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Extension of association models to complex chemicals

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Preface

This thesis is submitted in partial fulfilment of the requirements for the Ph.D. degree at the Technical University of Denmark (DTU). The work was carried out at the Department of Chemical and Biochemical Engineering, DTU from August 2007 to September 2010, including a six month stay at Rice University. The project was funded by DTU.

During the course of the work presented in the thesis, a number of people have provided their help and support, for which I am very grateful. First of all, I would like to thank my supervisors at DTU, Georgios M. Kontogeorgis and Michael L. Michelsen for their guidance, encouragement and many valuable inputs. I would also like to thank my friends and colleagues in CERE for providing a fun and stimulating research environment. In particular I want to thank my office mate Sidsel Nielsen with whom I have had daily discussions, of which some were research related.

During my project I had the opportunity to spend six month at Rice University, Texas, at the Department of Chemical and Biomolecular Engineering. A very special thank you to Professor Walter G. Chapman for kindly hosting my visit, and taking the time to discuss the theory with me. I have benefitted tremendously from the time at Rice University, both academically and personally, and for that I am very grateful.

I wish to thank my family and friends for continuous support. Especially Casper Hadsbjerg for helping me out in Houston, and Annette Sørensen for being there

even when we were in different continents. Finally I would like to thank my parents for always being there and supporting every decision I make.

Kongens Lyngby, January 2011

Ane Søgaard Avlund

Summary

The subject of this thesis is application of SAFT type equations of state (EoS). Accurate and predictive thermodynamic models are important in many industries including the petroleum industry. The SAFT EoS was developed 20 years ago, and a large number of papers on the subject has been published since, but many issues still remain unsolved. These issues are both theoretical and practical. The SAFT theory does not account for intramolecular association, it can only treat flexible chains, and does not account for steric self-hindrance for tree-like structures. An important practical problem is how to obtain optimal and consistent parameters. Moreover, multifunctional associating molecules represent a special challenge.

In this work two equations of state using the SAFT theory for association are used; CPA and sPC-SAFT. Phase equilibrium and monomer fraction calculations with sPC-SAFT for methanol are used in the thesis to illustrate the importance of parameter estimation when using SAFT. Different parameter sets give similar pure component vapor pressure and liquid density results, whereas very different mixture results are obtained. The performance of the theory, therefore depends significantly on the parameter estimation, and this is important to consider if different theories (or association schemes) are compared.

The CPA EoS has been applied for alkanolamines, as a continuation of a previous study, were only the simple 2 (1:1) and 4 (2:2) association schemes were investigated. It is in this work investigated for MEA (monoethanolamine) how the results with CPA is effected if a more advanced association scheme is used, where different association parameters are used for the different functional groups. It is also tested whether increasing the number of sites for DEA (diethanolamine)

improves the results.

It can be shown from experimental data that intramolecular association is dominating compared to intermolecular association in certain systems, and that the intramolecular association can significantly alter the phase behavior of a mixture. Lattice theories have earlier on been extended to include intramolecular association for polyethoxyalcohols, while SAFT has only been extended to intramolecular association for chains with 2 associating sites. A general theory for intramolecular association is presented in the thesis, and compared to the corresponding lattice theory.

The theory for intramolecular association is then applied in connection with sPC-SAFT for mixtures containing glycol ethers. Calculations with sPC-SAFT (without intramolecular association) are presented for comparison, and the results with sPC-SAFT are moreover compared to results with CPA and SAFT-HS. The comparisons show that while the improved theory does improve the predictive performance of the model, the choice of association scheme and the parameter estimation are at least as important.

In general it is found in this project that the parameter estimation is very important for the performance of a SAFT EoS, and that emphasis should be put on that area as well as on improving the theory.

Dansk resumé

Emnet for afhandlingen er anvendelse af tilstandslingniner af SAFT typen. Præcise og prædiktive termodynamiske modeller er vigtige i mange industrier, inklusiv olie og gas industrien. SAFT tilstandsligningen blev udviklet for 20 år siden, og et stort antal artikler er blevet publiceret om emnet siden, men der er stadig mange uløste problemstillinger. Disse problemstillinger er både teoretiske og praktiske. SAFT teorien tager ikke højde for intramolekylær associering, den kan kun beskrive fleksible kæder og tager ikke højde for sterisk afskærming i træ-lignende strukturer. Et vigtigt praktisk problem er hvordan man estimerer optimale og konsistente parametre. Desuden udgør multifunktionelle associerende molekyler en særlig udfordring.

To tilstandsligninger der begge bruger SAFT teorien for association er blevet benyttet i dette arbejde; CPA og sPC-SAFT. Faseligevæts og monomer fraktion beregninger med sPC-SAFT for metanol bruges i afhandlingen til at illustrere vigtigheden af parameter estimering ved anvendelse af SAFT. Forskellige parameter sæt giver tilsvarende resultater for damptryk og væskedensitet, mens meget forskellige resultater opnås for blandinger. De resultater der opnås med teorien afhænger derfor væsentligt af parameter estimeringen, og det er vigtigt at have dette in mente hvis forskellige teorier (eller associerings skemaer) skal sammenlignes.

CPA tilstandslinginen er blevet anvendt for alkanolaminer, i en fortsættelse af et tidligere studie, hvor kun de simple 2 (1:1) og 4 (2:2) associerings skemaer blev undersøgt. Det er i dette arbejde blevet undersøgt for MEA (monoethanolamin) hvordan resultaterne med CPA påvirkes hvis man bruger et mere avanceret skema, hvor der differentieres mellem associerings parametrene for de forskellige funk-

tionelle grupper. Det er også blevet undersøgt hvorvidt det forbedrer resultaterne, hvis antallet af associerende sites for DEA (diethanolamin) øges.

Det kan påvises ud fra eksperimentelle data at intramolekylære associering er dominerende i forhold til intermolekylær associering i visse systemer, og at intramolekylær associering væsentligt kan ændre faseopførelsen af en blanding. Gitter teorier er tidligere blevet udvidet til at inkludere intramolekylær associering for polyethoxyalkoholer, mens SAFT kun er blevet udvidet til at omfatte kæder med to associerende sites. En general teori for intramolekylær associering er blevet præsenteret i afhandlingen, og sammenlignet med den tilsvarende gitter teori.

Teorien for intramolekylær associering er derefter anvendt i forbindelse med sPC-SAFT for blandinger der indeholder glykol æter. Beregninger med sPC-SAFT (uden intramolekylær associering) presenteres til sammenligning, og resultater med sPC-SAFT sammenlignes desuden med resultater med CPA og SAFT-HS. Sammenligningerne viser at selvom den forbedrede teori øger teoriens prædiktive egenskaber så er valget af associerings skema og parameter estimeringen mindst lige så vigtige for resultaterne.

Generelt viser dette projekt at parameter estimeringen er meget vigtig for nøjagtigheden af en SAFT tilstandsligning, og at der både bør lægges vægt på dette område og på at forbedre teorien.

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CHAPTER 1

Introduction

Thermodynamic models are important tools in any chemical process design in order to satisfy product specifications, ensure and optimize production and processing. Whether it is in the design of a distillation column, a flash or a pipeline it is important to be able to determine the thermodynamic properties of the fluids and solids involved. Experimental data is usually available for these properties at limited conditions, and are often expensive and time consuming to conduct. A thermodynamic model, which allows you to extrapolate or even predict the experimental data at other pressures and temperatures than those where data is available, is therefore very desirable. If a reliable model is available it is possible to determine the bubble point pressure, the critical solution temperature, the composition of coexisting phases, the energy required in a certain step in the process and many other things.

Some of the most commonly used thermodynamic models are two cubic equations of state (EoS); Soave-Redlich-Kwong (SRK, Soave, 1972) and Peng-Robinson (PR, Peng and Robinson, 1978), which were developed based on the van der Waals EoS [1] from 1873. SRK and PR are especially widely used in the petroleum industry where they even today are the preferred models due to the simplicity compared to newer models. Another advantage of SRK and PR is that model parameters over the years have been determined for a large number of compounds, as well as characterization methods for reservoir fluids.

This work will focus on modeling compounds of interest to the petroleum industry using equations of state. The petroleum industry uses a number of chemicals at various stages in the oil production, of which a few examples are mentioned here: Glycol ethers are used in chemical flooding of oil reservoirs to enhance the oil recovery by decreasing the interfacial tension between oil (the original fluid) and the displacing fluid (normally brine). Glycols or methanol are used to avoid gas hydrate formation in off-shore process equipment and transmission lines. Alkanolamines are used for removal of acid gases like CO_2 and H_2S from natural gas streams. The compounds mentioned here are all so-called associating compounds, which are capable of forming hydrogen bonds.

Hydrogen bonds have a significant influence on the phase behavior of associating compounds. The cubic EoS do not account explicitly for association, and the theories therefore perform very poorly for systems containing associating compounds. A large number of theories have been developed with explicit treatment of hydrogen bonding. Most of them fall in one of three categories; chemical theories, lattice-fluid theories and perturbation theories. One of the most important association theories is the SAFT (Statistical Associating Fluid Theory) EoS. It is a perturbation theory, which was originally presented in 1988 (Jackson et al. [2] and Chapman et al. [3]) but the association theory used in SAFT was presented by Wertheim in four papers from 1984-1986 [4–7].

A large number of different SAFT variants has been developed, and the theory has been improved by adding polar and quadrupolar contributions, and by extending it to electrolytes. Group-contribution procedures have been developed for estimation of pure component parameters for some of the versions for compounds where data is not available for the parameter estimation. Despite the extensive work on improving the SAFT theories, there are still a number of unsolved problems. Some of the problems and limitations of the theory are discussed in the next section.

1.1 Limitations and assumptions of SAFT and project objectives

Most of the work on improving SAFT has been on the non-associating part of the theory, but many of the remaining problems are related to the association term (and the chain formation term which was derived from the association term),

where most SAFT models still use the association theory by Wertheim. The theoretical problems are related to a number of assumptions and approximations made in the development of SAFT, of which some will be discussed below.

The thermodynamic perturbation theory (TPT) used by Wertheim is first-order, meaning that only two-body interactions are considered. All higher order interactions are neglected. Most of the theoretical limitations of the association theory is related to the use of a first-order TPT (TPT1), and the limitations could thus, in principle, be eliminated by using a higher order TPT, but because of the lack of correlation functions for four- (or more) body interactions it is really not possible to go higher than second-order TPT (TPT2) [8]. It is not possible to include angle dependency on the bonds when only two-body interactions are included. As a result, steric self-hindrance in tree-like structures is neglected. By extending the theory to second-order the bond angles can be included, but Wertheim [8] found that even though TPT2 give better agreement with simulation results than TPT1, the difference is small, and does not justify using the more complex expressions in TPT2.

Wertheim found that the TPT1 was adequate in most cases, but neglecting the structural influences on the phase behavior, makes the theory inadequate for compounds like proteins, where the properties depend strongly on the structure of the molecule.

The theory only allows sites to bond to one other site, that is, only single bonds are allowed, no double bonds. Moreover, the activity of a site is independent of bonding at other sites on the same molecule, and bond-cooperativity is therefore not possible. Because of this, organic acids are modeled with 1 site, in order to get the dimerization right, but it is not realistic that an organic acid molecule surrounded by water molecules would only form one cross-associating bond. A system like acetic acid - water is therefore a very challenging mixture to model with SAFT [9].

Wertheim only included intermolecular association in the theory. Two sites on the same molecule are not allowed to associate. In practice sites are treated as if independent of the molecule they belong to, so two sites on the same molecule can actually associate, but the bond is treated in the same way as intermolecular association. The inter- and intramolecular bonds, however, influence the phase behavior very differently, which is not accounted for by the association theory of SAFT. Limited work has been done on modeling intramolecular association with

SAFT, and even less on including intramolecular association in the modeling of real compounds (e.g. [10–13]).

The theoretical limitations and assumptions are, however, not the only problems that need to be addressed when using advanced thermodynamic models. There are also practical limitations. A very important practical problem is how to obtain pure component parameters. The parameters for the SAFT theories have physical meanings, but have traditionally been fitted to pure component vapor pressure and liquid density, and for non-associating compounds this works very well. Group-contribution methods have been developed to determine parameters for polymers based on the structure, confirming the physical basis of the parameters [14–19]. For associating compounds there are five parameters instead of three, and the parameters are highly correlated, when looking only at pure component vapor pressure and liquid density. Several parameter sets can therefore be obtained, which give similar pure component results, and the dependency of the parameters on the structure of the molecule is not as clear as for the non-associating compounds.

A group-contribution method for sPC-SAFT [20] (a simplified version of the PC-SAFT [21] version of SAFT) was developed for non-associating compounds by Tihic et al. [14], but a similar method has not been developed for associating compounds for sPC-SAFT. Grenner et al. [22, 23], however, showed that generalized association parameters can be used for alkanols and glycols. This is an obvious first step towards a group contribution method for associating compounds.

Another practical problem is how to determine the optimal association scheme. The association schemes are in principle obtained from the molecular structure of the compounds, but in reality it is not that simple, and different association schemes have to be investigated for each compound (or family of compounds).

The main objective of this project is to improve and to better understand the SAFT EoS. Is it the limitations of the theory which is the biggest problem or are the practical issues, like parameter estimation, more important? More specifically the objectives are:

- To investigate the influence of the parameter estimation.

- To investigate the influence of the association scheme.

- To develop a theory for intramolecular association for real compounds.

- To apply the theory for intramolecular association to compounds of industrial importance.

1.2 Thesis outline

The thesis is divided into the following chapters:

Chapter 1 gives an introduction to the subject, and presents the objective of the project.

Chapter 2 presents the models considered in the thesis, CPA and sPC-SAFT, including a discussion of different association schemes and a review of the derivation of the association theory used in SAFT type equations of state.

In Chapter 3 the sPC-SAFT EoS is applied for methanol containing systems. The importance of parameter estimation is discussed based on phase equilibrium and monomer fraction calculations.

Chapter 4 presents an investigation of different association schemes for two alkanolamines, MEA and DEA, including using different association parameters for the hydroxyl and amine groups of MEA. The calculations are performed with CPA.

Chapter 5 is about intramolecular association. Experimental data showing the presence of intramolecular bonds are presented, and previous work on modeling intramolecular association with SAFT and lattice theory is presented and discussed. A new general theory for intramolecular association in the framework of SAFT is derived and compared to lattice theory.

In Chapter 6 the new theory for intramolecular association is applied to binary mixtures containing glycol ethers. The new theory is used in connection with sPC-SAFT, and results are presented both with sPC-SAFT and with sPC-SAFT plus intramolecular association.

Finally in Chapter 7 the results and conclusions of the thesis are discussed and ideas for future work are presented

CHAPTER 2

sPC-SAFT and CPA

2.1 Introduction

In four papers published in 1984-1986 in Journal of Statistical Physics [4–7] Wertheim presented a theory for associating fluids, based on statistical thermodynamics and cluster expansions (graph theory), which explicitly accounts for hydrogen bonding. However, Wertheim did not present the theory in a form which can easily be applied in thermodynamic calculations. A couple of years later, in 1988-1990, Chapman, Jackson, Radosz and Gubbins at Cornell University published a number of papers ([2,3,24,25]) in which they transformed the theory into an engineering equation of state, called the Statistical Associating Fluid Theory (SAFT). Already in 1990 a new version of SAFT appeared, developed by Huang and Radosz [26]. This version is sometimes referred to as "original SAFT", but that term will in this study be used to refer to the model by Chapman et al. [24]. Besides some notational differences, the main difference between the two SAFT versions is in the dispersion term. Chapman et al. used an expression from Cotterman et al. [27], while Huang and Radosz used the dispersion term proposed by Chen and Kreglewski [28].

After this, a large number of different versions of SAFT has followed, with the most important being perhaps the PC-SAFT from 2001 by Gross and Sadowski [21] from Technical University of Berlin.

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The SAFT models are typically written as a sum of contributions to the Helmholtz free energy, e.g. as in (2.1) from Chapman et al. [24],

$$\tilde{a} \equiv \frac{A}{NkT} = \tilde{a}^{\text{ideal}} + \tilde{a}^{\text{seg}} + \tilde{a}^{\text{chain}} + \tilde{a}^{\text{assoc}} \tag{2.1}$$

where the energy is obtained from an ideal gas, a segment, a chain and an association contribution.

Several reviews of the different SAFT theories have been published (e.g. Müller and Gubbins [29], Economou [30] and Tan et al. [31]) and they will therefore not be described here. However, the biggest differences in these theories are the choice of reference fluid and the dispersion term. They all more or less use the same expressions for the contribution to the Helmholtz free energy from association and chain formation, as in the original SAFT EoS.

This chapter will present the two theories used in this work, sPC-SAFT and CPA, and will also describe the derivation of the association term.

2.2 PC-SAFT

PC-SAFT was as mentioned proposed in 2001 by Gross and Sadowski [21]. The theory was presented partly in terms of the compressibility factor and partly in terms of the Helmholtz free energy, but will here be given solely in terms of the Helmholtz free energy. The residual energy is divided into three corrections to the ideal gas:

$$\tilde{a} = \frac{A}{NkT} = \tilde{a}^{\text{id}} + \tilde{a}^{\text{hc}} + \tilde{a}^{\text{disp}} + \tilde{a}^{\text{assoc}} \tag{2.2}$$

where $\tilde{a}^{\text{id}}$ is the ideal gas contribution, $\tilde{a}^{\text{hc}}$ is the contribution of the hard-sphere chain reference system, $\tilde{a}^{\text{disp}}$ is the dispersion contribution from the modified square-well attractive potential and $\tilde{a}^{\text{assoc}}$ is the contribution from association. The difference between PC-SAFT and the SAFT theory of Huang and Radosz is the dispersion term, but it is not only a different expression. Where the dispersion term in the previous SAFT theories describe the dispersive interactions between spheres, in PC-SAFT it accounts for the dispersive interactions between chains. Figure 2.1 illustrates the combination of the terms in PC-SAFT.

The hard-sphere chain term accounts for the hard-sphere repulsion and the contribution from chain formation and is given by the following expression:
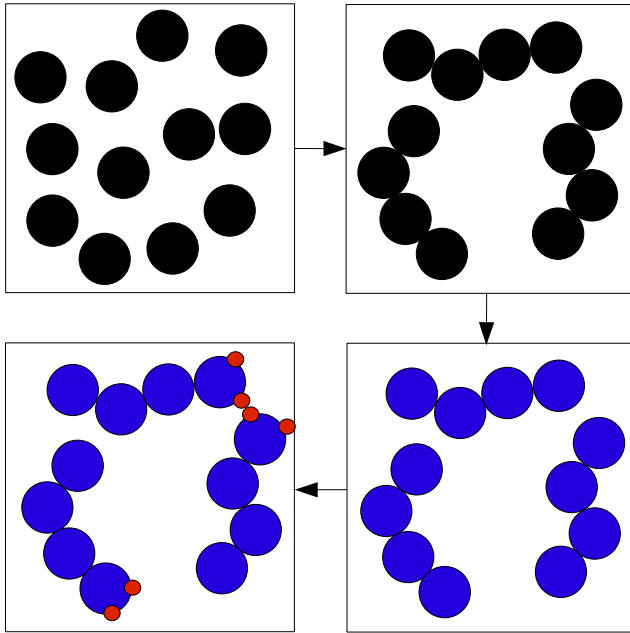
Figure 2.1: Schematic illustration of the PC-SAFT EoS. Hard spheres are connected to form hard chains. Dispersive forces are added to make the chains interact through a square-well potential. Associating sites are added to allow hydrogen bonding between chains. The illustration is freely adopted from [9].

$$\tilde{a}^{\mathrm{hc}} = \bar{m}\tilde{a}^{\mathrm{hs}} - \sum_i x_i(m_i - 1)\ln g_{ii}^{\mathrm{hs}}(d_{ii}) \tag{2.3}$$

where m_i is the chain-length of component i, $\bar{m} = \sum_i x_i m_i$ is a mean chain length and x_i is the mole fraction of component i.

The contribution from chain formation is derived from the association theory by imposing total bonding and setting the fraction of sites not bonded to zero (for the sites involved in the chain formation). In this way hydrogen bonds are replaced with covalent bonds [3].

