^{n_{seg}} x_i m_{seg_{ij}} d_{ij}^k \right], \quad k = 0,1,...,3
\]  

\( m_{seg_{ij}} \) is the contribution to the chain length due to segment type \( j \) in component \( i \),

\( \rho \) is the number density of molecules, \( \alpha_j \) is the ratio of the chain length to the molecular weight for segment type \( j \) and \( f_j \) is the mass fraction of the co-monomer (segment) type \( j \) in the copolymer, which is constant for all the copolymer pseudocomponents. \( x_p \) is the overall copolymer mole fraction defined by

\[
x_p = \sum_{j=1}^{p} x_j
\]

and \( \bar{M}_n \) is the number average molecular weight of the copolymer defined by

\[
\bar{M}_n = \sum_{j=1}^{p} x_j M_j / \sum_{j=1}^{p} x_j = \sum_{j=1}^{p} X_j M_j
\]

where \( M_j \) is molecular weight of component \( j \) and

\[
X_j = x_j / \sum_{k=1}^{p} x_k = x_j / x_p
\]
$X_j$ is the mole fraction of copolymer component $j$ in the copolymer mixture on a solvent free basis. Equation (6.3) shows that the reduced density depends only on the average copolymer properties and not on the detailed MWD. Thus,

$$\zeta_k = f(T, x_p, \bar{M}_n, \{x_s\}) \quad (6.7)$$

where $\{x_s\}$ is the vector of solvent compositions. Next we derive the various contributions to pressure and chemical potential to show the validity of equation (4.1) for molecular weight polydisperse heterosegmented chains.

The contact value of the hard sphere pair correlation function between segment type $i$ and $j$ is given by:\cite{78}

$$g_{ij}(d_{ij})^{hs} = \frac{1}{1-\zeta_3} + \left[ \frac{3d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right] \frac{\zeta_2}{(1-\zeta_3)^2} + 2 \left[ \frac{d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right]^2 \frac{\zeta_2^2}{(1-\zeta_3)^2} \quad (6.8)$$

It is a function of the reduced densities, therefore from equations (6.7) and (6.8),

$$g_{ij}(d_{ij})^{hs} = G(T, x_p, \bar{M}_n, \{x_s\}) \quad (6.9)$$

6.2.1 Hard Sphere Contribution

$$Z^{hs, res} = \frac{2}{3} \pi \rho \sum_{I=1}^{p+s} \sum_{J=1}^{p+s} \sum_{k=1}^{nseg} x_i mseg_{k,i} x_j mseg_{J,j} d_{kl}^3 g_{kl}^{hs}(d_{kl}) \quad (6.10)$$

The compressibility factor is residual to the ideal gas and is based on per mole of molecules. With the assumptions we have for the copolymer pseudocomponents, this becomes:
\[ Z^{hs} = \frac{2}{3} \pi \rho \left[ \sum_{i=1}^{p} \sum_{j=1}^{p} \sum_{k=1}^{nseg} \sum_{l=1}^{nseg} x_i f_j \alpha_k \alpha_j M_i f_j M_j d_{kl} g_{kl}^{hs} (d_{kl}) \right. \]

\[ + \sum_{i=1}^{nseg} \sum_{j=1}^{nseg} x_i \alpha_k x_j \alpha_j d_{kl} g_{kl}^{hs} (d_{kl}) \]

(6.11)

\[ Z^{hs} = \frac{2}{3} \pi \rho \left[ x_p^2 M_n \sum_{k=1}^{nseg} \sum_{j=1}^{nseg} f_k \alpha_k f_j \alpha_j d_{kl} g_{kl}^{hs} (d_{kl}) + 2 x_p M_n \sum_{j=1}^{nseg} \sum_{k=1}^{nseg} f_k \alpha_k x_j \alpha_j d_{kl} g_{kl}^{hs} (d_{kl}) \right. \]

\[ + \sum_{i=1}^{nseg} \sum_{j=1}^{nseg} x_i \alpha_k x_j \alpha_j d_{kl} g_{kl}^{hs} (d_{kl}) \]

(6.12)

The chemical potential contribution due to a segment of type \( l \) is given by:

\[ \mu_{l}^{seg} \left( \frac{X^{hs} + x_p M_n \sum_{k=1}^{nseg} f_k \alpha_k \sum_{j=1}^{nseg} x_j \alpha_j d_{kl} g_{kl}^{hs} (d_{kl})}{6} - \ln(1 - \zeta_3) + \frac{3 \zeta_2 d_{ll}}{(1 - \zeta_3)} \right) \]

\[ - \left\{ \frac{3 \zeta_1 d_{ll}^2}{(1 - \zeta_3)^2} + \frac{9 \zeta_2 d_{ll}^2}{2(1 - \zeta_3)^2} + \frac{3}{2} \left( \frac{\zeta_2 d_{ll}}{\zeta_3} \right)^2 \ln(1 - \zeta_3) + \frac{\zeta_3}{(1 - \zeta_3)} - \frac{\zeta_3^2}{2(1 - \zeta_3)^2} \right\} \]

(6.13)

The hard sphere contribution to the chemical potential for a copolymer pseudocomponent \( i \) is given by:

\[ \mu_{i}^{hs} \left( \frac{X^{hs}}{kT} \right) = \sum_{j=1}^{nseg} \alpha_j f_j M_i \mu_{i}^{seg} - M_i \sum_{j=1}^{nseg} \alpha_j f_j \mu_{i}^{seg} \]

(6.14)

Hence the hard sphere contribution to the compressibility factor depends on the number average molecular weight of the copolymer components. From equations (6.11) we see that
\[ Z^{hs} = Z^{hs}(\rho, T, x_p, \overline{M}_n, \{x_s\}) \]  \hspace{2cm} (6.15)

Also, the hard sphere contribution to the chemical potential of a copolymer component is proportional to its molecular weight.

\[ \mu^{hs}_i \frac{kT}{k} = M_i f(\rho, T, x_p, \overline{M}_n, \{x_s\}) \]  \hspace{2cm} (6.16)

Equations (6.15) and (6.16) are the key to the reduction of the system of nonlinear equations specifying phase equilibrium. We now derive similar equations for the chain and dispersion contributions.

### 6.2.2 Chain Contribution

In a copolymer, depending on the type of the copolymer; random, alternate or block the way the segments bond to form chains will vary. Here we derive the thermodynamic properties for the case of a random copolymer with segment ‘A’ (or 1) being the primary monomer of the copolymer and segment ‘B’ (or 2) the co-monomer. The total number of bonds in the chain is equal to one less the total number of segments. It is assumed that the comonomers are always separated by primary monomer so there are no bonds between the comonomers. Therefore the bonds between monomer and comonomer are twice the no. of comonomer segments present. This leads to the following equations for the number of bonds of each type in a random copolymer pseudocomponent \(i\).

\[ Bond_{\text{Total},i} = M_i (\alpha_B f_B + \alpha_A f_A) - 1 \]

\[ Bond_{B,B,i} = 0 \]  \hspace{2cm} (6.17)

\[ Bond_{A,B,i} = 2\alpha_B f_B M_i = C_{1,2} M_i \]  \hspace{2cm} (6.18)

\[ Bond_{A,A,i} = Bond_{\text{Total},i} - Bond_{B,B,i} - Bond_{A,B,i} = M_i (\alpha_A f_A - \alpha_B f_B) - 1 = C_{1,1} M_i - 1 \]  \hspace{2cm} (6.19)
The above result for random copolymer, that the number of bonds of each type varies linearly with the molecular weight of the copolymer (which is a key to the proposed simplification as shown in the next few equations) also hold for block and alternating copolymers as well as copolymers containing more than two comonomers.