The hard-sphere term is given by the mixture version of the Carnahan-Starling equation of state for hard-spheres [32]:

$$\tilde{a}^{\mathrm{hs}} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right] \tag{2.4}$$

where

$$\zeta_n = \frac{\pi\rho}{6}\sum_i x_i m_i d_i^n \tag{2.5}$$

d_i is the Chen and Kreglewski [28] temperature-dependent segment diameter,

$$d_i = \sigma_i \left[1 - 0.12 \exp \left(-\frac{3\varepsilon_i}{kT} \right) \right] \tag{2.6}$$

where ε_i is the potential depth, and σ_i is the temperature-independent segment diameter. The radial distribution of hard-spheres (hs) at contact is given by the following expression [32]:

$$g_{ij}^{\text{hs}}(d_{ij}) = \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3} \tag{2.7}$$

The radial distribution function expresses the probability density for finding a molecule of type j at a distance d_{ij} from a molecule of type i.

A second order perturbation theory is used to calculate the dispersion contribution. It is given by

$$\tilde{a}^{\text{disp}} = -2\pi\rho I_1 m^2 \left(\frac{\varepsilon}{kT} \right) \sigma^3 - \pi\rho m \left(1 + \tilde{a}^{\text{hc}} \rho \frac{\partial \tilde{a}^{\text{hc}}}{\partial \rho} \right)^{-1} I_2 m^2 \left(\frac{\varepsilon}{kT} \right)^2 \sigma^3 \tag{2.8}$$

The required integrals are approximated with the power series in density η, where the coefficients of the power series are functions of the chain length:

$$I_1(\eta, m) = \sum_{i=0}^{6} a_i(m)\eta^i \tag{2.9}$$

$$I_2(\eta, m) = \sum_{i=0}^{6} b_i(m)\eta^i \tag{2.10}$$

The dependency of the coefficients $a_i(m)$ and $b_i(m)$ on segment number is given by:

$$a_i(m) = a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m}\frac{m-2}{m} a_{2i} \tag{2.11}$$

$$b_i(m) = b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m}\frac{m-2}{m} b_{2i} \tag{2.12}$$

Equations (2.8) to (2.12) are for pure components, and are extended to mixtures by applying the van der Waals one-fluid mixing rules. This is done by replacing m with $\bar{m}$ and setting

$$m^2 \left(\frac{\varepsilon}{kT} \right)^y \sigma^3 = \sum_{i=1}^{\text{NC}} \sum_{j=1}^{\text{NC}} x_i x_j m_i m_j \left(\frac{\varepsilon}{kT} \right)^y \sigma_{ij}^3 \qquad y \in \{1, 2\} \tag{2.13}$$

The cross-parameters are obtained by employing the Lorentz-Berthelot combining

rules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}(1 - k_{ij}) \qquad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2.14}$$

A binary interaction parameter k_{ij} is introduced to correct the dispersion potential of unlike segments.

The constants in equations (2.11) and (2.12) are considered to be universal, and were obtained from an indirect regression to pure component vapor pressures and vapor, liquid and supercritical volumes of n-alkanes. The fitting procedure and values of the constants can be found in Ref. [21].

The association term is given by:

$$\tilde{a}^{\text{assoc}} = \sum_i x_i \sum_{A_i} \left[\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right] \tag{2.15}$$

where x_i is the mole fraction of component i and X_{A_i} is the fraction of molecules not bonded at site A_i given by:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta_{A_i B_j}} \tag{2.16}$$

where the summation over B_j is a summation over all sites. $\rho = N_{\text{AV}}/V_m$ is the number density and V_m is the molar volume. $\Delta_{A_i B_j}$ is the association strength between site A on molecule i and site B on molecule j, given by:

$$\Delta_{A_i B_j} = \sigma_{ij}^3 g_{ij}^{\text{hs}}(d_{ij}) \kappa^{A_i B_j} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT}\right) - 1 \right] \tag{2.17}$$

where $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume respectively.

The monomer fraction of a compound can be found from the fractions of non-bonded sites:

$$X_{0_i} = \prod_{A_i} X_{A_i} \tag{2.18}$$

2.2.1 Pure-component parameters

There are three pure component parameters for non-associating components and five for associating components. The three parameters for the non-associating

part are σ_i, the segment diameter of component i, m_i, the number of segments and ε_i, the depth of the potential well in the dispersion term. The two additional parameters for associating components are $\varepsilon^{A_iB_j}$, the association energy, and $\kappa^{A_iB_j}$ the association volume. The parameters are usually obtained by fitting pure component vapor pressure and liquid density.

2.2.2 Cross-association

When systems with more than one associating component are studied, combining rules are needed for the association energy and volume. Two different combining rules are used for the association parameters. In the first rule the arithmetic mean is used for the association energy and the geometric mean for the association volume. This corresponds to the CR-1 for CPA [33].

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \qquad \kappa^{A_iB_j} = \sqrt{\kappa^{A_iB_i}\kappa^{A_jB_j}} \qquad (2.19)$$

The second is the Elliott combining rule (ECR) [34]:

$$\Delta_{A_iB_j} = \sqrt{\Delta_{A_iB_i}\Delta_{A_jB_j}} \qquad (2.20)$$

2.2.3 Association schemes

The fraction of sites not bonded, X_A depends on the choice of association scheme. The association scheme gives the number and types of association sites in the associating components. In most papers the nomenclature of Huang and Radosz [26] is used to describe the association schemes, but that nomenclature is not systematical, and a different nomenclature is therefore used in this work: x (y:z), where x is the total number of sites, y is the number of proton acceptor sites, and z is the number of proton donor sites. This nomenclature was originally proposed by Yarrison and Chapman in 2004 [35].

It is normally assumed in SAFT that different sites on the same molecule are identical (have the same association parameters), but this assumption can be dropped. The assumptions for Δ (which sites are allowed to interact) for different association schemes are listed in Table 2.1 along with the resulting assumptions for the fraction of sites not bonded (for systems with one associating compound).

Table 2.1: Assumptions for Δ and X_A for different association schemes. After inspiration from Huang and Radosz [26].

scheme	Δ assumption	X_A
1 (0:1):	$\Delta_{AA} \neq 0$	
2 (1:1):	$\Delta_{AA} = \Delta_{BB} = 0$ $\Delta_{AB} \neq 0$	$X_A = X_B$
3 (1:2):	$\Delta_{AA} = \Delta_{BB} = \Delta_{CC} = \Delta_{BC} = 0$ $\Delta_{AB} = \Delta_{AC} \neq 0$	$X_A = 2X_B - 1$ and $X_B = X_C$
3 (2:1):	$\Delta_{AA} = \Delta_{BB} = \Delta_{CC} = \Delta_{AB} = 0$ $\Delta_{AC} = \Delta_{BC} \neq 0$	$X_A = X_B$ and $X_C = 2X_A - 1$
4 (2:2):	$\Delta_{AA} = \Delta_{AB} = \Delta_{BB} = \Delta_{CC} = \Delta_{CD} = \Delta_{DD} = 0$ $\Delta_{AC} = \Delta_{AD} = \Delta_{BC} = \Delta_{BD} \neq 0$	$X_A = X_B = X_C = X_D$
4 (1:1,1:1):	$\Delta_{AA} = \Delta_{AC} = \Delta_{BB} = \Delta_{CC} = \Delta_{BD} = \Delta_{DD} = 0$ $\Delta_{AB} \neq \Delta_{AD} = \Delta_{BC} \neq \Delta_{CD} \neq 0$	$X_A = X_B, X_C = X_D$
6 (3:3)	$\Delta_{AA} = \Delta_{BB} = \Delta_{CC} = \Delta_{DD} = \Delta_{EE} = \Delta_{FF} = 0$ $\Delta_{AB} = \Delta_{AC} = \Delta_{BC} = \Delta_{DE} = \Delta_{DF} = \Delta_{EF} = 0$ $\Delta_{AD} = \Delta_{AE} = \Delta_{AF} = \Delta_{BD} = \Delta_{BE} = \Delta_{BF} = \Delta_{CD}$ $= \Delta_{CE} = \Delta_{CF} \neq 0$	$X_A = X_B = X_C = X_D = X_E = X_F$
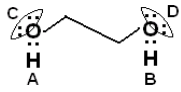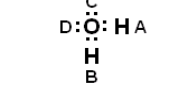
Possible association schemes for different families of compounds are shown in Table 2.2. Ethers and tertiary amines are not considered to be self-associating but they can cross-associate with other associating compounds.

In general X_A must be found iteratively, but with the assumptions in Table 2.1 explicit analytic expressions can be found (for systems with one associating compound) for most of the association schemes in the table:

$$1 \ (0:1): \qquad X_A = \frac{-1 + \sqrt{1 + 4\rho\Delta}}{2\rho\Delta}$$

$$2 \ (1:1): \qquad X_A = \frac{-1 + \sqrt{1 + 4\rho\Delta}}{2\rho\Delta}$$

$$3 \ (1:2): \qquad X_B = \frac{-(1 - \rho\Delta) + \sqrt{(1 + \rho\Delta)^2 + 4\rho\Delta}}{4\rho\Delta}$$

$$3 \ (2:1): \qquad X_A = \frac{-(1 - \rho\Delta) + \sqrt{(1 + \rho\Delta)^2 + 4\rho\Delta}}{4\rho\Delta}$$

$$4 \ (2:2): \qquad X_A = \frac{-1 + \sqrt{1 + 8\rho\Delta}}{4\rho\Delta}$$

$$6 \ (3:3): \qquad X_A = \frac{-1 + \sqrt{1 + 12\rho\Delta}}{6\rho\Delta}$$

When a compound contains different functional groups it is necessary to combine the schemes in Table 2.2. Alkanolamines for example contain both hydroxyl groups and an amine group, and we therefore need to look at the schemes for alcohols and amines. The structures of two alkanolamines are shown in Figure 2.2. The

Table 2.2: Association schemes for different families of compounds. After inspiration from Huang and Radosz [26].

Species	Formula	Scheme
Alcohol		3 (2:1)
		2 (1:1)
Glycols		4 (2:2)
Water		4 (2:2)
		3 (1:2)
		3 (2:1)
Amines		
Primary		2 (1:1)
		3 (1:2)
Secondary		2 (1:1)
Tertiary		1 (1:0)
Ethers		1 (1:0)
		2 (2:0)

simplest alkanolamine, MEA, contains one hydroxyl group and one primary amine, and according to Table 2.2 between 4-6 sites can therefore be assigned to MEA. Previous work on modeling alcohols and amines with CPA [36, 37] has however shown that 2 sites give as good or better results than 3 sites for both types of compounds, and 4 sites will therefore be used for MEA in this work. If the sites

are assumed to be identical this corresponds to the 4 (2:2) scheme. If different association parameters are used for the hydroxyl and amine groups in MEA it corresponds to the 4 (1:1,1:1) scheme, where the same parameters are used for the hydrogen donor and acceptor in a group, but different parameters are used for each group.

DEA contains two hydroxyl groups and one secondary amine and, according to the schemes for alcohols and amines, that corresponds to 6-8 sites. Using the same argument as for MEA we will use a 6 (3:3) scheme, with 2 sites for each group. Alcohols, however, associate stronger than amines, and a simplified scheme, where the amine sites were ignored, has therefore been applied in a previous work [38]. The simplified scheme where only the sites of the hydroxyl groups are accounted for corresponds to the 4 (2:2) scheme. Both schemes will be used for DEA in this work.

MEA: O–CH$_2$–CH$_2$–N:H
        H   H

DEA: O–CH$_2$–CH$_2$–N–CH$_2$–CH$_2$–O
      H   H   H
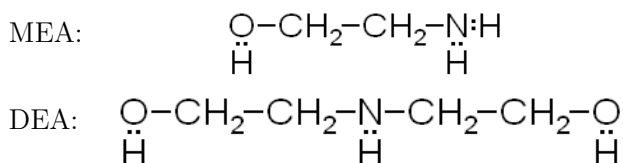
Figure 2.2: Structures of MEA and DEA.

Glycol ethers contain both a hydroxyl group and one or more ether oxygens. As for alkanolamines, the glycol ether hydroxyl groups will in this work be assigned two sites, while one site will be assigned for each ether oxygen. This work will only consider glycol ethers with one ether oxygen, and the glycol ethers will therefore all be modelled with three sites in total, in accordance with the 3 (2:1) scheme.

2.2.4   sPC-SAFT

In 2003 von Solms et al. [20] proposed a simplified PC-SAFT (sPC-SAFT). The simplifications only influences the hard-sphere chain and the association term and follow from the approximation that all segments in the mixture have the same diameter, with the constraint that the mixture volume fraction calculated using the new diameter gives the same volume fraction as the actual mixture (i.e. we

define $\eta \equiv \zeta_3$, where $\eta = \pi\rho d^3/6$). This average diameter is then given by

$$d = \left(\frac{\sum_i x_i m_i d_i^3}{\sum_i x_i m_i} \right)^{1/3} \tag{2.21}$$

If this diameter is introduced in (2.7) we get a much simpler expression for the radial distribution function in the chain and association terms

$$g^{\mathrm{hs}}(d) = \frac{1 - \eta/2}{(1 - \eta)^3} \tag{2.22}$$

Similarly if (2.21) is substituted into (2.4) the hard-sphere term reduces to the pure component Carnahan-Starling equation:

$$\tilde{a}^{\mathrm{hs}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \tag{2.23}$$

Moreover a slightly different but equivalent (except for the expression for the radial distribution function) expression is used for the association strength:

$$\Delta_{A_i B_j} = \frac{\pi}{6} \sigma_{ij}^3 g^{\mathrm{hs}}(d) \kappa^{A_i B_j} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT} \right) - 1 \right] \tag{2.24}$$

The difference between the expressions in (2.17) and (2.24) is the factor of $\pi/6$, which scales κ to the segment volume in sPC-SAFT. Because of this factor one needs to be careful when using PC-SAFT parameters in sPC-SAFT or sPC-SAFT parameters in PC-SAFT, even though the two theories are identical for pure components. If we transfer parameters we need to modify the κ parameter in accordance with the following expression:

$$\kappa^{\mathrm{PC\text{-}SAFT}} = \frac{\pi}{6} \kappa^{\mathrm{sPC\text{-}SAFT}} \tag{2.25}$$

2.3 CPA

The CPA (Cubic Plus Association) EoS [39] combines the cubic EoS SRK and the association term from SAFT. It can be given in terms of the Helmholtz free energy as

$$\frac{A}{NkT} = \frac{A^{\mathrm{SRK}}}{NkT} + \frac{A^{\mathrm{assoc}}}{NkT} \tag{2.26}$$

but will here be given in detail as an expression for the pressure, because this is the way SRK is usually presented (this form of the association term was proposed by Michelsen and Hendriks in 2001 [40]):

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \frac{1}{V_m}\frac{\partial \ln g}{\partial(1/V_m)}\right)\sum_i x_i \sum_{A_i}(1 - X_{A_i}) \quad (2.27)$$

with the same definitions as for PC-SAFT: V_m is the molar volume, X_{A_i} is the mole fraction of molecule i not bonded at site A and x_i is the mole fraction of component i, and the SRK parameters are a, the energy parameter, and b, the co-volume.

The expression for X_{A_i} is identical to the one in PC-SAFT

$$X_{A_i} = \frac{1}{1 + \frac{1}{V_m}\sum_j x_j \sum_{B_j} X_{B_j}\Delta_{A_i B_j}} \quad (2.28)$$

while $\Delta_{A_i B_j}$ is slightly different:

$$\Delta_{A_i B_j} = g(V_m)^{\text{ref}}\left[\exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1\right]b_{ij}\beta^{A_i B_j} \quad (2.29)$$

where $g(V_m)^{\text{ref}}$ is the radial distribution function for the reference fluid (a fluid of hard spheres). $\varepsilon^{A_i B_j}$ is again the association energy and $\beta^{A_i B_j}$ is the association volume. ($\Delta_{A_i B_j}$ in 2.29 is per mole, whereas $\Delta_{A_i B_j}$ in 2.17 and 2.24 is per molecule.)

In the original CPA EoS from 1996 Kontogeorgis et al. [39] used the radial distribution function from the Carnahan-Starling EoS,

$$g(V_m)^{ref} = \frac{1 - \eta/2}{(1 - \eta)^3} \text{ , with } \eta = \frac{1}{4V_m}b \quad (2.30)$$

but a simpler expression was proposed by Kontogeorgis et al. in 1999 [41],

$$g(V_m)^{ref} = \frac{1}{1 - 1.9\eta} \text{ , with } \eta = \frac{1}{4V_m}b \quad (2.31)$$

We will in this work use the CPA EoS with the simplified expression in equation (2.31) for the radial distribution function.

2.3.1   Pure component parameters

The energy parameter in the SRK part of equation (2.27) is given by

$$a(T) = a_0(1 + c_1(1 - \sqrt{T_r}))^2 \tag{2.32}$$

where T_r is the reduced temperature, T/T_c.

Five pure component parameters are needed in CPA; three in the physical (SRK) part (a_0, b, c_1), and two for the association part ($\varepsilon^{A_iB_i}$, $\beta^{A_iB_i}$). Only the three physical parameters are needed for non-associating components.

The five parameters for associating components are usually found by fitting experimental vapor pressure and liquid density data. The three parameters for non-associating components can either be calculated from critical temperature, pressure and the acentric factor in the conventional way or by fitting to experimental vapor pressure and liquid density data.

In the conventional way of using SRK the three non-association parameters are calculated from the following expressions

$$
\begin{aligned}
a_0 &= 0.42748 \, \frac{R^2 T_c^2}{P_c} \\
b &= 0.08664 \, \frac{R T_c}{P_c} \\
c_1 &= 0.48 + 1.57\omega - 0.176\omega^2
\end{aligned}
\tag{2.33}
$$

We replace the a_0 parameter with

$$\Gamma = \frac{a_0}{R \cdot b} = 4.93398 \, T_c \tag{2.34}$$

to get a dimension of temperature.

2.3.2   Mixing and combining rules

When the CPA EoS is extended to mixtures mixing rules are needed for the SRK part. The classical Van der Waals one-fluid mixing rules are used for a and b:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2.35}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{2.36}$$

where the combining rules are

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{2.37}$$

$$b_{ij} = \frac{b_i + b_j}{2} \tag{2.38}$$

k_{ij} is a binary interaction parameter. No mixing rules are needed in the association part.

2.3.3   Cross-association

Combining rules are again needed for the association parameters when systems with more than one associating component are modeled.

The two combining rules used for CPA are the Elliott combining rule (ECR) by Suresh and Elliott (1992) [34], shown in equation (2.39), which uses the geometric mean for the association strength,

$$\Delta_{A_i B_j} = \sqrt{\Delta_{A_i B_i} \Delta_{A_j B_j}} \tag{2.39}$$

and the so-called CR-1 rule by Derawi et al. (2003) [33], which uses the arithmetic mean for the association energy as shown in equation (2.40), and the geometric mean for the association volume, as shown in equation (2.41).

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \tag{2.40}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \tag{2.41}$$

If it is assumed, that $\exp[\varepsilon^{AB}/(RT)] \gg 1$, it can be shown that ECR corresponds to the following expressions for the cross-association energy and volume parameters:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \tag{2.42}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \frac{\sqrt{b_i b_j}}{b_{ij}} \tag{2.43}$$

Equations (2.40) to (2.43) show that ECR and CR-1 are very similar. The biggest difference between the two combining rules is the function of b in the

cross-association volume in ECR. The function of b is most important in size-asymmetric systems. In such systems ECR will give less cross-association than CR-1.

2.3.4 Solvation and the homomorph approach

Aromatic hydrocarbons are not self-associating, but some solvation occurs in mixtures with associating compounds like water or alcohols. This is a result of the π electrons in the aromatic ring which can interact with associating compounds. To account for this solvation, a modified CR-1 combining rule (mCR-1) was suggested by Folas et al. [42] for associating - aromatic systems. According to this rule the cross-association volume $\beta^{A_i B_j}$ is determined from experimental data (fitted) and the cross-association energy is equal to the value of the associating compound divided by two:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon_{\text{associating}}}{2} \tag{2.44}$$

$$\beta^{A_i B_j} = \beta^{\text{cross}}(\text{fitted}) \tag{2.45}$$

β^{cross} is usually fitted together with k_{ij}. Having two adjustable binary parameters will of course give a better fit to the experimental data, but is not necessarily an advantage. It is likely that the k_{ij} values for solvating systems found in this way do not follow general trends, which makes them difficult to generalise. It can moreover be unclear whether the successful correlation results for solvating systems are due to the explicit treatment of solvation or the additional adjustable parameter.

To avoid the problems described above Breil et al. [43] suggested using the homomorph approach for solvating systems, which reduces the number of binary adjustable parameters to one. Homomorph is a Greek word which means "same shape" ("omoia morfi"). In this approach the k_{ij} is taken from a corresponding homomorph system, leaving only one parameter, β^{cross}, to be fitted to the data for the solvating system. A homomorph is a non-associating compound of similar molecular weight, and, as much as possible, similar structure to the solvating compound. It is not always possible to use the most obvious homomorph if significant experimental data is not available. Then other compounds are used as homomorph. The obvious homomorph of benzene is cyclohexane, but since experimental data with n-hexane is more common, n-hexane is often used as homomorph for benzene.

2.4   Derivation of SAFT

This section will discuss how the association term in SAFT is obtained from Wertheim's papers, and will also present an alternative derivation of the Helmholtz free energy from association, presented by Chapman et al. [3].

The association term in PC-SAFT was presented in section 2.2:

$$\tilde{a}^{\text{assoc}} = \sum_i x_i \sum_{A_i \in \Gamma_i} \left[\ln X_{A_i} - \frac{X_{A_i}}{2} + \frac{1}{2} \right] \tag{2.46}$$

where X_{A_i}, the mole fraction of molecules i not bonded at site A, is given by

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta_{A_i B_j}} \tag{2.47}$$

and $\Delta_{A_i B_j}$, the association strength between site A on molecule i and site B on molecule j, is given by (for sPC-SAFT)

$$\Delta_{A_i B_j} = \frac{\pi}{6} \sigma_{ij}^3 g(d)^{\text{HS}} \kappa_{A_i B_j} \left[\exp\left(\frac{\varepsilon_{A_i B_j}}{kT} \right) - 1 \right] \tag{2.48}$$

2.4.1   From Wertheim

As mentioned in the beginning of the chapter, the theory for associating fluids was first presented by Wertheim in four papers in Journal of Statistical Physics [4–7] (referred to in the text as Wertheim I, II, III and IV). Wertheim presented the theory for pure components, which is also how the derivation is shown here, but it is straight forward to extent it to mixtures.

Wertheim considered hard-spheres with two directional attractive sites, as shown in Figure 2.3. The theory will however be derived here for any number of sites.
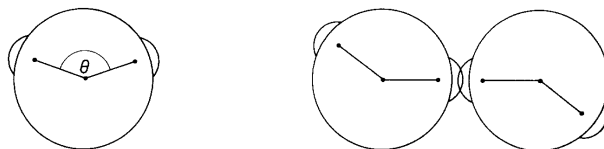
Figure 2.3: To the left, model molecule with two attraction sites. The large circle indicates the hard core. The radius of the small circular arcs is half the range of the attraction. To the right a bonded configuration of two such molecules. [6]

Before the equations are presented it is convenient to introduce the density definitions used by Wertheim; ρ_0 is the density of molecules with no sites bonded, ρ_A is the density of molecules where only site A is bonded, and similarly ρ_B is the density of molecules only bonded at site B, and finally ρ_{AB} is the density of molecules bonded at site A and B, but on no other sites. Wertheim used combinations of these densities in his derivation of thermodynamic functions in Wertheim III:

$$
\begin{aligned}
\sigma_0 &= \rho_0 \\
\sigma_A &= \rho_0 + \rho_A \\
\sigma_B &= \rho_0 + \rho_B \\
\sigma_\Gamma &= \rho
\end{aligned}
$$

where $\rho = N/V$ is the total number density, and Γ is the set of sites. $\sigma_{\Gamma-A}$ is the density of molecules not bonded at site A. We also define $\hat{\sigma}_A = \sigma_A/\sigma_0$.

The change in Helmholtz free energy from association is given in equation (5) from Wertheim IV:

$$
\beta(A - A_{\mathrm{R}}) = \int \left(\sigma_\Gamma \ln \frac{\sigma_0(1)}{\sigma_\Gamma(1)} + \sigma_\Gamma(1) + Q(1) \right) d(1) - c^{(0)} + c_{\mathrm{R}}^{(0)} \tag{2.49}
$$

where (1) represents the position and orientation of the molecule as well as the angle subtended by the sites, and $Q(1)$ is a summation over all possible bonding states given in equation (40) in Wertheim III:

$$
Q(1) = -\sum_{A \in \Gamma} \sigma_{\Gamma-A}(1) + \sigma_0(1) \sum_{P(\Gamma)=\{\gamma, M \geq 2\}} (-1)^M (M-2)! \prod_\gamma \hat{\sigma}_\gamma(1) \tag{2.50}
$$

where P is a partitioning of the sites in the set Γ (into M subsets). Only proper partitions of Γ into two or more sets are allowed.

$c^{(0)} - c_{\mathrm{R}}^{(0)}$ is the sum of graphs in the associating fluid subtracted the graphs in the non-associating reference fluid. For the system considered here $\Delta c^{(0)}$ is given by:

$$
\Delta c^{(0)} = c^{(0)} - c_{\mathrm{R}}^{(0)} = \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma} \int g_{\mathrm{R}}(12) f_{AB}(12) \sigma_{\Gamma-A}(1) \sigma_{\Gamma-B}(2) d(1) d(2) \tag{2.51}
$$

which is a sum over all possible interactions between two sites on two different molecules. An expression for $\Delta c^{(0)}$ is given for two sites in equation (15) in Wertheim IV, and in general with a different nomenclature in equation (6) in

Wertheim IV.

$g_{\mathrm{R}}(12)$ is the reference fluid pair correlation function, f_{AB} is the Mayer f-function:

$$f_{AB}(12) = \exp\left(\frac{-\phi_{AB}}{kT}\right) - 1 \tag{2.52}$$

and $d(1)d(2)$ denotes an unweighted average over all orientations and positions of molecules 1 and 2. ϕ_{AB} is the site-site potential.

The expression in (2.51) is based on a number of assumptions regarding steric incompatibility, which are illustrated in Figure 2.4.
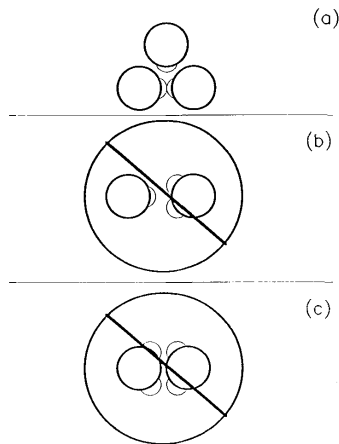
Figure 2.4: The three types of steric incompatibility: a) The repulsion of two associating molecules will prevent a third molecule from coming close enough to associate. b) No site on one molecule can bond simultaneously to two sites on another molecule. c) No double bonding between two molecules is allowed. The restriction of no double bonding can be relaxed. [2]

For a homogeneous fluid the densities are independent of position and if we assume that $r^2 g_R$ (where r is the distance between the interacting molecules) is constant in the overlap volume and equal to the value at contact then (2.49) becomes

$$\frac{\beta(A - A_{\mathrm{R}})}{V} = \sigma_\Gamma \ln \frac{\sigma_0}{\sigma_\Gamma} + \sigma_\Gamma + Q - \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma} g_{\mathrm{R,c}} f_{AB} K_{AB} \sigma_{\Gamma-A} \sigma_{\Gamma-B} \tag{2.53}$$

where $g_{\mathrm{R,c}}$ is the value of the pair correlation function at contact and K_{AB} is the bonding volume available for sites A and B.

According to equation (12) in Wertheim IV:

$$\hat{\sigma}_\alpha(1) = \prod_{A \in \alpha} \hat{\sigma}_A(1) \quad \text{for } \alpha \neq \emptyset \tag{2.54}$$

Using this (2.50) becomes

$$Q \;=\; -\sum_{A \in \Gamma} \sigma_{\Gamma-A} + \sigma_\Gamma \sum_{P(\Gamma)=\{\gamma, M \geq 2\}} (-1)^M (M-2)! \qquad (2.55)$$

In the limit of no bonding we have $\beta(A - A_R) = 0$ and all $\sigma_{\Gamma-\gamma}$ equal to σ_Γ, and from (2.53) we then find

$$0 \;=\; \sigma_\Gamma - \sum_{A \in \Gamma} \sigma_\Gamma + \sigma_\Gamma \sum_{P(\Gamma)=\{\gamma, M \geq 2\}} (-1)^M (M-2)!$$

$$\Rightarrow \sum_{P(\Gamma)=\{\gamma, M \geq 2\}} (-1)^M (M-2)! \;=\; n(\Gamma) - 1 \qquad (2.56)$$

where $n(\Gamma)$ is the number of sites in Γ.

Equation (2.56) is inserted in (2.55) and from (2.53) we then obtain:

$$\frac{\beta(A - A_R)}{V} \;=\; \sigma_\Gamma \ln \frac{\sigma_0}{\sigma_\Gamma} + \sigma_\Gamma n(\Gamma) - \sum_{A \in \Gamma} \sigma_{\Gamma-A} - \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma} g_{R,c} f_{AB} K_{AB} \sigma_{\Gamma-A} \sigma_{\Gamma-B}$$

$$(2.57)$$

We use (2.54) to find an expression for σ_0 / σ_Γ:

$$\hat{\sigma}_\Gamma = \prod_{A \in \Gamma} \hat{\sigma}_A \quad \Rightarrow \quad \frac{\sigma_\Gamma}{\sigma_0} = \frac{\sigma_A}{\sigma_0} \frac{\sigma_{\Gamma-A}}{\sigma_0} \quad \Rightarrow \quad \sigma_\Gamma = \frac{\sigma_A \sigma_{\Gamma-A}}{\sigma_0} \quad \Rightarrow \quad \frac{\sigma_A}{\sigma_0} = \frac{\sigma_\Gamma}{\sigma_{\Gamma-A}}$$

$$\Rightarrow \quad \frac{\sigma_\Gamma}{\sigma_0} = \prod_{A \in \Gamma} \frac{\sigma_A}{\sigma_0} = \prod_{A \in \Gamma} \frac{\sigma_\Gamma}{\sigma_{\Gamma-A}} \quad \Rightarrow \quad \frac{\sigma_0}{\sigma_\Gamma} = \prod_{A \in \Gamma} \frac{\sigma_{\Gamma-A}}{\sigma_\Gamma} \qquad (2.58)$$

which we then use to eliminate σ_0 from (2.57):

$$\frac{\beta(A - A_R)}{V} \;=\; \sigma_\Gamma \sum_{A \in \Gamma} \left[\ln \frac{\sigma_{\Gamma-A}}{\sigma_\Gamma} + 1 - \frac{\sigma_{\Gamma-A}}{\sigma_\Gamma} \right] - \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma} g_{R,c} f_{AB} K_{AB} \sigma_{\Gamma-A} \sigma_{\Gamma-B}$$

$$(2.59)$$

The energy of the system is at a minimum with respect to all bonding states at equilibrium. This means that the derivative of $A - A_R$ with respect to any σ_γ is zero, which we can use to eliminate the graph sum:

$$\frac{\partial \beta(A - A_R)/V}{\partial \sigma_{\Gamma-A}} \;=\; \frac{\sigma_\Gamma}{\sigma_{\Gamma-A}} - 1 - \sum_{B \in \Gamma} g_{R,c} f_{AB} K_{AB} \sigma_{\Gamma-B} \;=\; 0$$

$$\Rightarrow \sum_{A \in \Gamma} \sum_{B \in \Gamma} g_{R,c} f_{AB} K_{AB} \sigma_{\Gamma-A} \sigma_{\Gamma-B} \;=\; \sum_{A \in \Gamma} (\sigma_\Gamma - \sigma_{\Gamma-A}) \qquad (2.60)$$

which is inserted in (2.59)

$$\frac{\beta(A - A_{\mathrm{R}})}{V} = \sigma_\Gamma \sum_{A \in \Gamma} \left[\ln \frac{\sigma_{\Gamma - A}}{\sigma_\Gamma} + \frac{1}{2} \left(1 - \frac{\sigma_{\Gamma - A}}{\sigma_\Gamma} \right) \right] \tag{2.61}$$

We divide with σ_Γ and introduce the fraction of molecules not bonded at a specific site, $X_A = \sigma_{\Gamma - A}/\sigma_\Gamma$ from Chapman [44], to obtain the pure component version of (2.46):

$$\frac{\beta(A - A_{\mathrm{R}})}{N} = \sum_{A \in \Gamma} \left[\ln X_A - \frac{X_{A_i}}{2} + \frac{1}{2} \right] \tag{2.62}$$

Similarly X_A is introduced in (2.60) to give the pure component version of (2.47):

$$\frac{1}{X_A} - 1 - \rho g_{R,c} \sum_{B \in \Gamma} f_{AB} K_{AB} X_B = 0$$

$$\Rightarrow X_A = \frac{1}{1 + \rho \sum_{B \in \Gamma} g_{R,c} f_{AB} K_{AB} X_B} \tag{2.63}$$

with

$$\Delta_{AB} = g_{R,c} f_{AB} K_{AB} \tag{2.64}$$

Jackson et al. [2] showed how a theoretical expression for K_{AB} can be obtained through a number of assumptions and approximations, but in practice the bonding volume is fitted together with the other parameters. In sPC-SAFT the bonding volume is given as a fraction of the segment volume, $K_{AB} = \kappa_{AB} \frac{\pi}{6} \sigma^3$, and the hard-sphere radial distribution function is used for the reference fluid. With these assumptions the expression in (2.64) is identical to (2.48) for a pure component.

As shown in Figure 2.4 Wertheim did not allow double bonding between molecules, and the theory was derived using this assumption. The restriction was maintained through certain limits for the bonding volume K (e.g. cut-off distance and ratio of site diameter to segment diameter). The bonding volume is however usually fitted to experimental data for vapor pressure and liquid density, together with the other parameters, without considering the limits which was imposed in the development of the theory. The physical meaning of the K parameter is therefore somewhat lost in the parameter estimation.

2.4.2 Chapman et al.

A different derivation was presented by Chapman et al. in 1988 [3]. The contribution to the Helmholtz free energy from association is derived as the difference

between the free energy of an associating mixture and that of a non-associating reference fluid, denoted $A_{\text{bond}}^{\text{Mix}}$ (the notation in the paper by Chapman et al. is slightly different from the one used in this work):

$$\tilde{a}^{\text{assoc}} = \frac{A_{\text{bond}}^{\text{Mix}}}{NkT} = \frac{A^{\text{Mix}} - A_{\text{R}}^{\text{Mix}}}{NkT} \tag{2.65}$$

where A^{Mix} is the Helmholtz free energy of the associating mixture, and $A_{\text{R}}^{\text{Mix}}$ is the Helmholtz free energy of the corresponding non-associating reference fluid.

The Helmholtz free energy of a mixture can be obtained from the thermodynamic identity

$$A = \sum_i N_i \mu_i - PV \tag{2.66}$$

where $N_i = x_i N$ is the number of molecules of component i.

For a low density fluid the pressure depends on the number of molecules present (an associated complex counts as one molecule in this context):

$$P = \frac{kT\bar{N}}{V} \tag{2.67}$$

From statistical mechanics we have for an ideal monatomic gas

$$\mu(T, P) = -kT \ln \frac{q}{N} = -kT \ln \frac{q_{\text{trans}}}{N} - kT \ln \ q_{\text{elec}} q_{\text{nucl}} \tag{2.68}$$

where q_{trans}, q_{elec} and q_{nucl} are the translational, electronic and nuclear partition functions respectively. q_{trans} is given as

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{V}{\Lambda^3} \tag{2.69}$$

where Λ is the de Broglie wavelength.

The electronic and nuclear contributions to the chemical potential are small compared to the translational, and if they are ignored we get the following approximation for the chemical potential of species i present as monomers

$$\mu_i^{\text{mono}} = kT \ln \left(\rho_{0_i} \Lambda_i^3\right) \tag{2.70}$$

where $\rho = N/V$ is the number density and ρ_{0_i} is the monomer density of molecules of species i.

The monomers in the associating mixture can bond to form dimers, trimers and larger complexes, which will decrease the number of molecules in the fluid. If we assume that only branched chains are formed, and no ring-like structures then the number of molecules present will decrease by one every time a bond is formed. The number of molecules are then

$$\bar{N} = \sum_i N_i - N^{\text{bond}} = \sum_i \left[N_i \left(1 - \frac{1}{2} \sum_{A_i \in \Gamma_i} (1 - X_{A_i}) \right) \right] \qquad (2.71)$$

where N^{bond} is the number of bonds and Γ_i is the set of sites for component i.

At equilibrium the chemical potential of the monomer must be equal to that of the associated complexes

$$\mu_i^{\text{mono}} = \mu_i^{\text{dimer}} = \mu_i^{\text{trimer}} \text{ etc.}$$

and from (2.66) we then find

$$
\begin{aligned}
A^{\text{Mix}} &= \sum_i N_i \mu_i^{\text{mono}} - kT\bar{N} \\
&= NkT \sum_i x_i \ln \left(\rho_{0_i} \Lambda_i^3 \right) - NkT \sum_i x_i \left(1 - \frac{1}{2} \sum_{A_i \in \Gamma_i} (1 - X_{A_i}) \right) \\
&= NkT \sum_i x_i \left[\ln \left(\rho_{0_i} \Lambda_i^3 \right) - 1 + \frac{1}{2} \sum_{A_i \in \Gamma_i} (1 - X_{A_i}) \right] \qquad (2.72)
\end{aligned}
$$

In the reference fluid all molecules are monomers and we therefore have $\bar{N} = N$. Moreover all molecules have the same chemical potential $\mu_i = \mu_i^{\text{mono}}$ and the monomer density is equal to the overall number density, $\rho_{0_i} = \rho_i$. The free energy of the reference fluid is then given as

$$
\begin{aligned}
A_{\text{R}}^{\text{Mix}} &= \sum_i N_i \mu_i - kTN \\
&= NkT \sum_i x_i \ln \left(\rho_i \Lambda_i^3 \right) - kTN \\
&= NkT \sum_i x_i \left[\ln \left(\rho_i \Lambda_i^3 \right) - 1 \right] \qquad (2.73)
\end{aligned}
$$

The contribution to the free energy from association can now be found

$$
\begin{aligned}
\tilde{a}^{\text{assoc}} &= \frac{A^{\text{Mix}}_{\text{bond}}}{NkT} = \frac{A^{\text{Mix}} - A^{\text{Mix}}_{\text{R}}}{NkT} = \sum_i x_i \left[\ln \left(\frac{\rho_{0_i}}{\rho_i} \right) + \frac{1}{2} \sum_{A_i \in \Gamma_i} (1 - X_{A_i}) \right] \\
&= \sum_i x_i \left[\ln X_{0_i} + \frac{1}{2} \sum_{A_i \in \Gamma_i} (1 - X_{A_i}) \right] = \sum_i x_i \sum_{A_i \in \Gamma_i} \left[\ln X_{A_i} - \frac{X_{A_i}}{2} + \frac{1}{2} \right]
\end{aligned}
$$

$$(2.74)$$

which is identical to (2.46).

For the formation of a chemical complex, where site A on component i and site B on component j form a hydrogen bond, we have from the mass action law for chemical reactions that:

$$
\Delta_{A_i B_j} = \frac{\rho_{A_i B_j}}{\rho_{A_i} \rho_{B_j}} = \frac{\rho x_i X_{A_i}^{B_j}}{\rho x_i X_{A_i} \rho x_j X_{B_j}} = \frac{X_{A_i}^{B_j}}{\rho X_{A_i} x_j X_{B_j}}
\tag{2.75}
$$

where $X_{A_i}^{B_j}$ is the fraction of component i bonded at site A to site B on component j, and $\Delta_{A_i B_j}$ is the equilibrium constant for this interaction, that is the association strength between site A on component i and site B on component j.