The chain contribution to the compressibility factor is given below. To prevent double counting of bonds note the index for the second summation over segment types.

\[
Z_{\text{chain}} = \frac{P_{\text{chain}}}{\rho_{\text{mol}} kT} = \sum_{i=1}^{p+sN_{\text{seg}}} \sum_{j=1}^{N_{\text{seg}}} \sum_{k=j}^{N_{\text{seg}}} x_i (-\text{Bond}_{j,k,i}) \rho \left[ \frac{\partial \ln(g_{j,k}(d_{j,k}))}{\partial \rho} \right]
\]

\[
= x_p M_n \sum_{j=1}^{N_{\text{seg}}} \sum_{k=j}^{N_{\text{seg}}} C_{j,k} \rho \left[ \frac{\partial \ln(g_{j,k}(d_{j,k}))}{\partial \rho} \right] + x_p \rho \left[ \frac{\partial \ln(g_{11}(d_{11}))}{\partial \rho} \right] + \sum_{\text{solvents}} \sum_{j=1}^{N_{\text{seg}}} \sum_{k=j}^{N_{\text{seg}}} x_i (-\text{Bond}_{j,k,i}) \rho \left[ \frac{\partial \ln(g_{j,k}(d_{j,k}))}{\partial \rho} \right]
\]

where

\[
\rho \frac{\partial g_{j,k}}{\partial \rho} = \frac{\xi_2}{(1-\xi_3)^2} + \frac{3}{2} d_{j,k} \left[ \frac{\xi_2}{(1-\xi_3)^2} + \frac{2\xi_2^2 \xi_3}{(1-\xi_3)^3} \right] + \frac{d_{j,k}^2}{2} \left[ \frac{2\xi_2^2}{(1-\xi_3)^3} + \frac{3\xi_2^2 \xi_3}{(1-\xi_3)^4} \right]
\]

The densities \( \xi_k \) depend on the total copolymer composition and number average molecular weight (equation (6.7)). Thus, we see that

\[
Z_{\text{chain}} = f(\rho, T, x_p, M_n, \{x_i\})
\]

The chain contribution to the chemical potential is given by:

\[
\frac{\mu_{\text{chain}}}{kT} = \sum_{k=1}^{N_{\text{seg}}} \sum_{l=1}^{N_{\text{seg}}} (-\text{bond}_{k,l}) \ln(g_{k,l}(d_{k,l})) + \sum_{i=1}^{p+s} \sum_{k=1}^{N_{\text{seg}}} \sum_{l=1}^{N_{\text{seg}}} x_i (-\text{bond}_{k,l,i}) g_{kl}(d_{kl}) \rho \left[ \frac{\partial (g_{kl}(d_{kl}))}{\partial \rho_i} \right]
\]

Note that the pair correlation function at contact, \( g_{kl}(d_{kl}) \) is only a function of \( \xi_k \). The density derivative of the reduced density from equation (6.3) is given by:
\[
\frac{\partial \xi_k}{\partial \rho_j} = \frac{\partial}{\partial \rho_j} \left[ \pi \rho, M_i \sum_{j=1}^{n_{seg}} (\alpha_j f_j) d_{ji}^k + \sum_{i=p+1}^{p_{seg}} \sum_{j=1}^{n_{seg}} \sum_{x,m_{seg_j}} \frac{d_{ji}^k}{d_{ji}^k} \right] \\
= \frac{\pi}{6} \left[ M_i \sum_{j=1}^{n_{seg}} (\alpha_j f_j) d_{ji}^k \right], \quad k = 0,1,\ldots,3 
\]  
(6.24)

which is a linear function of the copolymer pseudocomponent molecular weight. Hence

\[
\left[ \frac{\partial (g_{kl} (d_{kl}))}{\partial \rho_i} \right] = M_i f(I(T, \rho, x_p, M_n, \{x_i\}) 
\]  
(6.25)

The chain contribution to the chemical potential for a copolymer pseudocomponent \( j \) simplifies to

\[
\frac{\mu_j^{\text{chain}}}{kT} = M_j \left( \sum_{k=1}^{n_{seg}} \sum_{l=k}^{n_{seg}} -C_{kl} \ln(g_{kl} (d_{kl})) \right) + \ln(g_{11}(d_{11})) + \\
M_j \sum_{l=\text{solvol}} \sum_{k=1}^{n_{seg}} \sum_{l=k}^{n_{seg}} x_i (-\text{bond}_{k,l,i}) \frac{f(I(T, \rho, x_p, M_n, \{x_i\})}{g_{kl}} + \\
\rho x_p M_n M_j \sum_{k=1}^{n_{seg}} \sum_{l=k}^{n_{seg}} \frac{1}{g_{kl}} f(I(T, \rho, x_p, M_n, \{x_i\})) 
\]  
(6.26)

This can be written as:

\[
\frac{\mu_j^{\text{chain}}}{kT} = \mu_A^{\text{chain}}(T, \rho, x_p, M_n, \{x_i\}) + M_j \cdot \mu_B^{\text{chain}}(T, \rho, x_p, \bar{M}_n, \{x_i\}) 
\]  
(6.27)

where \( l=1,2,\ldots,p \) is the index that runs over the copolymer pseudocomponents and \( M_l \) is the molecular weight of the pseudocomponent \( l \). Thus, for a given solution, the chain contribution to the chemical potential of a copolymer component is a linear function of its molecular weight and the coefficients depend only on the number average molecular weight of the copolymer.
6.2.3 PC-Dispersion Contribution

van der Waals one fluid theory (VDW-1) is used for the dispersion term in mixtures. According to the VDW-1 mixing rules, for a mixture the chain length of the equivalent fluid is given by:

\[ m = \sum_{i=1}^{p+s} \sum_{j=1}^{nseg} x_i m_{seg,j,ij} = x_p M_n \sum_{j=1}^{nseg} f_j \alpha_j + \sum_{I-solv}^{l-solv} \sum_{j=1}^{nseg} x_i m_{seg,j,ij} \]  

(6.28)

The dispersion contribution to the compressibility factor is given by

\[ \frac{A_{\text{disp}}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \]  

(6.29)

\[ \frac{A_1}{RT} = -2\pi p I_1(\eta, m) \sum_i \sum_j x_i x_j m_i m_j \left( \frac{e_{ij}}{kT} \right) \sigma_{ij}^3 \]  

(6.30)

\[ \frac{A_2}{RT} = -\rho \pi n I_2(\eta, m) W \sum_i \sum_j x_i x_j m_i m_j \left( \frac{e_{ij}}{kT} \right) \sigma_{ij}^3 \]  

(6.31)

\[ W = 1 + m \left( \frac{8\eta - 27\eta^2}{(1-\eta)^4} + (1-m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \right) \]  

(6.32)

\[ e_{ij} = \sqrt{e_{ii} e_{jj}} \]  

(6.33)

\[ \sigma_{ij} = 0.5(\sigma_i + \sigma_j) \]  

(6.34)

\[ \frac{A_1}{RT} \] (and similarly \[ \frac{A_2}{RT} \]) simplifies as:

\[ \frac{A_1}{RT} = -2\pi p I_1(\eta, m) \left[ x_p M_n \sum_{k=1}^{nseg} \sum_{l=1}^{nseg} \alpha_k f_k \alpha_l f_l \left( \frac{e_{kl}}{kT} \right) \sigma_{kl}^3 + \right. \]  

\[ \left. 2x_p M_n \sum_{j=\text{solv}}^{l=\text{solv}} \sum_{k=1}^{nseg} \sum_{l=1}^{nseg} \alpha_k f_k x_j m_{seg,k,j} \left( \frac{e_{kl}}{kT} \right) \sigma_{kl}^3 + \right. \]  

\[ \sum_{I=\text{solv}}^{l=\text{solv}} \sum_{j=\text{solv}}^{l=\text{solv}} \sum_{k=1}^{nseg} \sum_{l=1}^{nseg} x_i x_j m_{seg,k,i} m_{seg,l,j} \left( \frac{e_{kl}}{kT} \right) \sigma_{kl}^3 \]  

(6.35)
while the composition derivative of $A_1$ and $A_2$ simplify as:

$$
\left( \frac{\partial}{\partial x_j} \frac{A_i}{RT} \right)_{T,Y,x_{n_{t,i}}} = -2\pi p I_1(\eta, m) \left[ \begin{array}{c} 2M \bar{M} \frac{1}{kT} \sum_{k=1}^{\text{nseg}} \sum_{l=1}^{\text{nseg}} \alpha_k f_k \alpha_l f_l \left( \frac{\sigma_k}{kT} \right)^2 + \\
2M \sum_{j=1}^{\text{nseg}} \sum_{k=1}^{\text{nseg}} \alpha_k f_k x_j \sigma_{ij} \left( \frac{\epsilon_{ij}}{kT} \right) \sigma_{ij} \end{array} \right] (6.36)
$$

$$
= M F_2(T, \rho, x_p, M_n, \{x_s\})
$$

since $I_1, I_2, W$ are functions of $m$ and $\eta$ (which is the same as $\zeta_3$), from equation (6.7) we get:

$$I_1, I_2, W = f(T, \rho, x_p, M_n, \{x_s\}) (6.37)$$

and hence

$$\frac{A_1}{RT}, \frac{A_2}{RT}, \frac{A_{\text{disp}}}{RT} = f(T, \rho, x_p, M_n, \{x_s\}) (6.38)$$

As shown in equation (6.21), the density derivative of a thermodynamic function has the same functional dependence as the original function, therefore:

$$Z_{\text{disp}} = \frac{P_{\text{disp}}}{\rho_{\text{mol}} kT} = \rho \left( \frac{A_{\text{disp}}}{NkT} \right) = f(T, \rho, x_p, M_n, \{x_s\}) (6.39)$$

The dispersion contribution to the chemical potential is given by

$$\frac{\mu_{\text{disp}}}{kT} = A_{\text{disp}} + Z_{\text{disp}} + \left( \frac{\partial A_{\text{disp}}}{\partial x_k} \right)_{T,Y,x_{n_{t,i}}} - \sum_{j=1}^{p} x_j \left( \frac{\partial A_{\text{disp}}}{\partial x_j} \right)_{T,Y,x_{n_{t,i}}} (6.40)$$

where the summation over the copolymer pseudocomponents is seen to depend only on the average copolymer properties as shown below:

$$\sum_{j=1}^{p} x_j \left( \frac{\partial A_{\text{disp}}}{\partial x_k} \right)_{T,Y,x_{n_{t,i}}} = \sum_{j=1}^{p} x_j M_j F_2(T, \rho, x_p, M_n, \{x_s\}) = x_p \bar{M}_n F_2(T, \rho, x_p, M_n, \{x_s\}) (6.41)$$
From equation (6.36) \( \left( \frac{\partial A^{\text{disp}}}{\partial x_k} \right)_{T,\varphi, x_{mk}} \) for a copolymer pseudocomponent varies linearly with its molecular weight. Since \( A^{\text{disp}}, Z^{\text{disp}} \) and \( \sum_{j=1}^{p+1} x_j \left( \frac{\partial A^{\text{disp}}}{\partial x_k} \right)_{T,\varphi, x_{mj}} \) depend only on the average properties of the copolymer, thus for a copolymer pseudocomponent

\[
\frac{\mu_k^{\text{disp}}}{kT} = \mu_A^{\text{disp}}(T, \rho, x_p, \overline{M}_n, \{x_s\}) + M_k \cdot \mu_B^{\text{disp}}(T, \rho, x_p, \overline{M}_n, \{x_s\}) \tag{6.42}
\]

Equations (6.12), (6.22) and (6.39) for compressibility factor show that

\[
Z = Z(T, \rho, x_p, \overline{M}_n, \{x_s\}) \tag{6.43}
\]

Combining equations for chemical potential, we see that

Equations (6.16), (6.27), and (6.42) show that for a copolymer pseudocomponent

\[
\frac{\mu_p^{\text{res}}}{kT} = \mu_A^{\text{res}}(T, \rho, x_p, \overline{M}_n, \{x_s\}) + M_p \mu_B^{\text{res}}(T, \rho, x_p, \overline{M}_n, \{x_s\}), \quad p \rightarrow \text{polymer} \tag{6.44}
\]

Where the functions \( \mu_A^{\text{res}} \) and \( \mu_B^{\text{res}} \) are the same for all the copolymer pseudocomponents.

Substituting equation (6.44) in equation (6.2) and equating the chemical potential of a copolymer pseudocomponent \( i \) in two equilibrium phases (\( \alpha \) and \( \beta \)) leads to the relation for the partition coefficient shown in equation (6.45) (and also equation 4.1). This enables us to use the numerical algorithms developed for phase equilibrium in polydisperse polymer solutions in Chapter 4, for polydisperse copolymer solutions.

\[
\ln(K_i) = \ln \left( \frac{x_i^\alpha}{x_i^\beta} \right) = A + M_i B \tag{6.45}
\]

\[
A, B = f(T, \rho, x_p, \overline{M}_n, \{x_s\}) \tag{6.46}
\]
6.3 Application to Polyethylene-co-octene solution

We perform calculations for polydisperse polyethylene-co-octene (PEO) in hexane to illustrate the effect of polydispersity on the phase behavior of copolymer solutions. The PC-SAFT parameters for each segment type in the solution are reported in Table 6.1. The number average molecular weight of the polymer is 33000. The polymer molecular weight distribution is represented by fitting the polydispersity to the Log-Normal distribution and discretizing the distribution with 10 pseudocomponents using quadrature. The pressure-composition phase equilibrium curve is calculated for polydispersity indices of 1.1, 2, 3.75, 5 and 20 to demonstrate the effect of polydispersity on phase equilibrium in polydisperse copolymer solutions. The polydispersity index is a measure of the width of a distribution, the higher the polydispersity index the wider the molecular weight distribution. In a process simulator, the type of molecular weight distribution is determined by the kinetics and type of polymerization reaction.

In Figure 6.2 we show results of our calculations illustrating the effect of polydispersity on the phase behavior of PEO solutions. At high polymer concentrations of the polymer in the solution the cloud point pressure is not influenced much by the polydispersity. At low polymer concentrations however there is a significant effect of polydispersity on the cloud point pressure. The maximum cloud point pressure increases by about 100% in going from an almost monodisperse polymer to a polymer with a polydispersity index of 20. The critical point (which is identified by the change in the slope of the curve in Figure 6.2) shifts to higher polymer compositions as the
polydispersity of the cloud phase increases. These features are similar to that observed for polydisperse homopolymer solutions.