We then sum over all interactions involving site A on component i:

$$
\sum_j \sum_{B \in \Gamma_j} \Delta_{A_i B_j} = \sum_j \sum_{B \in \Gamma_j} \left(\frac{X_{A_i}^{B_j}}{\rho X_{A_i} x_j X_{B_j}} \right) = \frac{1 - X_{A_i}}{\rho X_{A_i} \sum_j x_j \sum_{B \in \Gamma_j} X_{B_j}}
\tag{2.76}
$$

where the second equal sign is obtained from

$$
\sum_j \sum_{B \in \Gamma_j} X_{A_i}^{B_j} = 1 - X_{A_i}
\tag{2.77}
$$

We can rewrite this as:

$$
\rho X_{A_i} \sum_\gamma x_j \sum_{B_j \in \Gamma_j} \Delta_{A_i B_j} X_{B_j} = 1 - X_{A_i}
$$

$$
\Rightarrow X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j \in \Gamma_j} \Delta_{A_i B_j} X_{B_j}}
\tag{2.78}
$$

This expression is exactly the same as the one in (2.47).

2.5 Chapter summary

The last twenty years have seen many versions of SAFT. Different dispersion terms and reference fluids have been used, but the association term remains untouched in most versions. Two theories, which use the original SAFT association term, are used in this work; sPC-SAFT and CPA. The two theories were presented in this chapter, and the association schemes used were discussed. It was also shown how the association term of SAFT can be derived both from the Wertheim papers, and through a different approach presented by Chapman et al.

CHAPTER 3

Methanol

3.1 Introduction

One of the main issues, when using an advanced thermodynamic model like SAFT, is, as mentioned in Chapter 1, how to obtain pure component parameters. The pure component parameters in SAFT-type theories are often estimated solely on pure component vapor pressure and liquid density, but the parameters are very correlated, and a number of parameter sets give almost identical deviations in vapor pressure and liquid density. The parameter sets however often perform very differently for mixtures (e.g. [39, 45, 46]). Methanol contains one hydrogen-bonding proton and two lone pairs, and should "rigorously" be assigned 3 sites in accordance with the 3 (2:1) scheme. It can be argued that both lone pairs cannot be bonded simultaneously, and that methanol instead should be assigned 2 sites in accordance with the 2 (1:1) scheme. Both schemes have been applied for methanol with SAFT-type equations of state in the literature [20, 39, 47–49], and different conclusions have been made on which scheme is better.

PC-SAFT/sPC-SAFT parameters for methanol are available in the literature from three sources. Gross and Sadowski [48] and von Solms et al. [20] both use the 2 (1:1) scheme, while Tybjerg et al. [50] have estimated parameters for and applied both schemes with sPC-SAFT. The parameters from Tybjerg et al. [50] were estimated by fitting pure component vapor pressure and liquid density as well as enthalpy of vaporization and compressibility factor, and it was found that the

inclusion of the additional data in the parameter estimation improved the phase equilibrium results compared to the parameters from Gross and Sadowski [48].

The parameters from Gross and Sadowski [48], and von Solms et al. [20] are both (according to the authors) fitted to pure component vapor pressure and liquid density. The two parameter sets are however quite different, and it was decided to test and compare the performance of the parameters. A new parameter set was moreover estimated to further investigate the impact of the parameter estimation. This chapter will present phase equilibrium and monomer fraction calculations with sPC-SAFT with the parameter sets from Gross and Sadowski [48], von Solms et al. [20] and this work. Only the 2 sites scheme has been used for methanol in this work.

3.2   Parameters

The three parameter sets investigated in this work are listed in Table 3.1, along with the absolute relative deviations between sPC-SAFT and the experimental data and between sPC-SAFT and DIPPR correlations [51]. The temperature range of the experimental vapor pressure data for methanol is T=258-503 K (T_r=0.50-0.98) and of the liquid density data is T=176-440 K (T_r=0.34-0.86). The parameters are briefly described below. The parameters for other compounds considered in this chapter were taken from Gross and Sadowski [21]. They are listed in Appendix A. The κ^{AB} parameters listed are for sPC-SAFT (PC-SAFT parameters have been converted).

GS - Gross and Sadowski: According to the paper [48] the parameters from Gross and Sadowski were estimated by simultaneously fitting vapor pressure and liquid density data. Also according to the paper the literature data (of vapor pressure and liquid density) covers the temperature range $T = 200 - 512$ K ($T_r = 0.39$-1.00).

vSolms - Von Solms et al.: The parameters estimated by von Solms et al. [20] were fitted to experimental pure component vapor pressure and liquid density in the temperature range 200-500 K ($T_r = 0.39$-0.98). DIPPR correlations were used for the experimental data.

tw - this work: The tw parameters were estimated in this work. They were

estimated by fitting DIPPR correlations of pure component vapor pressure and liquid density in the temperature range T=215-487 K ($T_r = 0.42$-0.95).

Table 3.1: sPC-SAFT parameters for methanol and absolute relative deviations (ARD%) between sPC-SAFT and experimental data. The deviations compared to the DIPPR correlations for $T_r = 0.42 - 0.95$ are given in brackets.

set	σ [Å]	ε [K]	m	ε^{AB} [K]	κ^{AB}	T [K]	ARD% P^{sat}	ρ^L
GS [48]	3.230	188.9	1.526	2900	0.0672	200-512	2.21 (4.50)	0.42 (0.43)
vSolms [20]	2.651	186.6	2.792	2090	0.279	200-500	1.09 (1.03)	0.42 (0.52)
tw	2.611	179.2	2.876	2141	0.311	215-487	1.06 (0.87)	0.32 (0.12)

It is clear from Table 3.1 that the parameters from von Solms et al. (vSolms) and the parameters from this work (tw) are quite similar. The parameters from Gross and Sadowski (GS) are on the other hand rather different from the other sets, and the deviation in vapor pressure for that set is also significantly larger than for the other sets, while all sets have similar accuracy in liquid density. This indicates that other considerations might have been taken in the estimation of that parameter set than just minimizing the error in vapor pressure and liquid density.

3.3   Phase equilibrium calculations

In the paper where the GS parameters for methanol were published [48], they were used to model VLE and LLE for methanol - cyclohexane, with PC-SAFT with $k_{ij} = 0.051$. The results with sPC-SAFT for this system with the three different parameter sets for methanol are shown in Figure 3.1 with $k_{ij} = 0$.

As seen from Figure 3.1 the vSolms and tw sets give similar results especially for VLE. Both sets underestimate the extent of LLE in methanol - cyclohexane, while no LLE is predicted with GS. vSolms and tw both give a good prediction of the VLE, including the azeotrope. The temperature of the azeotrope (and the flat saturated liquid curve) is overestimated by only a couple of degrees compared to what the experimental data suggests. GS gives a larger overprediction of the azeotrope temperature, but gives a good prediction of the azeotrope composition.

Figure 3.2 shows the results for methanol - cyclohexane with a fitted interaction parameter. It is possible with all three sets to match the highest demixing temperature and the composition of one of the liquid phases with a k_{ij}, but none

of the sets can correlate the complete LLE curve. GS matches the solubility of methanol in cyclohexane, and vSolms and tw matches the solubility of cyclohexane in methanol. The interaction parameter was fitted to the highest demixing temperature. A positive value of the interaction parameter is needed for all three sets, to increase the immiscibility of methanol - cyclohexane. The three parameter sets perform equally well for VLE, with GS giving a slightly better correlation in the cyclohexane rich part than vSolms and tw, and vSolms and tw being slightly better for the methanol rich part.
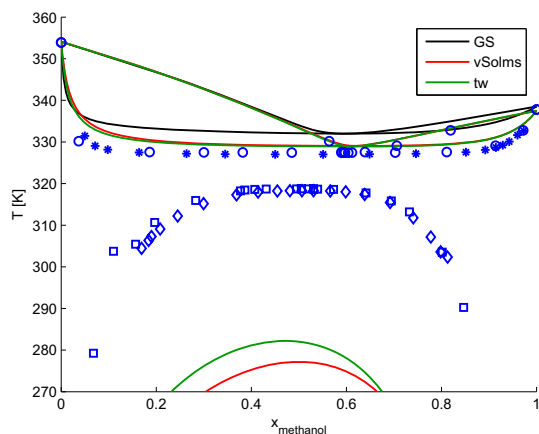
Figure 3.1: Methanol - cyclohexane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with $k_{ij} = 0$; black lines are GS, red lines are vSolms and green lines are tw for methanol. Experimental data: Marinichev and Susarev [52] (○), Madhavan and Murti [53] (∗), Jones and Amstell [54] (□) and Eckfeldt and Lucasse [55] (◇).
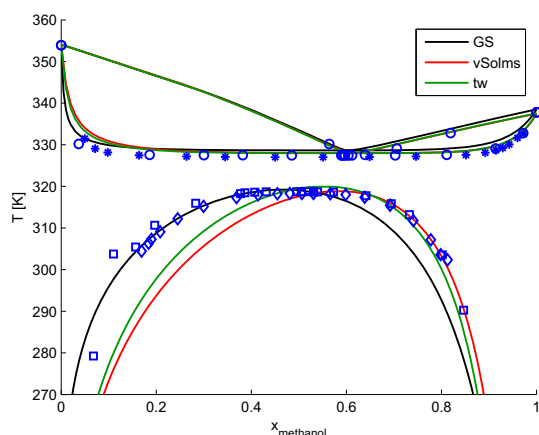
Figure 3.2: Methanol - cyclohexane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with fitted k_{ij}; black lines are GS (with $k_{ij} = 0.0365$), red lines are vSolms (with $k_{ij} = 0.0087$) and green lines are tw (with $k_{ij} = 0.0080$) for methanol. Experimental data: Marinichev and Susarev [52] (○), Madhavan and Murti [53] (∗), Jones and Amstell [54] (□) and Eckfeldt and Lucasse [55] (◇).

Two other methanol systems for which VLE and LLE data is available are methanol - *n*-hexane and methanol - *n*-heptane, two rather similar mixtures with similar phase behavior. sPC-SAFT performs not surprisingly almost identical for the two systems. Figure 3.3 shows the predictions with sPC-SAFT for methanol - *n*-hexane. Again no LLE is predicted with GS, whereas vSolms and tw for this system overestimate the LLE area. vSolms and tw again give good VLE predictions including the azeotrope, with some deviations in the liquid curve though in the dilute areas. The azeotrope temperature is again overestimated with GS, and neither the liquid or vapor curve therefore match the experimental data.
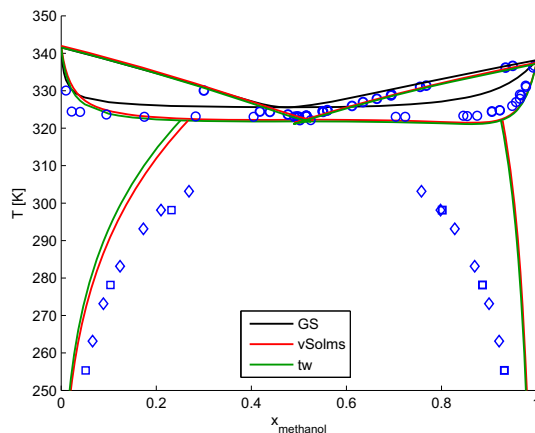

Figure 3.3: Methanol - *n*-hexane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with $k_{ij} = 0$: black lines are GS, red lines are vSolms and green lines are tw for methanol. Experimental data: Raal et al. [56] ($\circ$), Radice and Knickle [57] ($\square$) and DECHEMA (smoothed data) [58] ($\diamond$).
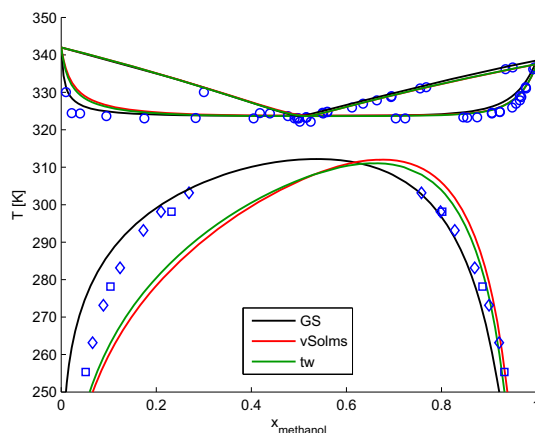

Figure 3.4: Methanol - *n*-hexane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with fitted k_{ij}: black lines are GS (with $k_{ij} = 0.0275$), red lines are vSolms (with $k_{ij} = -0.0137$) and green lines are tw (with $k_{ij} = -0.0135$) for methanol. Experimental data: Raal et al. [56] ($\circ$), Radice and Knickle [57] ($\square$) and DECHEMA (smoothed data) [58] ($\diamond$).

The results for methanol - n-hexane with an optimal interaction parameter are shown in Figure 3.4. The VLE results are very similar to the ones for methanol - cyclohexane. The GS set gives a significantly better correlation of the whole LLE curve than the vSolms and tw sets, which are both somewhat shifted towards higher methanol concentrations. A positive value of k_{ij} is again needed for GS, whereas a negative values are needed for vSolms and tw to increase the cross-attraction between methanol and hexane, and thereby decrease the immiscibility of the mixture.
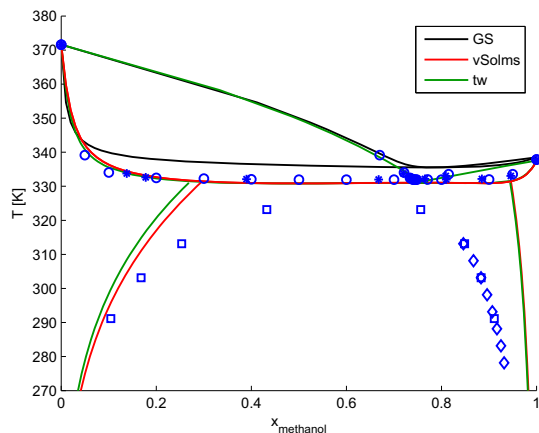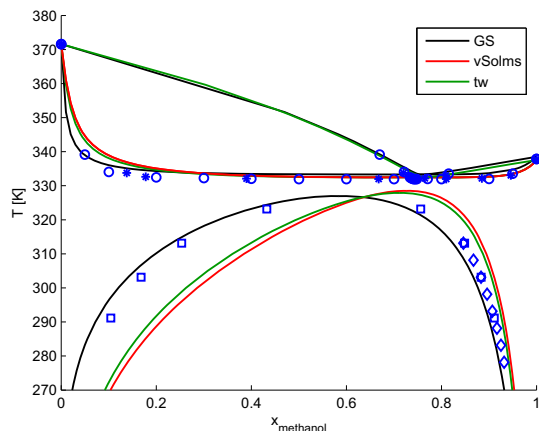

Figure 3.5: Methanol - n-heptane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with $k_{ij} = 0$: black lines are GS, red lines are vSolms and green lines are tw for methanol. Experimental data: Budantseva et al. [59] ($\circ$), Benedict et al. [60] ($*$), Tagliavini and Arich [61] ($\square$) and Kiser et al. [62] ($\diamond$).

Figure 3.6: Methanol - n-heptane VLE and LLE at $P = 1.013$ bar. Lines are sPC-SAFT with fitted k_{ij}: black lines are GS (with $k_{ij} = 0.026$), red lines are vSolms (with $k_{ij} = -0.0125$) and green lines are tw (with $k_{ij} = -0.0125$) for methanol. Experimental data: Budantseva et al. [59] ($\circ$), Benedict et al. [60] ($*$), Tagliavini and Arich [61] ($\square$) and Kiser et al. [62] ($\diamond$).

Figures 3.5 and 3.6 show the results for methanol - n-heptane. As for the other sys-

tems the predictive performance is best with vSolms and tw, whereas sPC-SAFT with the GS set for methanol clearly correlates the LLE of this mixture better than with the vSolms and tw sets. There is no big difference in the correlated results for VLE.

In general the phase equilibrium calculations show that the GS set gives significantly worse predictions than vSolms and tw, but correlates the LLE much more satisfactorily than the other sets. There is no big difference in the ability of the different sets to correlate VLE, with GS being marginally better than the other sets.

3.4   Monomer fraction

SAFT-type equations of state have an explicit treatment of hydrogen bonding in associating fluids, and the monomer fraction predicted by these models can therefore be determined directly. A monomer in this context is a molecule of an associating compound, which does not take part in any hydrogen bond, that is, all sites are unbonded. Von Solms et al. [63] argue that monomer fractions can be useful in the parameter estimation to obtain more physical parameters. It will not be included in the parameter estimation in this work, but a comparison between sPC-SAFT and experimental data will be used in the evaluation of the parameter sets.

An expression for the monomer fraction, X_0, was given in equation (2.18) in section 2.2 in terms of the fractions of sites not bonded:

$$X_{0_i} = \prod_{A_i} X_{A_i}$$

and the monomer fraction determined with sPC-SAFT therefore depends explicitly on the association scheme used for the associating compound. For the 2 (1:1) scheme, used in this work for methanol, the monomer fraction is given by $X_0 = X_A X_B = (X_A)^2$ (since $X_A = X_B$).

The amount of hydrogen bonding in a fluid can be measured using spectroscopy, but some interpretation of the data is necessary in order to obtain the monomer fraction. Luck [64] has presented spectroscopy data for the amount of hydrogen bonding in pure saturated liquid methanol at different temperatures. Von Solms

et al. [63] present a discussion of the data, where it was concluded that what Luck reports as fraction of free -OH groups is the fraction of nonbonded hydrogen atoms in the hydroxyl group. In the discussion in Luck [64] alcohols are assumed to be 3 sites molecules, which is the correct interpretation in terms of a "rigorous" atomic description of the molecules, and von Solms et al. [63] therefore use the 3 (2:1) scheme to convert the spectroscopic data to monomer fractions. Von Solms et al. [63] also compare the measured monomer fractions with calculated values from CPA and sPC-SAFT.

Figure 3.7 shows the results for methanol with sPC-SAFT with parameter sets GS, vSolms and tw, as well as the experimental results from Luck [64]. The figure shows that the vSolms and tw parameters match the experimental data significantly better than the GS parameters, though neither of the parameter sets can predict the steep increase in monomer fraction for temperatures above 400 K. The GS parameters underestimate the monomer fraction at all temperatures.
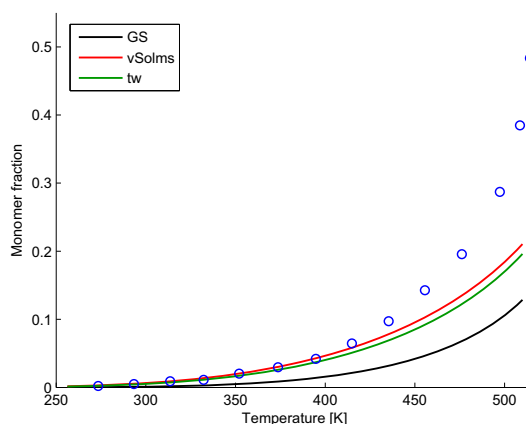
Figure 3.7: Monomer fraction for pure methanol. Lines are sPC-SAFT; black lines are GS, red lines are vSolms and green lines are tw for methanol. Experimental data: Luck [64] (∘).

Spectroscopy has also been used to measure the amount of hydrogen bonding in mixtures. Von Solms et al. [65] present experimental results as well as calculations with CPA and sPC-SAFT for a number of binary 1-alkanol + n-alkane systems. The only methanol mixture considered in the paper is methanol - n-hexane, and the results for this system with sPC-SAFT are shown in Figure 3.8. The experimental data and the sPC-SAFT calculations are not at the exact same temperature, but the small difference in temperature does not significantly influence the results.
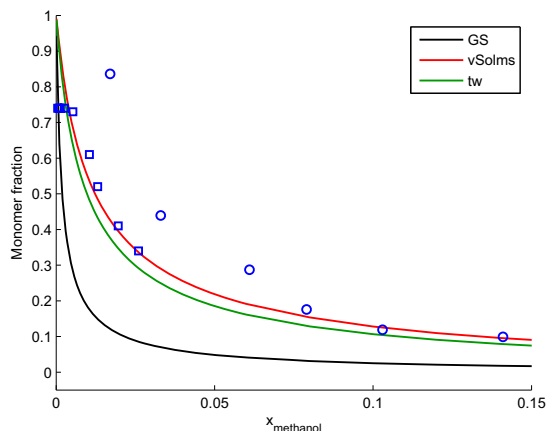
Figure 3.8: Monomer fraction for methanol - n-hexane. Lines are sPC-SAFT at $T = 298.15$ K; black lines are GS, red lines are vSolms and green lines are tw for methanol. Experimental data: von Solms et al. [65] at $T = 296.45$ K ($\circ$) and Martinez [66] at $T = 303.15$ K ($\square$).