<table>
<thead>
<tr>
<th>Component</th>
<th>σ(Å)</th>
<th>ε/k (K)</th>
<th>m/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>4.021767</td>
<td>252.0</td>
<td>0.0263</td>
</tr>
<tr>
<td>Polyoctene</td>
<td>4.390000</td>
<td>216.9</td>
<td>0.0227</td>
</tr>
<tr>
<td>Hexane</td>
<td>3.798300</td>
<td>236.77</td>
<td>0.0355</td>
</tr>
</tbody>
</table>

Table 6.1: PC-SAFT parameters for segments.

Figure 6.2: Effect of chain length polydispersity of the copolymer on the cloud point pressure at a temperature of 177 °C. in the Polyethylene-co-octene / Hexane system. The cloud point curve is shown for polydispersity indices of increasing value from 1.1 to 20
6.4 Conclusions

In this chapter we derive expressions demonstrating the generality of the algorithms presented in Chapter 4 for polydisperse copolymer solutions. The algorithm accumulates the pseudo-components so that the size of the system of equations specifying equilibrium is independent of the number of pseudo-components used to represent the copolymer molecular weight distribution. We present cloud point calculation results for a range of polydispersity indices to elucidate the effect of polydispersity on the phase behavior of polydisperse polyethylene-co-octene / hexane solution.
Chapter 7

Compositional Polydispersity in Dipolar Copolymer Solutions

In this chapter we present a novel algorithm to account for compositional polydispersity in dipolar copolymer solutions, where the size of the system of equations for phase equilibrium is independent of the number of pseudocomponents used to represent the comonomer distribution. Compositional polydispersity refers to the fact that the fraction of comonomer varies in the different pseudocomponents comprising the copolymer. To isolate the effect of compositional polydispersity, we treat the pseudocomponents as monodisperse in molecular weight. We apply the algorithm to the Polar-SAFT equation of state. Previous approaches in modeling compositional polydispersity in copolymers have used the framework of continuous thermodynamics. Since copolymers may have a multimodal comonomer distribution that cannot be adequately described using distribution functions and hence continuous thermodynamics, a pseudocomponent based method is more general.

7.1 Introduction

Recent publications\textsuperscript{66,67,85,110,112,153-157} have shown considerable interest in modeling the thermophysical properties of polymer solutions using molecular based equations of state viz. the Statistical Associating Fluid Theory (SAFT) formalism\textsuperscript{2,4}. The versatility of this
formalism allows for modeling phase behavior in solutions of monomer, associating liquids and polymers while accounting for comonomers, short chain branching, chain length polydispersity and polar groups. In this chapter we extend the applicability of Polar-SAFT\textsuperscript{68} by developing an efficient method for modeling the effect of compositional polydispersity on the phase behavior of dipolar copolymers solutions and blends. The method is in general valid for other equations of state based on the SAFT formalism such as the dipolar version of the PC-SAFT equation of state\textsuperscript{6,71}. To isolate the effect of compositional polydispersity, the pseudocomponents are monodisperse in molecular weight. This is also a representative physical situation where copolymers of the same length are found to differ in comonomer content\textsuperscript{158}.

Continuous thermodynamics has previously provided an elegant methodology for modeling multivariate polydispersity in polymer solutions\textsuperscript{159-164}. Ratzsch et al.\textsuperscript{162} have studied the effect of the breadth and asymmetry of the compositional distribution on the cloud and shadow curves while Bauer\textsuperscript{165} studied the effect of different comonomer distribution functions on the phase behavior of a random acrylonitrile butadiene melt. Nesarikar\textsuperscript{166} using a discrete comonomer distribution and Sollich\textsuperscript{121} using the moment free energy method which uses continuous distribution functions, performed model calculations for random copolymer systems to demonstrate the multiplicity of phases and critical points that can arise in such systems. Previous approaches to investigating compositional polydispersity in dipolar copolymers suffered from two drawbacks that have been addressed in this chapter.

First, compositional polydispersity in copolymer solutions has been previously studied in the framework of lattice based modified Flory-Huggins theory which does not
explicitly account for dipolar interactions. The recent development of molecular based continuum models for liquids based on the SAFT formalism\textsuperscript{2,6,68,71} allows for predictive modeling of phase behavior in polymer solution. Dipolar interactions have a significant effect on the thermophysical properties and phase behavior of mixtures containing polar components. Jog and Chapman\textsuperscript{68} have recently developed a statistical mechanical theory within the SAFT formalism (Polar-SAFT) for chains with dipolar functional groups. This allows for modeling of polymers with multiple dipolar functional groups where one can predict the effect of changing the concentration of dipolar functional groups in a copolymer as shown by Jog et al.\textsuperscript{70}. This physical continuum model for dipolar copolymers is used for the first time to understand the effect of compositional polydispersity on the phase behavior of dipolar copolymer solutions.

Secondly, a major drawback of continuous thermodynamics is that it is intimately tied to analytical distribution functions. Such functions are typically restricted to simple unimodal distribution functions because of the complication in representing multimodal distribution functions using analytical expressions. However, the increasing use of multisite catalysts in solution polymerization often leads to multimodal distributions\textsuperscript{145}. Experimental TREF characterization has revealed that comonomer distribution can often be broad and multimodal\textsuperscript{167} which cannot be adequately described using distribution functions and hence continuous thermodynamics. A pseudocomponent based method is more general for such cases. In the past, pseudocomponent based methods have been criticized as being crude and arbitrary since a limited number of pseudocomponents were retained to limit the computational expense. This is true when the computation time for phase equilibrium calculations scales non-linearly with the number of
pseudocomponents. For the methodology that we present in this chapter the size of the system of equations to be solved for phase equilibrium is independent of the number of pseudocomponents used to represent the comonomer distribution. Thus using this method there is no limit on the number of pseudocomponents that can be retained in the phase equilibrium calculation, leading to accurate description of the equilibrium polymer comonomer distribution in various phases. This was not possible previously when modeling compositional polydispersity in polar copolymers with pseudocomponent based methods.

In this chapter we first derive the equations that describe the computationally efficient algorithm for modeling phase equilibrium in dipolar copolymer solutions. Next we apply the algorithm to a compositionally polydisperse copolymer (with two pseudocomponents) to elucidate how phase behavior is affected by compositional polydispersity, molecular weight of the copolymer, average comonomer composition of the copolymer and pressure. Finally we address the question whether miscibility in compositionally polydisperse dipolar copolymers solutions is enhanced by the presence of pseudocomponents of intermediate composition. It is known that compositionally polydisperse systems are prone to multiphase separation as the polydispersity increases\textsuperscript{121}. This chapter will limit its purview to the two phase region and describe the sensitivity of the phase behavior in this region due to increasing compositional polydispersity. This is important to tune processing conditions during the manufacturing of dipolar copolymers to ensure that the polymer solution is in the single or two-phase region.
7.2 Model for dipolar copolymers

We model the polar copolymer as shown in Figure 5.1 as a chain of tangential spheres (segments) with a certain fraction of the segments having dipoles on them. All the segments are identical (same size and dispersion energy) except that some of the segments have dipoles. The assumption of equal size and dispersion energy for the primary monomer and the comonomer is a simplifying assumption made to minimize the number of parameters fitted to binary mixture data. This is a simplified model for a dipolar copolymer but this simplification allows us to accurately isolate and quantify the effect of polar interactions on phase behavior. This assumption has been tested and seen to provide a predictive model for polar copolymers\textsuperscript{70}. Since we account for compositional polydispersity, the comonomer incorporation (and hence the fraction of dipolar segments) will vary in the polymer pseudocomponents.

Consider the case where the monomer is a non-polar molecule and the comonomer is a polar molecule with a single dipole. Then the dipolar segment fraction is proportional to the mass fraction of comonomer present in a polymer pseudocomponent. Comonomer compositional polydispersity in this case is equivalent to polydispersity in the fraction of dipolar segments in the pseudocomponents. Hence here we treat the fraction of the dipolar segment as the distributed parameter. In the rest of the chapter, composition will refer to the fraction of dipolar segments ($\lambda$) in a copolymer pseudocomponent; and concentration will refer to the species concentration ($x$) in the copolymer/solvent solution. The comonomer incorporation in the copolymer is reported in percentage by mass.
7.3 Simplification from the Equation of State

The residual Helmholtz energy in the Polar-SAFT formalism is given by:

\[ a^{\text{res}} = a^{\text{hs}} + a^{\text{dispersion}} + a^{\text{polar}} + a^{\text{chain}} \]  \hspace{1cm} (7.1)

where the Helmholtz energy is residual to an ideal gas at the same temperature and density as the fluid of interest. The first term on the right hand side is the hard sphere contribution to the energy. SAFT has three pure component parameters for a pure fluid, namely segment volume \( (\nu^0) \), segment dispersion energy \( (u^0/k) \) and chain length \( (m) \). Dipolar fluids have an additional parameter \( (\chi) \) which is the fraction of dipolar segments in a chain. This parameter takes into account multiple dipolar sites in a molecule. We use the experimental value for dipole moment \( (\mu) \) of the molecule. As shown previously, the dipolar contribution to the Helmholtz energy is obtained by dissolving all the bonds in a chain and considering the resulting mixture of spherical segments with different dipole moments. The dipolar contribution is an infinite series of terms of order second, third and higher. The second and third order terms are calculated explicitly and the higher order terms are estimated by the Padé approximant of Rushbrooke et al.\(^{152} \).

\[ A^{\text{polar}} = \frac{A_2}{1 - A_3 / A_2} \]  \hspace{1cm} (7.2)

Consider a system consisting of a compositionally polydisperse copolymer (with \( p \) pseudocomponents of equal molecular weight) and \( s \) solvents. The copolymer pseudocomponents differ only in the dipolar (comonomer) fraction.
The terms $A_2$ and $A_3$ are given for mixtures by Gubbins and Twu\textsuperscript{168}. The expressions for the integrals over the two particle $I_2$ and three particle pair distribution function $I_3$ are given by Rushbrooke et al.\textsuperscript{152}.

\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \sum_i \sum_f x_i x_f m_i m_f X_i X_f \frac{\mu_i^2 \mu_f^2}{d_{ij}^3} I_2
\]  

(7.3)

where $\rho$ is the number density of the mixture and $d_{ij}$ is the mean diameter of component $i$ and $j$. Separating the copolymer and solvent contribution in the summation gives the following expression, where the subscript $p$ refers to the copolymer:

\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \left[ \sum_p m_p^2 \frac{\mu_p^4}{d_{pp}^3} I_2 \sum_p \sum_p x_i x_f X_i X_f + \sum_{i=1}^{p+1} \sum_{j=p+1}^{s+1} \sum_i x_i x_j m_i m_j X_i X_j \frac{\mu_i^2}{d_{ij}^3} I_2 + \sum_s \sum_s x_i x_j m_i m_j X_i X_j \frac{\mu_j^2}{d_{ij}^3} I_2 \right]
\]  

(7.4)

The first moment of the dipolar fraction $X_i$ (fraction of polar segments in component $i$) or the average dipolar fraction is given by the following expression, where $x_p$ in the denominator is the total copolymer concentration in the mixture:

\[
\bar{X}_p = \frac{\sum_i x_i x_i}{x_p}
\]  

(7.5)

\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \left[ m_p^2 \frac{\mu_p^4}{d_{pp}^3} I_2 x_p^2 + 2m_p \mu_p^2 \bar{X}_p x_p \sum_{j=p+1}^{s+1} x_j m_j \frac{\mu_j^2}{d_{ij}^3} I_2 \right] + \left[ \sum_s \sum_s x_i x_j m_i m_j X_i X_j \frac{\mu_j^2}{d_{ij}^3} I_2 \right]
\]  

(7.6)
\[
\frac{A_3}{NkT} = \frac{5}{162} \pi^2 \frac{\rho^2}{(kT)^3} \sum_i \sum_j \sum_k x_i m_i x_j m_j x_k m_k X_i X_j X_k \frac{\mu_i^2 \mu_j^2 \mu_k^2}{d_{ij} d_{jk} d_{ik}} I_3
\]

\[
\begin{aligned}
&\left[ m_p^3 \bar{X}_p x_p^3 \frac{\mu_p^6}{d_{pp}} I_3 + \\
&3m_p^2 \bar{X}_p^2 x_p^2 \mu_p^4 \sum_{k=p+1}^{p+s} x_k m_k X_k \frac{\mu_k^2}{d_{pk} d_{pk}} + \\
&3m_p \bar{X}_p x_p \mu_p \sum_{j=p+1}^{p+s} \sum_{k=p+1}^{p+s} x_j m_j x_k m_k X_j X_k \frac{\mu_j^2 \mu_k^2}{d_{pj} d_{jk} d_{pk}} I_3 + \\
&\sum_s \sum_s \sum_s x_i m_i x_j m_j x_k m_k X_i X_j X_k \frac{\mu_i^2 \mu_j^2 \mu_k^2}{d_{ij} d_{jk} d_{ik}} I_3
\end{aligned}
\]

(7.7)

We define an average diameter for the mixture as:

\[
d_x^3 = \sum_i x_i m_i d_{ii}^3
\]

(7.9)

Alternatively the average diameter can be defined using van der Waals one fluid approximation as:

\[
d_x^3 = \frac{\sum_i \sum_i x_i m_i x_j m_j d_{ij}^3}{\sum_i \sum_j x_i m_i x_j m_j}
\]

(7.10)

The integrals \(I_2\) and \(I_3\) are related to the corresponding pure fluid integrals by van der Waals one fluid theory approximation.

\[
I_{2,ij} = I_2(\rho^*)
\]

(7.11)

\[
I_{3,ijk} = I_3(\rho^*)
\]

(7.12)

where \(\rho^* = \rho d_x^3\) and \(I_2\) and \(I_3\) are the corresponding pure fluid integrals. Other thermodynamic quantities like pressure and chemical potential can be obtained by differentiating equation (7.2). The dipolar contribution to the compressibility factor is given by:
\[
Z = \rho \frac{\partial \left( \frac{A_{\text{polar}}}{NkT} \right)}{\partial \rho} = \rho \left[ 2A_2 \frac{\partial \left( \frac{A_2}{NkT} \right)}{\partial \rho} - A_{\text{polar}} \frac{\partial \left( \frac{A_2 - A_3}{NkT} \right)}{\partial \rho} \right] \frac{A_2 - A_3}{A_2 - A_3}
\]  
(7.13)

\[
\frac{\partial \left( \frac{A_2}{NkT} \right)}{\partial \rho} = \frac{A_2}{NkT} \frac{1}{\rho l_2} \left( \rho \frac{\partial l_2}{\partial \rho} + I_2 \right)
\]  
(7.14)

\[
\frac{\partial l_k}{\partial \rho} = \frac{\partial l_k}{\partial \rho} \left( \rho \frac{\partial l_k}{\partial \rho} + I_3 \right) = \frac{\partial l_k}{\partial \rho} \sum x_i m_i d_{ii}^3 = \frac{\partial l_k}{\partial \rho} \left( x_p m_p d_{pp}^3 + \sum x_i m_i d_{ii}^3 \right) \quad k = 1, 2
\]  
(7.15)

\[
\frac{\partial l_k}{\partial \rho} \text{ is only a function of the reduced density } \rho^* \text{. The third order contribution is similarly given by:}
\]

\[
\frac{\partial \left( \frac{A_3}{NkT} \right)}{\partial \rho} = \frac{A_3}{NkT} \frac{1}{\rho l_3} \left( \rho \frac{\partial l_3}{\partial \rho} + I_3 \right)
\]  
(7.16)

Thus the compressibility factor as well as the Helmholtz energy only depends on the first moment of the conomer distribution or the average conomer composition in the system.