The assessment of the agrement between experimental results and calculations depends on which experimental data is considered. The results with vSolms and tw agree well with the data from von Solms et al. [65] around $x_{\mathrm{methanol}} = 0.1 - 0.15$, and with most of the data from Martinez [66], except for the data points at very dilute methanol. The results with the GS parameters do not agree with any of the experimental data.

3.5   Discussion

Based on the phase equilibrium results presented here for three methanol mixtures it seems reasonable to assume that some mixture data has been included in the parameter estimation by Gross and Sadowski [48]. The GS set performs in general very satisfactorily for all three systems with a fitted interaction parameter, and markedly better than the vSolms and tw sets. The predictive performance is however poor, whereas the two other sets give reasonable results without an interaction parameter. The impression is enhanced by the monomer fraction results, which show that the GS parameters are incapable of predicting the amount of hydrogen bonding both in pure methanol and in methanol - n-hexane.

The perception that mixture data was included in the parameter estimation by Gross and Sadowski was also based on previous work on CPA (e.g. [38,45]), which has shown that an implicit inclusion of LLE data for one mixture in the parameter estimation gives parameters which can successfully be applied for other mixtures.

The results presented here show how important it is to know how parameters were estimated, particularly when comparing different theories, since the performance of the theories depends markedly on the parameters. Parameters should be estimated using the same data and the same criteria in order to give a fair comparison of theories. The same is the case when examining different association schemes for associating compounds.

The results for methanol - cyclohexane with sPC-SAFT with the GS parameters are very similar to the results presented by Gross and Sadowski with PC-SAFT with the same parameters. A smaller value of the interaction parameter is however needed with sPC-SAFT. It is therefore found that the conclusions for the GS parameter set for methanol presented in this work would be the same if original PC-SAFT had been used.

3.6   Chapter summary

Phase equilibrium results have in this chapter been presented with sPC-SAFT for three methanol mixtures. Three different parameter sets were investigated, and it was found that even though similar pure component results are obtained with the three sets, very different mixture results are obtained. The parameters from Gross and Sadowski [48] were found to correlate the experimental data significantly better than the parameters from von Solms et al. [20] and a new parameter set estimated in this work. The predictive performance of the parameters from Gross and Sadowski is however poor, while the other sets perform reasonably well without an interaction parameter. The parameters from von Solms et al. and those from this work gave very similar results.

Monomer fractions were calculated using sPC-SAFT, with each of the three parameter sets and compared to spectroscopy data, both for pure methanol and for methanol - n-hexane. The parameters from von Solms et al. and from this work were found to perform satisfactorily, while the parameters from Gross and Sadowski in both cases significantly underestimated the number of monomers.

Based on the phase equilibrium results it was argued that some mixture data might have been considered in the estimation of the parameters from Gross and Sadowski. It was also argued that it is important to know how parameters were obtained especially if used for comparisons between for example models or asso-

ciation schemes.

Finally we can conclude that the parameters which perform best for monomer fraction calculations may not necessarily be best for phase behavior.

Alkanolamines

4.1 Introduction

Although alkanolamines are widely used in many industrial sectors and are considered promising solvents for removal of acid gases from natural gas streams and from power plant flue gases, relatively little attention has been given to applying advanced thermodynamic models to systems with alkanolamines. Button and Gubbins [67] have applied SAFT to modeling mixtures of MEA (monoethanolamine) and DEA (diethanolamine) with water and CO_2 but very few results are presented, mostly for ternary mixtures. There has been no follow up on this work. An initial study on modeling mixtures of MEA, DEA and MDEA (methyl diethanolamine) with hydrocarbons, water and alcohols with CPA has recently been published [38,46], and the work on alkanolamines presented here is a continuation of that work.

Alkanolamines contain both hydroxyl and amine groups and therefore have properties of both alcohols and amines, and can react as both. They react as amines with acids to form salts or soap, and as alcohols they are hygroscopic and can be esterified. This combination of properties makes them widely used in the industry, and very common in acid gas stripping (H_2S and CO_2 removal). Because of the multifunctionality of alkanolamines, determining the right association scheme is not as straightforward as for the monofunctional compounds previously modeled with CPA and SAFT.

The structures of MEA and DEA were shown in Figure 2.2 with an indication of all sites on the hydroxyl and amine groups. Two different association schemes were used for MEA in the previous work [38, 46]; 2 (1:1) and 4 (2:2). When using the 2 sites scheme, the association of the amine group is neglected, with the argument that alcohols associate stronger than amines. The 4 sites scheme for MEA was described in section 2.2.3. It assigns 2 sites to the hydroxyl group and 2 sites to the amine group. It was found that 4 (2:2) gave significantly better results than 2 (1:1), and the 2 sites scheme will therefore not be investigated in this work. It will instead be tested whether differentiating the association parameters for the two associating groups improves the results with CPA. This correspond to the 4 (1:1,1:1) scheme, which was also explained in section 2.2.3.

DEA contains two hydroxyl groups and one secondary amine and it was decided in the previous work [38, 46] to neglect the amine group, and model DEA with 4 sites (the 4 (2:2) scheme), again with the argument that alcohols associate stronger than amines. It will in this work be investigated whether including 2 sites for the amine improves the results. DEA will thus be modeled with the 4 (2:2) and 6 (3:3) schemes. Based on the results for MEA, it was decided not to differentiate the association parameters for DEA.

This chapter will present a discussion of how the parameters were estimated as well as results with CPA with the different association schemes.

4.2   Parameter estimation

The pure component parameters for CPA are typically obtained by fitting pure component vapor pressure and liquid density. An often used procedure is to use DIPPR (or other) correlations for the pure component data in the parameter estimation. This was done in the estimation of the parameters presented by Avlund et al. [38]. The experimental liquid density data for both alkanolamines is however confined to a narrow temperature range, and by using the extrapolated DIPPR correlations we risk transferring errors from the correlations to the parameters. The temperature ranges of the experimental data, and the number of data points available for MEA and DEA are listed in Table 4.1. To avoid transferal of error it was decided in this work to use the actual experimental data in the parameter estimation.

Table 4.1: Temperature range of experimental data for MEA and DEA. NP is the number of data points available in DIPPR [51]

	data type	T [K]	T_r	(NP)
MEA	Vapor pressure	190.00 - 565.00	0.42-0.92	(75)
	Liquid density	293.15 - 413.15	0.43-0.61	(26)
DEA	Vapor pressure	293.15 - 432.13	0.45-0.88	(46)
	Liquid density	303.15 - 355.10	0.41-0.48	(22)

The five pure component parameters in CPA are however highly correlated, and different parameter sets give almost equal results for the pure component vapor pressure and liquid density. Additional data is therefore needed in order to determine the optimal sets. Using LLE data of the associating compound with an inert compound in the parameter estimation was investigated in the previous work for alkanolamines [38, 46]. The parameters determined using LLE data were found to give better results also for mixtures not included in the parameter estimation, compared to the parameters obtained solely from pure component data. Such data is available for MEA (with n-heptane) and DEA (with hexadecane), and the LLE data was used as guidance to determine the association energy, while the remaining parameters were fitted to vapor pressure and liquid density. LLE data was not included directly in the parameter estimation.

To avoid increasing the number of adjustable parameters when different association parameters are used for the hydroxyl group and the amine group for MEA, the association parameters for the hydroxyl group were taken from alkanols [36]. In this way the number of variable parameters is the same as for the 4 (2:2) scheme and the remaining five parameters were fitted to experimental data in the same way as for the other schemes.

Table 4.2: Pure component CPA parameters for MEA and DEA and absolute relative deviations (ARD%) between CPA and experimental data (deviations between CPA and DIPPR correlations for $T_r = 0.55 - 0.90$ are listed in brackets).

							ARD%	
compound	scheme	b (L/mol)	Γ (K)	c_1	ε/R (K)	$\beta \times 10^3$	P^{sat}	ρ^L
MEA [38]	4 (2:2)	0.05656	3001	0.7012	2186	5.35	4.1 (0.53)	3.2 (0.68)
MEA (tw)	4 (2:2)	0.05458	2675	0.8316	1970	13.0	2.2 (1.2)	0.53 (3.6)
MEA (tw)	4 (1:1,1:1)	0.05452	2803	0.7588	1545^a	10.6^a	2.9 (1.9)	0.52 (3.6)
					2526^b	8.00^b		
DEA [38]	4 (2:2)	0.09435	2670	1.574	1944	33.2	3.2 (1.5)	4.9 (1.6)
DEA (tw)	4 (2:2)	0.08964	3583	0.9338	2442	7.4	4.2 (5.1)	0.41 (6.4)
DEA (tw)	6 (3:3)	0.09010	3472	0.911	2010	6.8	5.5 (6.5)	0.44 (7.2)

^{a} amine group, ^{b} hydroxyl group

The pure component parameters for MEA and DEA are listed in Table 4.2, together with the absolute relative deviation (ARD%) between CPA and the experimental data. CPA parameters for other compounds considered in this chapter are listed in Appendix A. Table 4.2 also lists the MEA and DEA parameters from Avlund et al. [38] for comparison and the deviations between CPA and DIPPR for $T_r = 0.55 - 0.90$ (the temperature interval used in the parameter estimation by Avlund et al. [38]) are shown in brackets. The use of actual experimental data in the parameter estimation instead of DIPPR correlations influences the liquid density results more than the vapor pressure, as seen in Table 4.2. This is perhaps not so surprising since liquid density is where the amount of data is most scarce, and most of the data is outside the temperature interval used in the parameter estimation by Avlund et al. [38].

4.3   Application of CPA to mixtures of alkanolamines

Alkanolamines are as mentioned of great interest in different industries, in particular the mixtures with water are of great importance in the removal of CO_2 and H_2S from natural gas streams and flue gases. This section will present a further investigation of the capability of CPA to model the phase equilibrium of two alkanolamines; MEA and DEA, with the parameters described in the previous section. Results will be presented for self-associating and solvating LLE systems and cross-associating VLE systems, including the mixtures with water.

4.3.1   Liquid - liquid equilibrium

LLE is more sensitive to the pure component parameters than VLE, which is why LLE data was used in the parameter estimation, and we will begin the investigation of the different association schemes by looking at the LLE results. The deviations in calculated solubility compared to the experimental values and k_{ij} values for the LLE systems considered are summarised in Table 4.3.

The only available LLE data for MEA with an alkane is for MEA - n-heptane, which was the data used in the parameter estimation. The results with CPA, with each of the two association schemes are shown in Figure 4.1.

Table 4.3: LLE results with CPA for MEA and DEA.

					ARD%		
component 1	component 2	scheme	k_{ij}	β_{ij}	x_{12}	x_{21}	average
MEA	n-heptane	4 (2:2)	0.0145		8.8	18.4	13.6
		4 (1:1,1:1)	0.0175		9.6	18.7	14.2
MEA	benzene	4 (2:2)	0.0062	0.021	8.4	1.27	4.8
			0.0145*	0.027	8.9	11.4	10.1
		4 (1:1,1:1)	0.0063	0.011	11.7	1.24	6.5
			0.0175*	0.018	11.7	14.1	12.9
DEA	hexadecane	4 (2:2)	-0.0875		10.8	14.5	12.7
		6 (3:3)	-0.118		11.2	14.8	13.0

*) Homomorph approach using the k_{ij} for MEA - n-heptane

It is clear from Figure 4.1 that the performance of CPA with the two schemes is very similar for this system. Both schemes give satisfactory results, but the temperature dependency of the experimental data is not completely captured. There is not a big difference in the k_{ij} values for the two schemes.
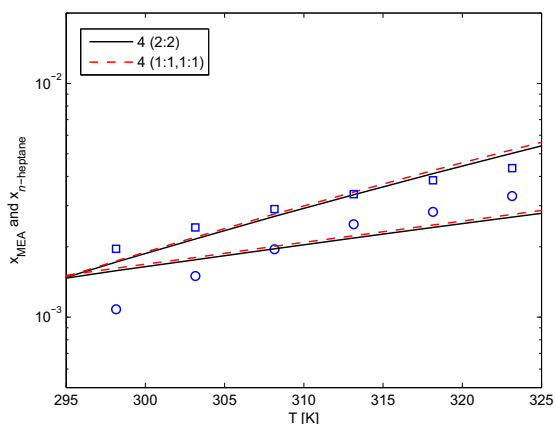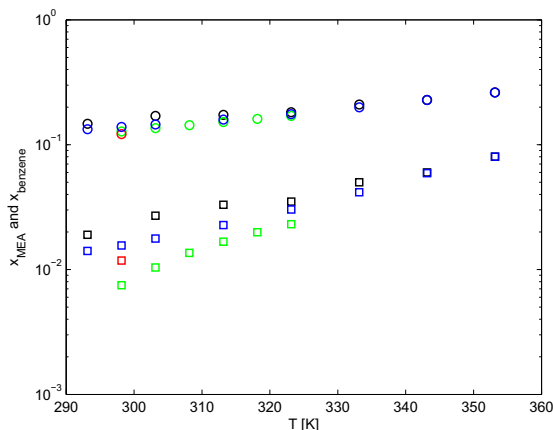

Figure 4.1: LLE calculations of MEA - n-heptane. The full (black) lines are CPA with 4 (2:2) for MEA and $k_{ij} = 0.0145$. The dashed (red) lines are CPA with 4 (1:1,1:1) for MEA and $k_{ij} = 0.0175$. MEA solubility in n-heptane ($\square$) and n-heptane solubility in MEA ($\circ$). Experimental data: Gustin and Renon [68].
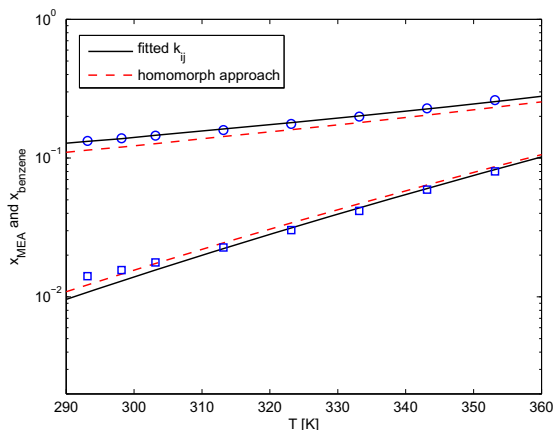
Experimental data for MEA-benzene is available from three papers; Gustin and Renon, 1973 [68], Zaretskji et al., 1970 [69] and Fabries et al., 1977 [70]. There is some discrepancy between the data from the different papers, but DECHEMA [58] has presented smoothed data. All experimental and smoothed data are shown in Figure 4.2.

Because of the discrepancy in the experimental data we will use the smoothed data from DECHEMA in the evaluation of CPA. As mentioned in section 2.3.4

it is necessary to fit the cross-association volume, β^{cross} for solvating systems like MEA - benzene. The interaction parameter, k_{ij} can either be fitted as well or obtained using the homomorph approach. Since no LLE data is available for MEA - cyclohexane or MEA - n-hexane, the best homomorph for benzene in this case is n-heptane.
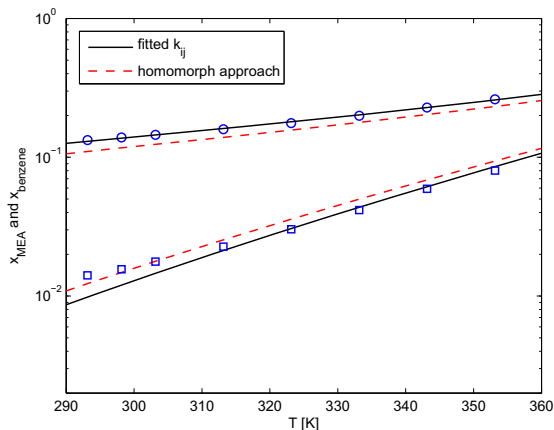

Figure 4.2: Experimental LLE data for MEA - benzene. MEA solubility in benzene ($\square$) and benzene solubility in MEA ($\circ$). Green points are ref. [68], black points are ref. [69], red points are ref. [70] and blue points are the smoothed data from ref. [58].

Figure 4.3: LLE calculations of MEA - benzene. Lines are CPA with 4 (2:2) for MEA. Full (black) lines are with $k_{ij} = 0.0062$ and $\beta^{\text{cross}} = 0.021$. Dashed (red) lines are using the homomorph approach, i.e. with $k_{ij} = 0.0145$ (from MEA - n-heptane) and $\beta^{\text{cross}} = 0.027$. Experimental data: DECHEMA [58] (smoothed data).

Figures 4.3 and 4.4 show the results with each of the two association schemes for MEA respectively both with fitted k_{ij} and with the k_{ij} values obtained from MEA - n-heptane. Only one β^{cross} value is estimated for the 4 (1:1,1:1) scheme, so the same association volume is used for the hydroxyl and amine groups in this case,

but different association energy parameters are still used. β^{cross} (and k_{ij}) is fitted to minimize the average absolute relative deviation in solubility.

Figure 4.4: LLE calculations of MEA - benzene. Lines are CPA with 4 (1:1,1:1) for MEA. Full (black) lines are with $k_{ij} = 0.0063$ and $\beta^{\text{cross}} = 0.011$. Dashed (red) lines are using the homomorph approach, i.e. with $k_{ij} = 0.0175$ (from MEA - n-heptane) and $\beta^{\text{cross}} = 0.018$. Experimental data: DECHEMA [58] (smoothed data).

It is seen from Figures 4.3 and 4.4 that similar results are again obtained with the two association schemes, though slightly lower deviations are obtained with the 4 (2:2) scheme. The results are, for both schemes, slightly worse with the homomorph approach than with the fitted k_{ij}, but the results are in all cases satisfactory, and within the experimental uncertainty illustrated in Figure 4.2.
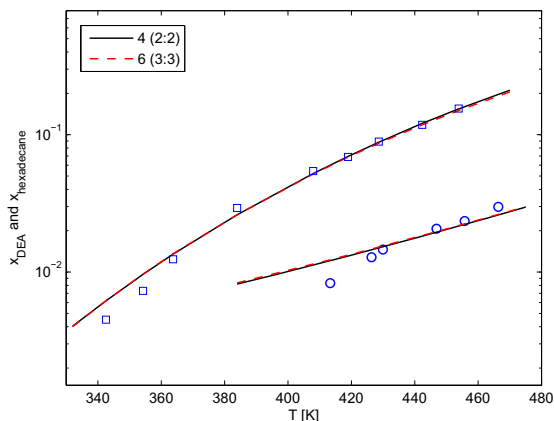
Figure 4.5: LLE calculations of DEA - hexadecane. Full (black) lines are CPA with 4 (2:2) for DEA and $k_{ij} = -0.0875$. Dashed (red) lines are CPA with 6 (3:3) for DEA and $k_{ij} = -0.118$. Experimental data: Abdi and Meisen [71]. MEA solubility in hexadecane ($\square$) and hexadecane solubility in DEA ($\circ$).

For DEA the only available binary LLE data is with hexadecane, which was used

in the parameter estimation. Figure 4.5 shows the results for this mixture with CPA with 4 and 6 sites for DEA. There is essentially no difference between the results with 4 and 6 sites, though a larger negative interaction parameter is needed for the 6 sites scheme. Both schemes match the data satisfactorily, with larger deviations though at lower temperatures.

CPA in general performs satisfactorily for these systems. The accuracy of the experimental data was illustrated with a comparison of data for MEA - benzene from three different papers, and though contradicting data has not been found for the other systems it does not mean that the accuracy for those systems is better. The LLE data is thus very well correlated with CPA, with the accuracy of the experimental data in mind.