The polar contribution to the chemical potential is given by:

\[
\frac{\mu_i^{\text{polar}}}{kT} = \frac{\partial \left( \frac{A_{\text{polar}}}{kT} \right)}{\partial N_i}
\]  
(7.17)

\[
\frac{\mu_i^{\text{polar}}}{kT} = 2A_2 \frac{\partial \left( \frac{A_2}{kT} \right)}{\partial N_i} - A_{\text{polar}} \frac{\partial \left( \frac{A_2 - A_3}{kT} \right)}{\partial N_i} \frac{A_2 - A_3}{A_2 - A_3}
\]  
(7.18)
\[
\frac{A_2}{NkT} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \left[ m_p^2 \frac{\mu_p^4}{d_{pp}^3} I_{2,p} X_p x_p^2 + 2m_p \mu_p^2 \overline{X}_p x_p \sum_{j=p+1}^{p+2} X_j m_j \frac{\mu_j^2}{d_{pj}^3} I_2 \right] \\
+ \sum_i \sum_j x_i x_j m_i m_j X_i X_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} I_2
\]

\[
\frac{\partial(A_2)}{\partial N_i} = -\frac{2\pi}{9} \frac{\rho}{(kT)^2} \left[ 2m_p \mu_p^2 \frac{\mu_i^2}{d_{pp}^3} I_{2,ij} \overline{X}_p X_p x_p x_{pi} + 2m_p \mu_p^2 \overline{X}_p X_{pi} \sum_{j=p+1}^{p+2} x_j m_j X_j \frac{\mu_j^2}{d_{pj}^3} I_{2,ij} \right] \\
+ \left( \sum_i \sum_j x_i x_j m_i m_j X_i X_j \frac{\mu_i^2 \mu_j^2}{d_{ij}^3} \right) \frac{\partial I_2}{\partial N_i}
\] (7.19)

\[
N \frac{\partial I_2}{\partial N_i} = \frac{\partial I_2}{\partial \rho^*} N \frac{\partial \rho^*}{\partial N_i}
\] (7.20)

\[
N \frac{\partial \rho^*}{\partial N_i} = N \frac{\partial \left( \rho \sum_i x_i m_i d_{ii}^3 \right)}{\partial N_i} = \frac{Nm_i d_{ii}^3}{V} = \rho m_i d_{ii}^3
\] (7.21)

Substituting equation (7.21) in equation (7.19) gives

\[
\frac{\partial(A_2)}{\partial N_i} = K_1 + X_{pi} K_2
\] (7.22)

Similarly the third order contribution to the polar contribution to the chemical potential is given by:

\[
\frac{\partial(A_3)}{\partial N_i} = \frac{5}{162} \frac{\pi^2 \rho^3}{(kT)^3} \left[ 3m_p^3 \overline{X}_p x_p^2 \frac{\mu_p^6}{d_{pp}^6} X_{pi} I_3 + \\
6m_p^2 \overline{X}_p x_p \mu_p^4 \frac{I_3}{d_{pp}^6} X_{pi} \sum_{k=p+1}^{p+2} x_k m_k X_k \frac{\mu_k^2}{d_{pk}^3} d_{pk} d_{pk} + \\
3m_p X_{pi} \mu_p^2 \sum_{j=p+1}^{p+2} \sum_{k=p+1}^{p+2} x_j m_j x_k m_k X_j X_k \frac{\mu_j^2 \mu_k^2}{d_{pj}^3 d_{jk}^3} d_{pk}^3 \\
+ \sum_i \sum_j \sum_k x_i x_j m_j x_k m_k X_i X_j X_k \frac{\mu_i^2 \mu_j^2 \mu_k^2}{d_{ij}^3 d_{jk}^3} \frac{\partial I_3}{\partial \rho^*} \rho m_p d_{pp}^3 \right]
\] (7.23)
\[
\frac{\partial \left( \frac{A_i}{kT} \right)}{\partial N_i} = K_3 + X_{pi}K_4
\]  \hspace{1cm} (7.24)

where \( K_1, K_2, K_3 \) and \( K_4 \) depend only on the average composition of the copolymer and not on the particular composition distribution of the comonomer in the various copolymer pseudocomponents.

\[
K_1, K_2, K_3, K_4 = f(T, \rho, \bar{X}_p, x_p, \{x_s\})  \hspace{1cm} (7.25)
\]

where \( \{x_s\} \) is the vector of solvent concentrations. The polar contribution to the chemical potential for a polymer pseudocomponent, from equation (7.18) is:

\[
\frac{\mu_{i}^{\text{polar}}}{kT} = \frac{2A_2 \left( K_1 + X_{pi}K_2 \right) - A_{i}^{\text{polar}} \left( K_1 + X_{pi}K_2 - K_3 - X_{pi}K_4 \right)}{A_2 - A_3}  \hspace{1cm} (7.26)
\]

\[
\frac{\mu_{i}^{\text{polar}}}{kT} = \mu_A(T, \rho, x_p, \{x_s\}, \bar{X}_p) + \bar{X}_p \mu_B(T, \rho, x_p, \{x_s\}, \bar{X}_p)  \hspace{1cm} (7.27)
\]

where

\[
\mu_A(T, \rho, x_p, \{x_s\}, \bar{X}_p) = \frac{2A_2K_1 - A_{i}^{\text{polar}}(K_1 - K_3)}{A_2 - A_3}  \hspace{1cm} (7.28)
\]

\[
\mu_B(T, \rho, x_p, \{x_s\}, \bar{X}_p) = \frac{2A_2K_2 - A_{i}^{\text{polar}}(K_2 - K_4)}{A_2 - A_3}  \hspace{1cm} (7.29)
\]

Equation (7.27) shows that the dipolar contribution to the residual chemical potential for a copolymer pseudocomponent varies linearly with the dipolar fraction in the copolymer. This is the key result that simplifies phase equilibrium calculations in compositionally polydisperse dipolar copolymer solutions.
7.4 Simplification of phase equilibrium conditions

At equilibrium the chemical potentials are equal in the two coexisting phases $\alpha$ and $\beta$ for each of the $p$ pseudocomponents of the copolymer.

\[
\frac{\mu_{i,\alpha}^{\text{res}}}{kT} + \ln(\rho_{\alpha}x_{i}^{\alpha}) = \frac{\mu_{i,\beta}^{\text{res}}}{kT} + \ln(\rho_{\beta}x_{i}^{\beta})
\]  

(7.30)

where the second term $\ln(\rho x_i)$ is the ideal gas contribution.

Equation (7.30) can be rearranged as

\[
\ln(K_i) = \ln(\rho_{\alpha} / \rho_{\beta}) + \frac{\mu_{i,\alpha}^{\text{res}}}{kT} - \frac{\mu_{i,\beta}^{\text{res}}}{kT}
\]

(7.31)

where we define the partition coefficient of a component $i$ as:

\[
K_i = \frac{x_i^{\beta}}{x_i^{\alpha}}
\]

(7.32)

Since the residual chemical potential for a polar copolymer is linear with the fraction of polar comonomer in the copolymer from equation (7.27), therefore we can write the partition coefficient of the $i^{th}$ polymer pseudocomponent as:

\[
\ln(K_i) = K_A + X_p \cdot K_B
\]

(7.33)

Where:

\[
K_A = \ln(\rho_{\alpha} / \rho_{\beta}) + \mu_{\alpha}^{\text{res}}(T, \rho_{\alpha}, x_{p}, \{x_{s}\}, \overline{X}_{p})
\]

\[
- \mu_{\alpha}^{\text{res}}(T, \rho_{\beta}, x_{p}^{\beta}, \{x_{s}\}, \overline{X}_{p})
\]

(7.34)

and

\[
K_B = \mu_{\alpha}^{\text{res}}(T, \rho_{\alpha}, x_{p}, \{x_{s}\}, \overline{X}_{p}) - \mu_{\beta}^{\text{res}}(T, \rho_{\beta}, x_{p}^{\beta}, \{x_{s}\}, \overline{X}_{p})
\]

(7.35)
This satisfies the condition for the equality of chemical potential for all polymer pseudocomponents. Thus, the $p$ equations of the form of equation (7.31) for each copolymer pseudocomponent are reduced to two equations (7.34 and 7.35).

Equation (7.33) is of the form of equation (4.1) except that the variable $M_i$ (molecular weight of pseudocomponent $i$) is replaced by the variable $X_{pi}$ (dipolar fraction in pseudocomponent $i$). Thus the algorithms presented in Chapter 4 for stability analysis and phase equilibrium calculations can be directly used for compositionally polydisperse dipolar copolymer solution by substituting the variable $X_{pi}$ for the distributed variable $M_i$. The problem size for phase equilibrium is now independent of the number of copolymer pseudocomponents ($p$) used to represent the comonomer composition distribution.

### 7.5 Results

We now demonstrate the effect of compositional polydispersity on the phase behavior of dipolar copolymer solutions. Polar-SAFT has previously been shown to be a predictive model for Polyethylene-co-methyl acrylate (EMA). Hence here we show the effect of increasing compositional polydispersity on the phase behavior of EMA (molecular weight 33000) in butane (parameters in Table 7.1). In EMA, ethylene is the primary monomer and methyl acrylate is the comonomer. Scott\textsuperscript{169} pointed out that the qualitative nature of occurrence of phase separation in copolymer blends is independent of the solvent used. The solvent acts as a diluent and mediates the interaction between the copolymers but does not qualitatively affect the phase behavior. In a sense, the solvent
dilutes the interaction between the polymer pseudocomponents and mitigates the onset of phase separation due to the presence of pseudocomponents with differing composition. Due to lack of experimental work on compositionally polydisperse dipolar copolymer solutions we will qualitatively relate our model predictions to those experimentally determined for copolymer blends.

We consider the simplest model of a compositionally polydisperse dipolar copolymer. The copolymer consists of two pseudocomponents with differing amounts of comonomer in each pseudocomponent. We generate the two pseudocomponents by perturbing a monodisperse copolymer that has 31% comonomer by mass. The comonomer fraction in the polydisperse copolymer is equally divided between the pseudocomponents so that the average comonomer fraction in the copolymer is 31%. The pseudocomponents have a 1:1 concentration in the cloud phase. The copolymer system is labeled in the figures with the comonomer percent by mass of the polar rich pseudocomponent. For example 33.07% refers to a system with two pseudocomponents with comonomer incorporation of 33.07% and 28.93%.

<table>
<thead>
<tr>
<th>Component</th>
<th>$v^0$(ml/mol)</th>
<th>$u^0/k$ (K)</th>
<th>$m$</th>
<th>$\mu$ (Debye)</th>
<th>$X_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMA$_{31}$</td>
<td>12.0</td>
<td>216.15</td>
<td>1681.7</td>
<td>1.77</td>
<td>0.15</td>
</tr>
<tr>
<td>Butane</td>
<td>12.599</td>
<td>195.11</td>
<td>3.458</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.1: Polar-SAFT Parameters for monodisperse EMA and Butane.
In Figure 7.1 we show the effect of increasing compositional polydispersity on the cloud point pressure. As the difference in the fraction of dipolar segments in the two pseudocomponents widens, the maximum of the cloud point curve shifts to higher pressures. Also the critical pressure is no longer at the highest pressure and shifts to higher compositions as shown in Figure 7.2. In Figure 7.2 the shadow curve is seen to deviate from the standard dome shape and shows the formation of a shoulder. This shoulder forewarns the presence of three phase equilibria in the neighborhood on further increasing the compositional heterogeneity between the two pseudocomponents.

Figure 7.1: Effect of compositional polydispersity on the pressure-composition phase space at a temperature of 220 °C. in the EMA/Butane system. The cloud point curve is shown for increasing breadths of the compositional distribution. The shadow curve is not displayed.
Figure 7.2: Effect of compositional polydispersity on the pressure-composition phase space at a temperature of 220 °C. The shoulder in the shadow curve (the curve on the left) forewarns the presence of 3 phase equilibria on further increasing the compositional polydispersity.

In Figure 7.3 we exhibit the Upper Critical Solution Temperature (UCST) behavior for the monodisperse copolymer and the polydisperse copolymer solutions. As the compositional polydispersity in the copolymer increases the critical concentration shifts to higher polymer concentrations and the maximum temperature in the two phase region increases to higher temperatures. Next we elucidate the sensitivity of the phase behavior of compositionally polydisperse solutions to the molecular weight of the copolymer, the average comonomer content of the copolymer and the presence of compatibilizing species.
Figure 7.3: Effect of compositional polydispersity on the temperature-composition phase space at a pressure of 575 bar.

Effect of compositional polydispersity on phase behavior - Sensitivity to molecular weight: In Figure 7.4 we display the Pressure-Temperature (PT) phase boundary for a monodisperse and 2 compositionally polydisperse solutions. Over the range of polymer molecular weights considered here, as the molecular weight increases the sensitivity of the phase behavior to the compositional polydispersity increases. This is consistent with what others\textsuperscript{170} have experimentally observed. Figure 7.5 shows the effect of increasing molecular weight of the copolymer on the cloud point temperature for a monodisperse EMA in butane. At constant pressure the cloud point temperature increases and eventually levels off.
Figure 7.4: Effect of compositional polydispersity on the PT phase boundary at two different molecular weights of the polymer. The polymer has a mass fraction of 0.05 in the cloud phase.

*Effect of compositional polydispersity on phase behavior - Sensitivity to average comonomer composition:* As Figure 7.6 shows the sensitivity of the phase behavior to the average comonomer composition depends on the pressure. At low pressure the phase behavior is insensitive to the compositional polydispersity at a given average comonomer composition. At higher pressures the sensitivity of phase separation to the compositional polydispersity decreases with increasing average comonomer composition. One reason for this is that even though the absolute width of the comonomer distribution remains the same as the average comonomer composition increases, the % polydispersity decreases with increasing average composition. This is also consistent with what Kollinsky and Markert\(^{171}\) observed for some dipolar copolymers. They observed that as the average
comonomer composition increased the susceptibility to phase separation could increase, decrease or remain unchanged depending on the nature of the comonomer. Koningsveld et al.\textsuperscript{170} attributed these differences to the size disparity between the monomers. The

![Graph](image)

**Figure 7.5:** Effect of molecular weight of the polymer on the cloud point temperature at different pressures. The comonomer content in the copolymer is 31\% by mass and the mass fraction of polymer in the cloud phase is 0.05.