4.3.2 Vapor - liquid equilibrium

To further test the performance of the different association schemes for MEA and DEA, CPA was also applied to VLE of binary cross-associating mixtures containing MEA or DEA. (Only bubble point pressures have been located for these systems. No dew point pressures.) It was found in the previous study of modeling alkanolamines with CPA [38, 46] that CR-1 performs as good or better than ECR for the systems considered here, and only that combining rule will therefore be applied for alkanolamines in this work. The VLE results are summarised in Table 4.4.
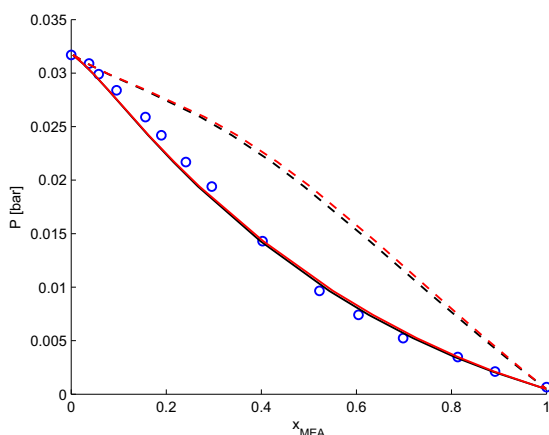
Figure 4.6: VLE calculations of MEA - water at $T = 298.15$ K. Black lines are CPA with 4 (2:2) for MEA; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.165$. Red lines are CPA with 4 (1:1,1:1) for MEA; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.165$. Experimental data: Nath and Bender [72].
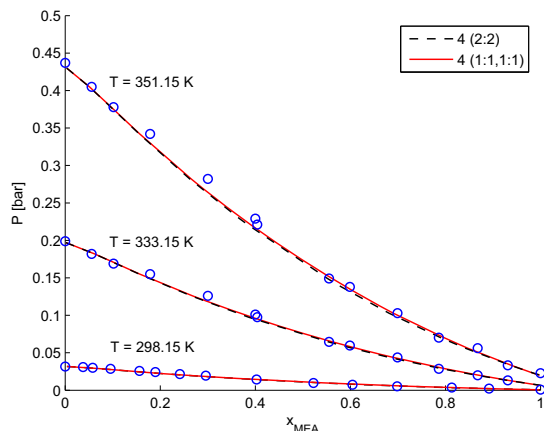
Figure 4.7: VLE calculations of MEA - water. Full (black) lines are CPA with 4 (2:2) for MEA and $k_{ij} = -0.165$. Dashed (red) lines are CPA with 4 (1:1,1:1) for MEA and $k_{ij} = -0.165$. Experimental data: $T = 298.15$ K: Touhara eta al. [73], $T = 333.15$ K and $T = 351.15$ K: Nath and Bender [72].

Table 4.4: VLE results for MEA and DEA. Deviations are given as absolute average deviation (AAD) in the liquid composition.

comp 1	comp 2	scheme	T [K]	k_{ij}	AAD x_1 $\times100$
MEA	water	4 (2:2)	298.15	0	11.4
				-0.165	1.66
			333.15	-0.165	1.35
			351.15	-0.165	1.65
		4 (1:1,1:1)	298.15	0	12.0
				-0.165	1.69
			333.15	-0.165	1.19
			351.15	-0.165	1.43
MEA	ethanol	4 (2:2)	338.15	0	3.3
				-0.031	0.57
			358.15	0	3.7
				-0.031	0.42
		4 (1:1,1:1)	338.15	0	3.1
				-0.029	0.56
			358.15	0	3.5
				-0.029	0.42
DEA	water	4 (2:2)	365.15	0	6.8
				-0.118	0.83
		6 (3:3)		0	2.0
				-0.048	0.85

Figure 4.6 shows the results for MEA - water at $T = 298.15$ K, both with $k_{ij} = 0$ and with fitted k_{ij}. The figure shows that CPA satisfactorily correlates this system

with both association schemes for MEA, and that the two schemes give very similar results, with similar values of the interaction parameter. For both schemes a large negative interaction parameter is necessary in order to model the negative deviation from Raoult's law. Figure 4.7 shows the results for MEA - water at three different temperatures. As seen in this figure, the interaction parameter estimated at $T = 298.15$ K can successfully be applied at other temperatures.

Figure 4.8 shows the CPA results for MEA - ethanol. Very similar results are obtained with the two schemes. Very good predictive results are obtained for this system with CPA in both cases, and only a small negative k_{ij} is needed to correlate the data points.
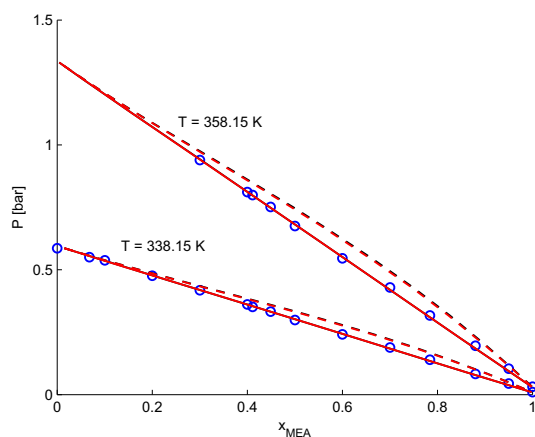
Figure 4.8: VLE calculations of MEA - ethanol. Black lines are CPA with 4 (2:2) for MEA ; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.031$. Red lines are CPA with 4 (1:1,1:1) for MEA; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.029$. Experimental data: Nath and Bender [72].

Finally Figure 4.9 shows the results for DEA - water. The 4 and 6 sites schemes for DEA both give very satisfactory results for DEA - water, and the results with a fitted k_{ij} are very similar. The predictive results with the 6 (3:3) scheme are however better than with the 4 (2:2) scheme, and a smaller k_{ij} is therefore needed to correct the results.

In general CPA very satisfactorily correlates the VLE of cross-associating mixtures with alkanolamines, though large negative interaction parameters are needed for the mixtures with water.
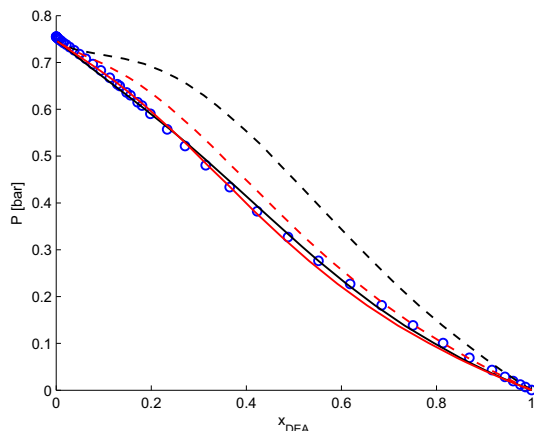
Figure 4.9: VLE calculations of DEA - water at $T = 365.15$ K. Black lines are CPA with 4 (2:2) for DEA ; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.118$. Red lines are CPA with 6 (3:3) for DEA; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.048$. Experimental data: Touhara et al. [73]

4.4   Chapter summary

CPA was in this chapter applied to model binary mixtures of alkanolamines with alkanes, benzene, ethanol and water. Two different association schemes were used for each alkanolamine. Previous work has shown that MEA should be modeled with 4 sites, and it was in this work investigated whether differentiating between the hydroxyl and amine association parameters improved the results compared to using the same association parameters for all sites. DEA has previously been modeled with 4 sites, but it was here examined whether using 6 sites gives better results. For the solvating system MEA - benzene the homomorph approach was compared to fitting both the cross-association volume and the interaction parameter.

For MEA it was found that the simple association scheme 4 (2:2) (with the same association parameters for all sites) perform as good or better than the more extensive association scheme 4 (1:1,1:1) (with differentiated association parameters). The homomorph approach was found to give good results for MEA - benzene, within the experimental uncertainty. The 4 sites and 6 sites schemes give similar results for DEA with a fitted interaction parameter, but rather different values are needed for the interaction parameter for the two schemes.

It was found that a temperature independent interaction parameter in general gives satisfactory results both for LLE and VLE. The predictive performance is

however poor and a non-zero interaction parameter is needed in all cases. A large negative value of the interaction parameter is needed for the alkanolamine - water VLE systems, in agreement with results in the literature for similar aqueous systems with SAFT models.

Based on the results presented here it is concluded that the simple 4 (2:2) scheme is adequate for both MEA and DEA.

CHAPTER 5

Intramolecular Association

5.1 Introduction

As mentioned in Chapter 1, one of the main limitations of the association theory in SAFT is that intramolecular association is not accounted for.

While intermolecular association is interactions between different molecules, that are bonded to form dimers or larger chain- or tree-like clusters, intramolecular association is interactions between sites on the same molecule, which lead to the formation of ring structures (with or without side-chains, depending on the positions of the sites on the molecule). The difference between inter- and intramolecular association is illustrated in Figure 5.1.
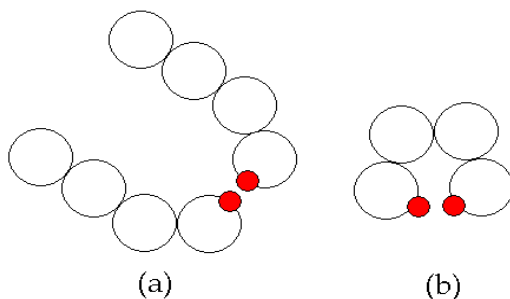
Figure 5.1: (a) Intermolecular and (b) intramolecular association of model chain molecules. The illustration is freely adopted from [74].

When Wertheim originally presented his theory for "Fluids with highly directional attractive forces" [4–7], he only included the interactions which lead to the formation of chain- or tree-like structures, and the association term from SAFT, which was developed based on that theory, therefore only accounts for intermolecular association. There are, however, cases where it is important to take ring formation into account.

Experimental data suggest that the intramolecular association in some systems is an important contribution to the overall hydrogen bonding in the system, and for some systems the phase behavior can only be explained with the competition between inter- and intramolecular association.

In mid 1990's two groups extended the SAFT association term to include intramolecular association, but neither have done it in a general form [10, 12], and the theory presented is limited to spheres or chains with 2 sites. On the other hand a theory for intramolecular association has been presented for lattice fluid theories [75], and the theory has in a number of papers been applied for glycol ethers (e.g. [76–78]).

This chapter will present experimental results for systems with significant amounts of intramolecular association and a brief presentation of the work done with lattice theory on the subject. The previous work on modeling intramolecular association with SAFT will also be discussed and a general theory (in the SAFT framework) is derived.

5.2   Experimental results

Experimental data showing the presence of intramolecular hydrogen bonds and the influence of these bonds on the phase behavior is shown for two examples; dilute solutions of glycol ethers in non-associating solvents and telechelic polymers in polar and non-polar solvents.

5.2.1   Glycol ethers

Glycol ethers contain one hydroxyl group and one or more ether oxygens, and are some of the simplest compounds that form intramolecular bonds. Intramolecular

bonds are formed between the hydroxyl hydrogen and an ether oxygen.

Fourier transform infrared (FTIR) spectroscopy can be used to measure the amount of hydrogen bonding in a solution. The free -OH groups and the hydrogen bonded groups have different stretching frequencies, and the peak areas of the different frequencies can therefore be used to determine the concentrations of free, intermolecularly bonded and intramolecular bonded molecules. The free and the intramolecularly bonded groups have distinct peaks, whereas the intermolecularly bonded groups lie in a range of frequencies, as seen from Figure 5.2.
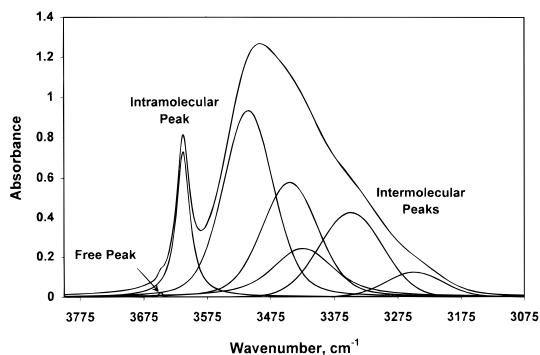

Figure 5.2: Curve-fit of FTIR spectra of 2-methoxyethanol - n-hexane at $T = 35^oC$. The small peak at 3648 cm^{-1} corresponds to the free -OH stretch. The sharp peak at 3612 cm^{-1} is due to intramolecular bonding, and the remaining peaks are due to intermolecular bonding. [79]

Spectroscopy data for glycol ethers in n-hexane is available in two papers; Missopolinou et al. [76] present spectroscopy data for 2-methoxyethanol and 2-ethoxy-ethanol, while Brinkley and Gupta [79] present results for 2-methoxyethanol and 2-butoxyethanol. The results for 2-methoxyethanol from both groups are shown in Figure 5.3.

Figure 5.3 shows that as the concentration of the glycol ether decreases the amount of intermolecular bonds also decreases, because the distance between the glycol ether molecules increases, and the probability of being within bonding range of another glycol ether molecule therefore decreases. The intramolecular association does not explicitly depend on concentration (or density), but when the competition from intermolecular association decreases the amount of intramolecular association increases. It is clear from Figure 5.3 that there is a large amount of intramolecular bonds in the dilute solution of 2-methoxyethanol in the non-associating solvent.

The data from the two papers [76, 79] do not agree very well with each other.

One reason is that in order to interpret the spectra both groups assume no inter-molecular bonds up to a certain concentration of the glycol ether, but they have not chosen the same limiting concentration; Missopolinou et al. use a limit of $c = 0.008$ mol/L $\Leftrightarrow x = 0.001$ and Brinkley and Gupta use a limit of $x = 0.006$ (at $T = 308.15$ K). So for example at $x = 0.006$ where Brinkley and Gupta assumes no intermolecular bonds at $T = 308.15$ K, Missopolinou et al. finds 15% intermolecularly bonded -OH groups at $T = 303.15$ K and 7% at $T = 313.15$ K. We also see from Figure 5.3 that the density and temperature dependency of the data from the two papers do not agree very well.
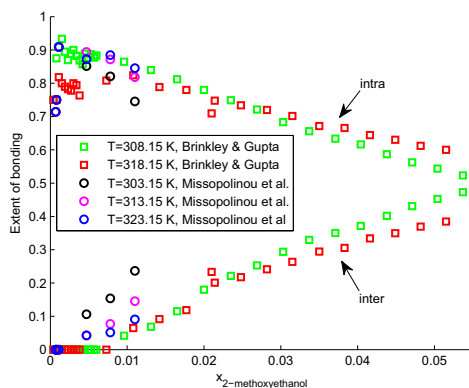
Figure 5.3: Amount of hydrogen bonding from FT-IR spectroscopy for 2-methoxyethanol - n-hexane. Data from [76] and [79].

5.2.2   Telechelic polymers

Telechelic polymers are polymers with functional (associating) end-groups, and can for example be used for the synthesis of block co-polymers, and they can form intramolecular hydrogen bonds through interactions between the end-groups.

Gregg et al. have published four papers [80–83] on the phase behavior of telechelic polyisobutylene (PIB) in subcritical and supercritical solvents. Experimental cloud-point curves are presented for blank (nonfunctional), monohydroxy and di-hydroxy PIB in both non-polar and polar solvents. They also modeled the systems with SAFT (the version of Huang and Radosz [26]).

The three most typical types of cloud-point curves are; upper critical solution temperature (UCST), lower critical solution temperature (LCST) and upper-lower critical solution temperature (U-LCST). The three types of curves are sketched in

Figure 5.4. The curve represents the miscibility limit; the solution is stable above it, but splits into two phases below it. If the dissimilarities of the system increases the UCST curve shifts to higher temperatures, and the LCST curve shifts to lower temperatures, this might cause them to merge in to a U-LCST curve. These shifts increase the two-phase region.
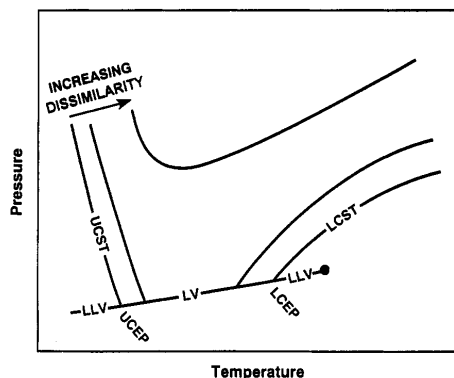

Figure 5.4: Qualitative cloud-point curves for binary polymer solutions at various degrees of polymer-solvent dissimilarities. [81]

In the first paper [80] Gregg et al. measured the cloud-point pressure of CH_3-PIB-CH_3, CH_3-PIB-OH and OH-PIB-OH (all with a molecular weight around 1000 g/mol) in 5 different solvents; ethane (non-polar), propane (non-polar), chlorodifluoromethane (polar), dimethyl ether (polar) and carbon dioxide (polar). They found that in non-polar solvents going from CH_3-PIB-CH_3 to CH_3-PIB-OH and from CH_3-PIB-OH to OH-PIB-OH the cloud-point pressure increased. This can be explained by intermolecular association, which results in agglomerate formation. CH_3-PIB-OH forms dimers, while OH-PIB-OH can form even larger agglomerates. The agglomerate formation increases the size asymmetry, and therefore decreases the solubility. Figure 5.5 shows the cloud-point pressure of CH_3-PIB-CH_3, CH_3-PIB-OH and OH-PIB-OH in propane.

In the polar solvents the cloud-point pressure of CH_3-PIB-OH is again increased compared to that of CH_3-PIB-CH_3 but the experimental points for OH-PIB-OH are almost coinciding with those for CH_3-PIB-CH_3 (see the SAFT curve for OH-PIB-OH in Figure 5.6). This cannot be explained with intermolecular association, which as for the non-polar solvent would result in large insoluble agglomerates.

The lower cloud-point pressure of OH-PIB-OH can instead be explained with intramolecular association. As explained earlier in this chapter intramolecular association occurs between different associating groups on the same molecule,

and only OH-PIB-OH is therefore capable of intramolecular association (and not CH$_3$-PIB-OH).
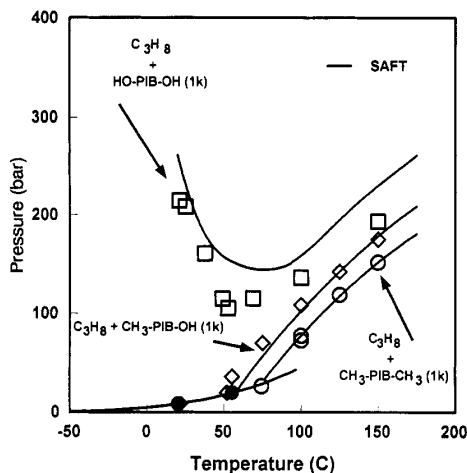
Figure 5.5: Binary pressure-temperature diagram for C$_3$H$_8$ + CH$_3$-PIB-CH$_3$ (1000 g/mol), CH$_3$-PIB-OH (1000 g/mol) and HO-PIB-OH (1000 g/mol). Points are experimental data and curves are calculated by SAFT. [80]

In a non-polar solvent the polymer backbone likes the solvent and the molecule will stretch out, and thus increase the distance between the two terminal segments on the molecule. Intramolecular association is therefore not very pronounced for this type of molecules in non-polar solvents, and does not significantly influence the phase behavior of the polymer.
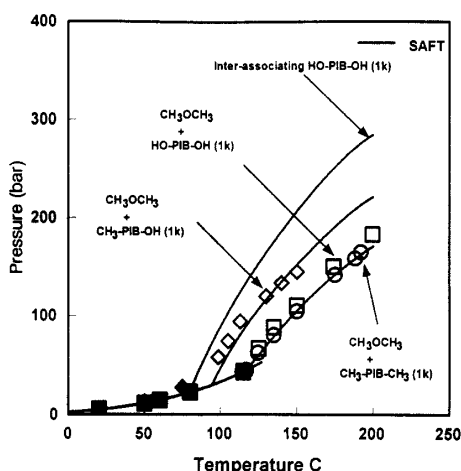
Figure 5.6: Binary pressure-temperature diagram for CH$_3$OCH$_3$ + CH$_3$-PIB-CH$_3$ (1000 g/mol), CH$_3$-PIB-OH (1000 g/mol) and HO-PIB-OH (1000 g/mol). Points are experimental data and curves are calculated by SAFT assuming only intermolecular association. [80]

When the polymers are placed in a polar solvent the polymer backbone will curl up to diminish the interactions with the solvent. In this way the likelihood of the two end hydroxyl groups to be within bonding range is greatly increased resulting in a large degree of ring formation. Figure 5.6 shows the cloud-point pressures of the three polymers in dimethyl ether.