The homosegmented nature of the model we are using precludes probing the effect of comonomer size disparity but the heterosegmented form of SAFT (Copolymer SAFT)\textsuperscript{108,109} can be used to study this.

*Compatibilization effect:* To a 1:1 mixture of a 33.07\% and a 28.93\% copolymer, 10\% mass fraction of a 31\% copolymer is added. As seen in Figure 7.7 this causes the cloud point pressure for the compatibilised quaternary (28.93\%, 31\%, 33.07\% and butane) to reduce as compared to the ternary system (28.93\%, 33.07\% and butane). This
behavior is explained by the fact that on addition of an intermediate component here the polydispersity index of the copolymer reduces and hence the resulting solution behaves more like the monodisperse polymer solution.

Figure 7.6: PT phase boundary for a polymer solution with 0.05 mass fraction polymer. Effect of compositional polydispersity with increasing average comonomer composition.

A more interesting question is if two distributions have the same polydispersity index (and the same first and second moments of the distribution function) but different number of pseudocomponents then do they have identical behavior with respect to the cloud point and shadow point curve. Paricaud\textsuperscript{131} showed that for polymers with chain length polydispersity while the cloud point curve is not affected significantly by the
number of pseudocomponents used to represent the molecular weight distribution, the shape of the shadow curve changes in going from a discrete distribution to a continuous

![Graph showing cloud point pressure (P(bar)) vs. wp (wp)](image)

Figure 7.7: The cloud point pressure (at 220 °C) reduces indicating miscibility enhancement on addition of a molecule of intermediate composition.

distribution. We test this phenomenon for compositionally polydisperse dipolar copolymers by comparing two distributions one with two pseudocomponents and the other with eight pseudocomponents, both with the same first and second moment. While the former system exhibits two-phase equilibria the latter phase splits into three phases. Even with a small quantity of high dipolar fraction pseudocomponent the system is destabilized and can split into multiple phases. This is consistent with what Scott observed, that when the difference between the pseudocomponents at the extremities of the distribution increases the system is destabilized and phase splits into multiple phases.
Thus the species at the extreme of the polymer distribution have a major influence on the propensity of the copolymer solution to split into multiple phases.

7.6 Conclusions

Compositional polydispersity in dipolar copolymers significantly affects the phase behavior of their solutions. In a polar copolymer comprised of a polar and a non-polar monomer the composition of the polar comonomer in a copolymer pseudocomponent is proportional to the fraction of dipolar segments (dipolar fraction) in the pseudocomponent. Using the dipolar fraction as the distributed parameter we have presented a new efficient algorithm in this chapter for calculating phase equilibria in compositionally polydisperse copolymer solutions where the size of the system of equations specifying phase equilibrium is independent of the number of pseudocomponents used to represent the comonomer distribution. This is accomplished using the Polar-SAFT equation of state which allows for predicting phase behavior in polar mixtures while explicitly accounting for the presence of multiple polar groups in a molecule. Further, we applied Polar-SAFT to solutions of the copolymer Polyethylene-co-methyl acrylate in butane to quantify the effect of compositional polydispersity on phase behavior in the two phase region with changing pressure, average comonomer composition in the copolymer, average molecular weight and the kind of comonomer distribution function of the copolymer. The extent of the two phase region increases with increasing compositional polydispersity in the copolymer. Increasing polydispersity is accompanied by the shifting of the critical concentration to higher compositions. As the
average comonomer composition in the copolymer increases the effect of compositional polydispersity becomes weaker. Increasing molecular weight of the copolymer intensifies the effect of polydispersity leading to enhanced two phase immiscibility. There is slight miscibility enhancement on adding a pseudocomponent of intermediate composition to two pseudocomponents. However the presence of even a small concentration of pseudocomponent with high enough comonomer content destabilizes the two phase region leading to three or more phases. Hence the composition difference between the extreme pseudocomponents \((cd)\) plays an important role in deciding whether single, dual or multiple phases will be stable. Therefore two distributions with the same polydispersity index can have qualitatively different phase behavior (wrt. the number of phases present) if \(cd\) is large enough.
Chapter 8

Conclusions and Future Directions

In this chapter I conclude the dissertation by summarizing the contributions of this thesis and also present some interesting directions for future research that build on the accomplishments of this dissertation.

8.1 Conclusions

The goal of this thesis is the development of methodologies to provide robust and efficient modeling of polydispersity effects on polymer solution phase behavior. The incorporation of these methodologies in polymer process simulators will allow for improved process optimization of polymer manufacturing processes. In particular this thesis has four major contributions.

First, we develop a model for predicting agglomeration in polymer slurry reactors. The model is based on the hypothesis that agglomeration in polymer reactors correlates with the onset of solid-liquid equilibrium (SLE) in the reactor. This hypothesis is validated by comparing model results with experimental data for carriers (solvents) of different shapes (linear, branched and cyclic). The success of the model depends on the equation of state distinguishing between linear, branched and cyclic carriers. This allows us to identify the best carrier for polymer slurry reactors.
Secondly, we validate the ability of the perturbed chain extension (PC-SAFT) to SAFT to accurately model and predict phase behavior in chain length asymmetric mixtures. PC-SAFT is able to do this more effectively than other equations of state because it accounts for the effect of the chain length on dispersive interactions. The ability to accurately model chain length effects provides the impetus to model chain length polydispersity in polymer solutions.

Thirdly, we propose novel numerical algorithms and initiation methodologies that simplify the calculation of phase equilibria and thermodynamic stability analysis in molecular weight (chain length) polydisperse polymer solutions. This allows us to perform the aforementioned calculations in molecular weight polydisperse polymer solutions that were previously intractable because of the difficulty of converging large systems of highly non-linear and non-convex equations. We demonstrate the applicability of these algorithms to molecular weight polydisperse homopolymer solutions and copolymer (polar as well as non-polar) solutions.

Finally, we present an efficient methodology to account for compositional polydispersity in dipolar copolymer solutions. Compositional polydispersity refers to the fact that different pseudocomponents of a copolymer have different amounts of comonomer incorporation. The proposed methodology is achieved by deriving that the log of the partition coefficient of a polar copolymer pseudocomponent varies linearly with the fraction of polar content in the pseudocomponent. Hence solving for the coefficients in the above stated linear relation ensures that the conditions of phase equilibria are satisfied for all the pseudocomponents. We then consider the system polyethylene-co-methyl acrylate in solution with butane and elucidate the effect of
compositional polydispersity on phase behavior and the sensitivity of phase behavior to molecular weight, pressure, average comonomer composition and type of comonomer distribution for compositionally polydisperse polymer solutions.

8.2 Future directions

Some future directions that are motivated by advances in this dissertation are:

- Extending the algorithms for two phase equilibrium for polydisperse polymer solutions developed here to three phase equilibrium.

- Extending the efficient algorithm proposed for compositional polydispersity to the heterosegmented (Copolymer-SAFT) model for copolymers. This will allow for more accurate modeling of non-polar copolymers.

- Accounting for two dimensional polydispersity (chain length as well as compositional polydispersity) in copolymers. This will lead to a well characterized model for copolymers.

- Utilizing the simplification for polydisperse polymers to probe the effect of polydispersity on polymer-colloid solutions.

- TPT1 is applicable to linear chains hence the equation of state cannot account for the effect of polymer conformation on phase behavior. Polymer conformation plays an important role for polymers at low concentration where the polymer may exist in a collapsed form. Modeling this behavior will require the inclusion of information about the polymer conformation in the equation of state.
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