Studies of the phase behavior of n-alkanes and the corresponding cycloalkanes have according to Gregg et al. [80] showed that the chain and the ring structure have similar miscibility in polar solvents, but unlike miscibility in non-polar solvents. This confirms that the behavior seen for OH-PIB-OH is the result of ring formation, and thus of intramolecular association.

5.3   Lattice theory

Missopolinou and Panayiotou presented in 1999 [75] a formalism for modeling systems with both inter- and intramolecular association in the frame of the lattice-fluid/hydrogen-bonding (LFHB) model [84]. The same formalism has later been presented in connection with the Non-Random Hydrogen-Bonding (NRHB) model by the same research group [85]. The theory is (in both cases) presented for polyethoxyalcohol (PEA) with x ether oxygen sites.

Even though it is stated in the paper from 1999 [75] that the theory easily can be extended to more complex systems, the theory has not been published for other types of systems, and it has only been applied to glycolether systems [76, 85, 86].

The theory is briefly described here.

The hydroxyl group in PEA is described with 2 sites, and each ether oxygen with 1 site. N_1 is the number of PEA molecules and N_2 is the number of solvent molecules ($N = N_1 + N_2$). The number of proton donors of type 1 (-OH) and proton acceptors of type 1 is N_1 and of proton acceptors of type 2 (-O-) is xN_1.

N_{11} is the number of $-OH-OH$ hydrogen bonds, N_{12} is the number of intermolecular $-OH-O-$ bonds and B is the number of intramolecular bonds. $N_H = N_{11} + N_{12}$ is the total number of intermolecular bonds. The number of free proton donors are then

$$N_{10} = N_1 - N_H - B = N_1 - N_{11} - N_{12} - B \qquad (5.1)$$

The Gibbs free energy for this system is

$$
\begin{aligned}
\frac{G_{\mathrm{H}}}{kT} = \frac{N_1 \mu_{\mathrm{H},1}}{kT} &= N_{\mathrm{H}} + N_1 \ln \left(1 - \frac{N_{\mathrm{H}} + B}{N_1} \right) + N_1 \ln \left(1 - \frac{N_{11}}{N_1} \right) \\
&+ x N_1 \ln \left(1 - \frac{N_{12}}{x N_1 - B} \right)
\end{aligned}
\tag{5.2}
$$

where $\mu_{\mathrm{H},1}$ is the hydrogen bonding contribution to the chemical potential of component 1.

This description of PEA (2 sites for the hydroxyl group and 1 for the ether oxygen) is the same as what will be used with sPC-SAFT in this work (Chapter 6) for three different glycolethers.

Other groups have presented similar lattice theories, but no groups have applied it to other compounds than glycolethers. [77, 78, 87]

A comparison between the LFHB formalism and the SAFT formalism derived in this work is given in section 5.6.

5.4 Intramolecular association with SAFT

Two groups have independently derived theories for intramolecular association within the SAFT framework, for the simple case of a chain with one associating site on each terminal segment. The two theories will be presented and compared in this section.

5.4.1 Ghonasgi, Perez and Chapman

Ghonasgi, Perez and Chapman at Rice University [11, 12] used an infinite dilution result for intramolecular association in combination with mass balances for the competition between inter- and intramolecular association. The nomenclature from the papers has been adopted here.

The derivation starts by considering chains, with one associating site on each terminal segment, that can only bond intramolecularly [11]. This fluid has the same number of "molecules" as the non-associating reference fluid and following the

arguments in section 2.4.2 the change in Helmholtz free energy due to association in this system is then given by

$$\frac{A^{\text{assoc}}}{NkT} = \frac{A - A^R}{NkT} = \ln\left(\frac{\rho_0}{\rho}\right) = \ln X_0 \tag{5.3}$$

where N is the total number of molecules, $\rho = N/V$ is the number density, ρ_0 is the monomer number density (density of unbonded molecules) and X_0 is the monomer fraction.

From classical thermodynamics we know that the internal energy is given by

$$U = \frac{\partial A/T}{\partial 1/T} = Nk\frac{\partial \ln(X_0)}{\partial 1/T} \tag{5.4}$$

The only contribution to the configurational energy is due to the square well potential between two sites, which is equal to $N'_{\text{bond}}\varepsilon_{\text{intra}}$, where N'_{bond} is the number of molecules in the bonding orientation given by:

$$N'_{\text{bond}} = N(1 - X_0) + NDX_0 \tag{5.5}$$

$\varepsilon_{\text{intra}}$ is the depth of the square well potential and D is the fraction of molecules in the reference system in the bonding orientation given by

$$D = \frac{1}{(4/3)\pi(m-1)^3\sigma^3} \int_{\text{Bond Volume}} g_{R,\text{intra}}(1m)d(1m) \tag{5.6}$$

where $g_{R,\text{intra}}$ is the intramolecular distribution function in the reference fluid.

If we equate $N'_{\text{bond}}\varepsilon_{\text{intra}}$ with (5.4) and separate the variables we obtain the following equation:

$$\int \frac{dX_0}{X_0(1 - X_0 + DX_0)} = \int \frac{\varepsilon_{\text{intra}}}{k}d(1/T) \tag{5.7}$$

The left and right hand sides of (5.7) are solved separately:

$$\text{LHS} = \int \frac{dX_0}{X_0(1 - X_0 + DX_0)} = \ln\frac{X_0}{1 - X_0 + DX_0} + C_1 \tag{5.8}$$

$$\text{RHS} = \int \frac{\varepsilon_{\text{intra}}}{k}d(1/T) = \frac{\varepsilon_{\text{intra}}}{kT} + C_2 \tag{5.9}$$

$$\Rightarrow \ln\frac{X_0}{1 - X_0 + DX_0} = \frac{\varepsilon_{\text{intra}}}{kT} + \ln C \tag{5.10}$$

$$\Leftrightarrow \frac{X_0}{1 - X_0 + DX_0} = C \exp\left(\frac{\varepsilon_{\text{intra}}}{kT}\right) \tag{5.11}$$

(where $\ln C = C_2 - C_1$)

When $\varepsilon_{\text{intra}}/kT = 0$ there is no association and $X_0 = 1$

$$\Rightarrow \frac{1}{D} = C$$

Equation (5.11) is rewritten to obtain an expression for X_0:

$$X_0 \left[1 - (D - 1)\frac{1}{D}\exp\left(\frac{\varepsilon_{\text{intra}}}{kT}\right)\right] = \frac{1}{D}\exp\left(\frac{\varepsilon_{\text{intra}}}{kT}\right)$$

$$\Rightarrow X_0 = \frac{1}{D\exp(-\varepsilon_{\text{intra}}/kT) - D + 1} = \frac{1}{1 + DF} \tag{5.12}$$

where $F = \exp(-\varepsilon_{\text{intra}}/kT) - 1$.

The theory was then extended to chains that can bond either inter- or intramolecularly [12]. The density contains two sites, A and B, and only $A - B$ interactions are allowed. For that system the Helmholtz free energy is given by:

$$\frac{A^{\text{assoc}}}{NkT} = \frac{A - A^R}{NkT} = \ln\left(\frac{\rho_0}{\rho}\right) + \frac{N_{\text{bonds}}^{\text{inter}}}{N} = \ln X_0 + 1 - X_A^{\text{inter}} \tag{5.13}$$

where $N_{\text{bonds}}^{\text{inter}}$ is the number of intermolecular bonds and X_A^{inter} is the fraction of molecules not bonded intermolecularly at site A, which in terms of densities is given by:

$$\rho X_A^{\text{inter}} = \rho_0 + \rho_B + \rho_{AB}^{\text{intra}} \tag{5.14}$$

where ρ_0 is the density of monomers, ρ_B the density of molecules bonded (only) at site B, and ρ_{AB}^{inter} is the density of molecules bonded intermolecularly on both sites A and B.

Similarly we can define X_A, the fraction of molecules not bonded at site A, and X_A^{intra}, the fraction of molecules not bonded intramolecularly at site A:

$$\rho X_A = \rho_0 + \rho_B \tag{5.15}$$

$$\rho X_A^{\text{intra}} = \rho_0 + \rho_A + \rho_B + \rho_{AB}^{\text{inter}} \left(= \rho X_B^{\text{intra}}\right) \tag{5.16}$$

The three quantities are related as

$$X_A^{\text{inter}} + X_A^{\text{intra}} - X_A = 1 \tag{5.17}$$

Equation (5.17) is inserted in (5.13):

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 + X_A^{\text{intra}} - X_A \tag{5.18}$$

The fraction of molecules not bonded intermolecularly at site A, given that site A is not bonded intramolecularly, $X_A^{\text{inter'}}$, is equivalent to X_A when there is no intermolecular association, and from equation (2.16) in section 2.2 we therefore have the following:

$$X_A^{\text{inter'}} = \frac{X_A}{X_A^{\text{intra}}} = \frac{1}{1 + \rho X_B^{\text{intra}} X_B^{\text{inter'}} \Delta^{\text{inter}}} = \frac{1}{1 + \rho X_B \Delta^{\text{inter}}} \tag{5.19}$$

$\Delta^{\text{inter}} = \Delta_{AB}^{\text{inter}}$ is the intermolecular association strength, for which the following approximate expression has been derived:

$$\Delta_{AB}^{\text{inter}} = 4\pi g_{\text{HS}}(\sigma) K_{AB} F_{AB}^{\text{inter}} \tag{5.20}$$

where $g_{\text{HS}}(\sigma)$ is the distribution function of hard spheres at contact, K_{AB} is the bonding volume between sites A and B and $F_{AB}^{\text{inter}} = \exp(\varepsilon_{AB}^{\text{inter}}/kT) - 1$ again is the Mayer f-function for the interaction between sites A and B.

When chains that can form both inter- and intramolecular bonds are considered equation (5.12) gives the fraction of molecules not bonded intramolecularly, given that the molecule is not bonded intermolecularly:

$$\Rightarrow X_0^{\text{intra'}} = \frac{X_0}{X_0^{\text{inter}}} = \frac{1}{1 + \Delta^{\text{intra}}} \tag{5.21}$$

where $\Delta^{\text{intra}} = DF$ is the intramolecular association strength between site A and B.

Similar to (5.17) we have for X_0

$$X_0^{\text{inter}} + X_0^{\text{intra}} - X_0 = 1 \tag{5.22}$$

Equation (5.21) is inserted in (5.22):

$$X_0^{\text{intra}} = 1 + X_0 - X_0(1 + \Delta^{\text{intra}}) = 1 - X_0\Delta^{\text{intra}} \tag{5.23}$$

For this system, we have

$$X_A^{\text{intra}} = X_B^{\text{intra}} = X_0^{\text{intra}} \tag{5.24}$$

From (5.19) and (5.23) we can therefore obtain:

$$X_A[1 + \rho X_B\Delta^{\text{inter}}] = 1 - X_0\Delta^{\text{intra}} \tag{5.25}$$

From the theory of chains that can only bond intermolecularly, we know that

$$X_0^{\text{inter'}} = \prod_{A\in\Gamma} X_A^{\text{inter'}} \tag{5.26}$$

Using the definition of $X_A^{\text{inter'}}$ given in (5.19) we can then find that

$$X_0 = X_A^{\text{inter'}} X_B^{\text{inter'}} X_0^{\text{intra}} = \frac{X_A X_B}{X_0^{\text{intra}}} \tag{5.27}$$

and inserting the relation for $X_B/X_0^{\text{intra}} = X_B/X_B^{\text{intra}}$ from (5.19) we obtain

$$X_0 = \frac{X_A}{1 + \rho X_A\Delta^{\text{inter}}} \tag{5.28}$$

which inserted in (5.25) (realizing that $X_A = X_B$) gives an expression for X_A given in terms of Δ^{inter} and Δ^{intra}:

$$1 = X_A\left[1 + \rho X_B\Delta^{\text{inter}}\right] + \frac{X_A}{1 + \rho X_A\Delta^{\text{inter}}}\Delta^{\text{intra}} \tag{5.29}$$

In the paper by Ghonasgi et al. [12] this is rewritten as

$$\left(\frac{1}{X_A}\right)^3 + (\rho\Delta^{\text{inter}} - \Delta^{\text{intra}} - 1)\left(\frac{1}{X_A}\right)^2 - 2\rho\Delta^{\text{inter}}\frac{1}{X_A} - \rho^2(\Delta^{\text{inter}})^2 = 0 \tag{5.30}$$

The theory was in the original and a later paper [12, 74] compared to molecular simulation results. The comparison showed good agreement between theory and simulations. D in the intramolecular association strength was determined from simulation results.

5.4.2 Sear and Jackson

Sear and Jackson at Imperial College have in their paper in Physical Review E from 1994 [10] adopted the formalism of Wertheim in their derivation for intramolecular association.

This section will present the derivation from that paper, though in a slightly modified way. Sear and Jackson considered segments, with two associating sites, which associate into chains, which could then associate inter- or intramolecularly. The derivation presented here will consider flexible chains, with one associating site on each terminal segment, that can bond inter- or intramolecularly. It was decided to consider chains instead of spheres because it makes the extension to more associating sites easier.

A nomenclature similar to the one in the paper by Sear and Jackson has been used in this section.

The two associating sites are distinguishable and are labeled A and B. A and B sites are allowed to associate with each other, but no $A - A$ or $B - B$ bonds are allowed.

There are four possible bonding states, here given with the corresponding number densities: neither of the two sites bonded with the density ρ_0; site A bonded but not site B with the density ρ_A; site B bonded but not site A with density ρ_B; and both sites bonded with density ρ_{AB}. The following combinations of these densities are used:

$$\begin{aligned} \sigma_0 &= \rho_0 \\ \sigma_A &= \rho_A + \rho_0 \\ \sigma_B &= \rho_B + \rho_0 \\ \sigma_\Gamma &= \rho_A + \rho_B + \rho_0 = \rho \end{aligned}$$

where $\rho = N/V$ is the total number density.

The difference in Helmholtz free energy between the system of associating chains and a reference fluid of identical chains, but without the attractive sites (from Wertheim IV), was presented in section 2.4.1:

$$\beta(A - A_R) = \int \left(\sigma_\Gamma(1) \ln \frac{\sigma_0(1)}{\sigma_\Gamma(1)} + \sigma_\Gamma(1) + Q(1) \right) d(1) - c^{(0)} + c_R^{(0)} \qquad (5.31)$$

$Q(1)$ depends on the number of sites, but for 2 sites it is given by:

$$Q_2(1) = -\sigma_A(1) - \sigma_B(1) + \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)} \tag{5.32}$$

and $\Delta c^{(0)}$ is the sum of all irreducible graphs in the associating system subtracted the ones in the non-associating reference system. In section 2.4.1 only interactions between two sites on two different molecules were included in the graph sum, but in order to allow intramolecular association, interactions between two sites on the same molecule must be included.

$$\Delta c^{(0)} = c^{(0)} - c_R^{(0)} = \int \sigma_A(1)\sigma_B(2)F_{AB}(12)y(12)d(1)d(2) + \int \sigma_0(1)F_{AB}(1)y(1)d(1) \tag{5.33}$$

The first term on the right hand side in (5.33) is the chain graphs, which accounts for intermolecular association between site A on a molecule with position 1 and site B on a molecule with position 2 and the second term is the ring graphs, which accounts for intramolecular association between sites A and B in a molecule with configuration and position 1. y is the reference fluid cavity distribution function.

The Mayer f-function for the interaction between two attractive sites (either on the same or different molecules) is given by:

$$F_{AB} = \exp\left(\frac{-\varepsilon_{\mathrm{SW}}}{kT} - 1\right) \tag{5.34}$$

where $\varepsilon_{\mathrm{SW}}$ is the potential depth of the square well interactions between two sites, A and B.

The expressions for Q and $\Delta c^{(0)}$ are inserted in (5.31):

$$\beta(A - A_R) = \int \left(\sigma_\Gamma(1)\ln\frac{\sigma_0(1)}{\sigma_\Gamma(1)} + \sigma_\Gamma(1) - \sigma_A(1) - \sigma_B(1) + \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)}\right) d(1)$$

$$- \int \sigma_A(1)\sigma_B(2)F_{AB}(12)y(12)d(1)d(2)$$

$$- \int \sigma_0(1)F_{AB}(1)y(1)d(1) \tag{5.35}$$

At equilibrium the free energy is at a minimum with respect to any variation in the densities σ_a, σ_B and σ_0. By functional differentiation of (5.35) with respect to σ_0 and σ_A we therefore find:

$$\frac{\sigma_\Gamma(1)}{\sigma_0(1)} - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)^2} = F_{AB}(1)y(1) \tag{5.36}$$

and

$$-1 + \frac{\sigma_B(1)}{\sigma_0(1)} = \int \sigma_B(2)F_{AB}(12)y(12)d(2) \tag{5.37}$$

For a homogenous fluid the densities are independent of position, and if we more-over assume that the cavity distribution function, y is constant in the overlap volume (the variation is small) we can simplify the expressions in (5.35), (5.36) and (5.37):

$$\frac{\beta(A - A_R)}{N} = \ln \frac{\sigma_0}{\sigma_\Gamma} + 1 - \frac{\sigma_A}{\sigma_\Gamma} - \frac{\sigma_B}{\sigma_\Gamma} + \frac{\sigma_A\sigma_B}{\sigma_0\sigma_\Gamma} - \frac{\sigma_0}{\sigma_\Gamma}\Delta_{AB}W_{n-1} - \frac{\sigma_A\sigma_B}{\sigma_\Gamma}\Delta_{AB} \tag{5.38}$$

$$\frac{\sigma_\Gamma}{\sigma_0} - \frac{\sigma_A\sigma_B}{\sigma_0^2} = KF_{AB}y_cW_{n-1} = \Delta_{AB}W_{n-1} \tag{5.39}$$

$$-1 + \frac{\sigma_B}{\sigma_0} = \sigma_B KF_{AB}y_c = \sigma_B\Delta_{AB} \tag{5.40}$$

where y_c is the value of y at contact, K is the bonding volume (per molecule) and Δ_{AB} is the association strength between sites A and B given by:

$$\Delta_{AB} = KF_{AB}y_c \tag{5.41}$$

W_m is the end-to-end distribution function of a freely jointed chain of $m = n - 1$ links. Sear and Jackson proposed the expression of Treolar [88]:

$$W_m = \frac{m(m - 1)}{\sigma^3 8\pi} \sum_{j=0}^{l} \frac{(-1)^j}{j!(m - j)!} \left[\frac{m - 1 - 2j}{2}\right]^{m-2} \tag{5.42}$$

where σ is the segment diameter and l is the smallest integer satisfying

$$l \geq \frac{m - 1}{2} - 1 \tag{5.43}$$

There was a misprint in the expression for W_m in the paper from 1994 [10], which was corrected in a later paper by Galindo et al. [13]. Unfortunately a new misprint appeared in the expression in that paper. Both misprints have been corrected in (5.42). Moreover the factor of σ^3 is missing in both papers, giving the impression that W_m is dimensionless. This is however because a hard-sphere diameter $\sigma = 1$ was used as unit of length.

Equation (5.40) is inserted in (5.38) to obtain

$$\frac{\beta(A - A_R)}{N} = \ln \frac{\sigma_0}{\sigma_\Gamma} + 1 - \frac{\sigma_B}{\sigma_\Gamma} - \frac{\sigma_0}{\sigma_\Gamma} \Delta_{AB} W_{n-1}$$
$$= \ln X_0 + 1 - X_A - X_0 \Delta_{AB} W_{n-1} \qquad (5.44)$$

where $X_0 = \sigma_0/\sigma_\Gamma$ is the fraction of molecules not bonded at any site, i.e. the monomer fraction, and $X_A = \sigma_B/\sigma_\Gamma$ is the fraction of molecules not bonded at site A.

(5.40) gives a relationship between σ_0 and σ_B (and therefore also between X_0 and X_A):

$$\sigma_0 = \frac{\sigma_B}{1 + \sigma_B \Delta_{AB}} \qquad \Rightarrow \qquad X_0 = \frac{X_A}{1 + \rho X_A \Delta_{AB}} \qquad (5.45)$$

This relationship can be used to obtain an expression for X_A from (5.39) given only in terms of Δ_{AB} and W_m:

$$\sigma_\Gamma = \frac{\sigma_A \sigma_B}{\sigma_0} + \sigma_0 \Delta_{AB} W_{n-1} = \sigma_B(1 + \sigma_B \Delta_{AB}) + \frac{\sigma_B}{1 + \sigma_B \Delta_{AB}} \Delta_{AB} W_{n-1}$$

$$\Rightarrow 1 = X_A(1 + X_A \Delta_{AB}) + \frac{X_A}{1 + \rho X_A \Delta_{AB}} \Delta_{AB} W_{n-1} \qquad (5.46)$$

If (5.45) is inserted in (5.44) we obtain the following expression:

$$\frac{\beta(A - A_R)}{N} = \ln \frac{X_A}{1 + \rho X_A \Delta_{AB}} + 1 - X_A - \frac{X_A}{1 + \rho X_A \Delta_{AB}} \Delta_{AB} W_{n-1} \qquad (5.47)$$

This expression is similar to the expression presented by Sear and Jackson in their equation (37), the only difference being

$$-(n - 1) \ln(\sigma_\Gamma \lambda y_c) + n - 1$$

which is the contribution to the free energy from chain formation.

The theory was in the original paper not compared to either experimental data or molecular simulations, but results were discussed qualitatively. In a paper from 2002 by Galindo et al. [13] the theory was used to model the phase behavior of hydrogen fluoride, a compound known to form ring aggregates both in the liquid and vapor phase.

5.4.3   Comparison of the theories from the two groups

The purpose here is to show that the equations presented in Ghonasgi and Chapman, 1995, J. Chem. Phys. [12] and in Sear and Jackson, 1994, Phys.Rev. E [10]

are identical under certain assumptions.

In the paper by Sear and Jackson they present the following equation, which accounts for inter- and intramolecular association as well as chain formation:

$$\frac{\beta(A - A_R)}{N} = -(n-1)\ln(\sigma_\Gamma \lambda y_c) + \ln\left(\frac{X}{1 + X\sigma_\Gamma \Delta}\right) + n - X - \frac{X}{1 + X\sigma_\Gamma \Delta} W_{n-1}\Delta$$
(5.48)

and this expression for the bonding state densities:

$$\sigma_\Gamma^1(1) = \sigma_B^1(1) + \sigma_B^1(1)\sigma_B^1(1^*)\Delta + \frac{\sigma_B^1(1)}{1 + \sigma_B^1(1)\Delta} W_{n-1}\Delta$$
(5.49)

This expression is rewritten for a homogeneous fluid in terms of $X = \sigma_B^1/\sigma_\Gamma^1$, the fraction of molecules not bonded at site A, by dividing with σ_Γ:

$$1 = X + \sigma_\Gamma X^2 \Delta + \frac{X}{1 + \sigma_\Gamma X\Delta} W_{n-1}\Delta$$
(5.50)

To isolate the contribution from chain formation we assume that the sites not involved in the chain formation cannot associate, meaning that we set $\Delta = 0$. If this is inserted in (5.50) we find (not surprisingly) that $X = 1$. The Helmholtz free energy is then:

$$\frac{\beta(A - A_R)^{\text{chain}}}{N} = -(n-1)\ln(\sigma_\Gamma \lambda y_c) + n - 1$$
(5.51)

If we subtract the contribution from chain formation we get the following equation for the change in free energy from inter- and intramolecular association:

$$\frac{\beta(A - A_R)^{\text{assoc}}}{N} = \ln\left(\frac{X}{1 + X\sigma_\Gamma \Delta}\right) + 1 - X - \frac{X}{1 + X\sigma_\Gamma \Delta} W_{n-1}\Delta$$
(5.52)

(which is identical to equation (5.47) in section 5.4.2).

From the paper of Ghonasgi et al. we have the following expression for the Helmholtz free energy:

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 - X_A^{\text{inter}} + 1 = \ln X_0 + X_0^{\text{intra}} - X_A$$
(5.53)

and the following four equations, which in the paper are combined to give an expression for X_A in terms of Δ^{inter} and Δ^{intra}:

$$X_A = \frac{X_0^{\text{intra}}}{1 + \rho X_A \Delta^{\text{inter}}} \tag{5.54}$$

$$\frac{X_0}{X_0^{\text{inter}}} = \frac{1}{1 + \Delta^{\text{intra}}} \tag{5.55}$$

$$X_0 = \frac{X_A^2}{X_0^{\text{intra}}} \tag{5.56}$$

$$X_0^{\text{inter}} + X_0^{\text{intra}} - X_0 = 1 \tag{5.57}$$

$$\Rightarrow \left(\frac{1}{X_A}\right)^3 + (\rho \Delta^{\text{inter}} - \Delta^{\text{intra}} - 1)\left(\frac{1}{X_A}\right)^2 - 2\rho \Delta^{\text{inter}} \frac{1}{X_A} - \rho^2 (\Delta^{\text{inter}})^2 = 0 \tag{5.58}$$

From (5.54) we find that:

$$X_0^{\text{intra}} = X_A(1 + \rho X_A \Delta^{\text{inter}}) \tag{5.59}$$

which inserted in (5.56) gives:

$$X_0 = \frac{X_A}{1 + \rho X_A \Delta^{\text{inter}}} \tag{5.60}$$

Rewriting (5.55) gives

$$X_0^{\text{inter}} = X_0(1 + \Delta^{\text{intra}}) \quad \Rightarrow \quad X_0^{\text{inter}} - X_0 = X_0 \Delta^{\text{intra}} \tag{5.61}$$

and from (5.57) we then find

$$X_0^{\text{intra}} = 1 - (X_0^{\text{inter}} - X_0) = 1 - X_0 \Delta^{\text{intra}} \tag{5.62}$$

After inserting (5.60) and (5.62) in (5.53) we obtain the following expression for the change in the Helmholtz free energy:

$$\frac{A^{\text{assoc}}}{NkT} = \ln\left(\frac{X_A}{1 + \rho X_A \Delta^{\text{inter}}}\right) + 1 - X_A - \left(\frac{X_A}{1 + \rho X_A \Delta^{\text{inter}}}\right)\Delta^{\text{intra}} \tag{5.63}$$

Remembering that $\rho = \sigma_\Gamma$, and that X in the paper by Sear & Jackson is identical to X_A in the paper by Ghonasgi et al. a comparison between equations (5.52) and (5.63) shows that the two approaches give identical expressions for the contribution to the Helmholtz free energy from association, in the case of associating chains with two attractive sites.

Similarly if we rewrite the expression in (5.58) we find that the expressions for the

fraction of molecules not bonded at a certain site are identical (compare (5.50) and (5.64))

$$1 = \left(-\rho \Delta^{\text{inter}} + \Delta^{\text{intra}} + 1\right) X_A + 2\rho \Delta^{\text{inter}} X_A^2 - \rho^2 (\Delta^{\text{inter}})^2 X_A^3$$

$$\Rightarrow 0 = \left(-1 + \rho \Delta^{\text{inter}} X_A\right) \left(1 + X_A + \rho \Delta^{\text{inter}} X_A^2\right) + X_A \Delta^{\text{intra}}$$

$$\Rightarrow 1 = X_A \left(1 + \rho X_A \Delta^{\text{inter}}\right) + \frac{X_A}{1 + \rho X_A \Delta^{\text{inter}}} \Delta^{\text{intra}}$$

$$\Rightarrow 1 = X_A + \rho X_A^2 \Delta^{\text{inter}} + \frac{X_A}{1 + \rho X_A \Delta^{\text{inter}}} \Delta^{\text{intra}} \tag{5.64}$$

The only real difference between the two approaches lie in the definition of the intramolecular association strength.

In the paper by Ghonasgi and Chapman [12] the intramolecular association strength is defined in terms of D, the fraction of molecules in the bonding orientation in the non-associating reference fluid, and an intramolecular distribution function:

$$\Delta^{\text{intra}} = DF = \frac{1}{(4/3)\pi(m-1)^3 \sigma^3} \int_{\text{Bond volume}} g_{\text{R,intra}}(12) d(12) F \tag{5.65}$$

(though in the results presented in the paper D has been determined from molecular simulations).

Sear and Jackson [10] define it in terms of the intermolecular association strength, multiplied with an intramolecular end-to-end distribution function

$$W_m \Delta = \frac{m(m-1)}{8\pi} \sum_{j=0}^{l} \frac{(-1)^j}{j!(m-j)!} \left[\frac{m-1-2j}{2}\right]^{m-2} K F_{AB} y_c \tag{5.66}$$

The two theories have the same definition of the Mayer f-function

$$F = \exp(-\varepsilon/kT) - 1 \tag{5.67}$$

Since Sear and Jackson define the intramolecular association strength in terms of the intermolecular association strength, the association parameters for the two types of association are the same, though differentiated parameters can be implemented, if wanted. The expressions by Ghonasgi and Chapman imply the use of two different association energies for the inter- and intramolecular association,

but the results in the paper are for $\varepsilon^{\text{inter}} = \varepsilon^{\text{intra}}$. It is not clear from the paper whether identical or different bond volumes should be used for the two types of association in the Ghonasgi and Chapman approach.

It seems reasonable that the bonding volume should be the same for inter- and intramolecular association since the same sites are involved in the two interactions. The same is true for the association energy, but there is an energy penalty involved in the chain-bend in an intramolecular association, which should be subtracted from the energy gain from association. (For simplicity the intramolecular association energy will here be understood as the actual association energy subtracted the energy penalty.) Using two different association energies however increases the number of pure component parameters, which in our opinion is not advantageous. In this work we have therefore decided to use the expression from Sear and Jackson [10], with identical association parameters for the two types of association.

5.5   Derivation of a general theory

As we just saw in the previous section the SAFT association term has already been extended to include intramolecular association, but only for chains with two attractive sites, and no real compounds forming intramolecular bonds can be modeled (physically reasonably) with this model. To model compounds like for example glycol ethers we need at least three sites, in order to describe the possible inter- and intramolecular interactions. In order to model real compounds with intramolecular association the theory must therefore be generalized. This section will present two approaches for deriving a general theory.

To simplify the expressions the derivation is shown for a pure component, but all expressions are easily extended to mixtures (by adding an index indicating which component the site belongs to, and summations over all components).

5.5.1   Approach #1

The theory for chains with two sites, that can associate inter- and intramolecularly, presented by Ghonasgi and Chapman [12] is in this section extended to chains with any number of sites.

For each site we have the following mass balance (see section 5.4.1):

$$X_A^{\text{inter}} + X_A^{\text{intra}} - X_A = 1 \tag{5.68}$$

The expression in (5.68) is general for any system and any site or subset of sites.

As for the case with 2 sites, the change in Helmholtz free energy from association is related to the monomer fraction and the number of clusters in the system:

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 + \frac{1}{2} \sum_{A \in \Gamma} \left(1 - X_A^{\text{inter}}\right) \tag{5.69}$$

Using the relation in (5.68) this can be rewritten as

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 + \frac{1}{2} \sum_{A \in \Gamma} \left(X_A^{\text{intra}} - X_A\right) \tag{5.70}$$

To calculate the free energy we need expressions for X_0, X_A and X_A^{intra}.

In the paper on competition between inter- and intramolecular association [12] Ghonasgi and Chapman consider the amount of intermolecular association after all intramolecular bonds have been formed, by introducing the fraction of molecules not bonded intermolecularly at site A, given that site A is not bonded intramolecularly, $X_A^{\text{inter'}}$. This means that we count the fraction of molecules not bonded at site A from the fraction of molecules not bonded intramolecularly at site A, and use the known relation for intermolecular association [3],

$$X_A^{\text{inter'}} \equiv \frac{X_A}{X_A^{\text{intra}}} = \frac{1}{1 + \rho \sum_{B \in \Gamma} X_B \Delta_{AB}^{\text{inter}}} \tag{5.71}$$

Rewriting (5.71) gives the following relation between X_A and X_A^{intra}:

$$X_A^{\text{intra}} = \frac{X_A}{1 + \rho \sum_{B \in \Gamma} X_B \Delta_{AB}^{\text{inter}}} \tag{5.72}$$

A second expression for X_A^{intra} is found by considering the intramolecular association as a chemical equilibrium with the intramolecular association strength Δ^{intra} as the equilibrium constant. Intramolecular association between sites A and B is thus an equilibrium between molecules with that intramolecular bond,

and molecules where the sites are unbonded:

$$\Delta_{AB}^{\text{intra}} = \frac{\rho_{AB}^{\text{intra}}}{\rho X_{AB}} \qquad \Leftrightarrow \qquad \rho_{AB}^{\text{intra}} = \rho X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.73}$$

(here ρ_{AB}^{intra} includes all molecules where A and B are bonded intramolecularly to each other, regardless of whether any other site is bonded or not). The same type of expression can be written for any two sites.

The total density must be equal to the density of molecules where site A is not bonded intramolecularly plus the density of molecules where site A is bonded intramolecularly. The following mass balance must therefore be satisfied:

$$\rho = \rho X_A^{\text{intra}} + \sum_{B \neq A} \rho_{AB}^{\text{intra}} = \rho \left(X_A^{\text{intra}} + \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \right)$$

$$\Rightarrow X_A^{\text{intra}} = 1 - \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.74}$$

A similar mass balance for both sites A and B gives an expression for X_{AB}^{intra}:

$$\rho = \rho X_{AB}^{\text{intra}} + \rho_{AB}^{\text{intra}}$$

$$\Rightarrow X_{AB}^{\text{intra}} = 1 - X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.75}$$

where X_{AB}^{intra} is the fraction of molecules on which sites A and B are not bonded intramolecularly to each other. This expression in combination with (5.74) gives us the obvious relation that the fraction of molecules bonded intramolecularly at site A is equal to the sum of the fraction of molecules where site A is bonded intramolecularly to a specific site:

$$1 - X_A^{\text{intra}} = \sum_{B \neq A} (1 - X_{AB}^{\text{intra}}) \tag{5.76}$$

If equation (5.74) is equated to (5.72) we then get

$$1 = X_A[1 + \rho \sum_B X_B \Delta_{AB}^{\text{inter}}] + \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.77}$$

from which X_A can be calculated if X_{AB} is known.

If equation (5.74) is inserted in (5.70) we moreover get an expression for the Helmholtz free energy only in terms of X_0, X_A and X_{AB} (and $\Delta_{AB}^{\text{intra}}$):

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 + \frac{1}{2} \sum_{A \in \Gamma} (1 - X_A) - \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.78}$$

Similar to the definition of $X_A^{\text{inter'}}$ in (5.71) the fraction of any subset of sites not bonded intermolecularly given that they are not bonded intramolecularly can be defined as

$$X^{\text{inter'}} = \frac{X}{X^{\text{intra}}} \qquad \Leftrightarrow \qquad X = X^{\text{inter'}} X^{\text{intra}} \tag{5.79}$$

From this definition we have that the monomer fraction is given by:

$$X_0 = X_0^{\text{inter'}} X_0^{\text{intra}} \tag{5.80}$$

and $X_0^{\text{inter'}}$ is according to the theory for only intermolecular association given by

$$X_0^{\text{inter'}} = \prod_{A \in \Gamma} X_A^{\text{inter'}} \tag{5.81}$$

In the case where only 2 sites (e.g. A and B) can associate intramolecularly we have

$$X_0^{\text{intra}} = X_A^{\text{intra}} = X_B^{\text{intra}} = X_{AB}^{\text{intra}} \tag{5.82}$$

which gives the following expression for X_0 and X_{AB}:

$$X_0 = X_{AB}^{\text{intra}} \prod_{A \in \Gamma} X_A^{\text{inter'}} = X_{AB} \prod_{C \in \Gamma \setminus \{A,B\}} X_C^{\text{inter'}} = \frac{\prod_A X_A}{X_0^{\text{intra}}} \tag{5.83}$$

$$X_{AB} = X_A^{\text{inter'}} X_B^{\text{inter'}} X_{AB}^{\text{intra}} = X_A X_B^{\text{inter'}} = \frac{X_A}{1 + \rho \sum_C X_C \Delta_{BC}^{\text{inter}}} \tag{5.84}$$

Examples of real compounds that can be modelled in this way are the glycolethers 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol, which all have one hydroxyl group and one ether oxygen.

If one site (e.g. A) can associate intramolecularly with a number of sites (e.g. B and C), which can only associate intramolecularly with that one site, then the fraction of molecules not bonded intramolecularly will be equal to the fraction of molecules not bonded at that site

$$X_0^{\text{intra}} = X_A^{\text{intra}} \tag{5.85}$$

$$X_0 = X_A^{\text{intra}} \prod_{A \in \Gamma} X_A^{\text{inter'}} = X_A \prod_{B \in \Gamma \setminus \{A\}} X_B^{\text{inter'}} \tag{5.86}$$

X_{AB} (or X_{AC}) is found from

$$X_{AB} = X_A^{\text{inter'}} X_B^{\text{inter'}} X_A^{\text{intra}} = X_A X_B^{\text{inter'}} = \frac{X_A}{1 + \rho \sum_C X_C \Delta_{BC}^{\text{inter}}} \qquad (5.87)$$

since X_A^{intra} in this case is equal to the fraction of molecules, where sites A and B (and C) are not bonded intramolecularly to any site.

One example of a real compound that can be modelled with this description is 2-(2-butoxyethoxy)ethanol, which has one hydroxyl group and two ether oxygens.

5.5.2 Approach #2

This section will present a different derivation of the general theory, where an approach similar to the one used by Sear and Jackson [10] has been applied.

The starting point is the expression for the Helmholtz free energy from Wertheims fourth paper on "Fluids with highly directional attractive forces" [7], which was presented in section 2.4.1:

$$\beta \left(A - A_R \right) = \int \left[\sigma_\Gamma(1) \ln \frac{\sigma_0(1)}{\sigma_\Gamma(1)} + \sigma_\Gamma(1) + Q(1) \right] d(1) - c^{(0)} + c_R^{(0)} \qquad (5.88)$$

where $Q(1)$ is the sum of all possible bonding states, given by

$$Q(1) = - \sum_{A \in \Gamma} \sigma_{\Gamma - A}(1) + \sigma_0(1) \sum_{P(\Gamma) = \{\gamma, M \geq 2\}} (-1)^M (M - 2)! \prod_\gamma \hat{\sigma}_\gamma(1) \qquad (5.89)$$

and

$$\Delta c^{(0)} = c^{(0)} - c_R^{(0)} = \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma} \int g_R(12) f_{AB}(12) \sigma_{\Gamma - A}(1) \sigma_{\Gamma - B}(2) d(1) d(2)$$

$$+ \frac{1}{2} \sum_{A \in \Gamma} \sum_{B \in \Gamma \backslash A} \int g_R(12) f_{AB}(12) \sigma_{\Gamma - AB}(1) d(12) \qquad (5.90)$$

For simplicity, in the rest of the section it will be implicit that a sum over A is for $A \in \Gamma$ (and similarly for any other site).

We will split Q(1) into two parts:

$$Q(1) = -\sum_A \sigma_{\Gamma-A}(1) + \sigma_\Gamma(1)K \tag{5.91}$$

where

$$K = \frac{\sigma_0(1)}{\sigma_\Gamma(1)} \sum_{P(\Gamma)=\{\gamma, M \geq 2\}} (-1)^M (M-2)! \prod_\gamma \hat{\sigma}_\gamma(1) \tag{5.92}$$

Similarly to section 5.4.2 we can write the Helmholtz free energy for a homogeneous fluid:

$$\frac{A^{\text{assoc}}}{NkT} = \left[\ln \frac{\sigma_0}{\sigma_\Gamma} + 1 + K - \sum_A \frac{\sigma_{\Gamma-A}}{\sigma_\Gamma} \right] - \frac{1}{2} \sum_A \sum_B \frac{\sigma_{\Gamma-A}\sigma_{\Gamma-B}}{\sigma_\Gamma} \Delta_{AB}^{\text{inter}}$$
$$- \frac{1}{2} \sum_A \sum_{B \neq A} \frac{\sigma_{\Gamma-AB}}{\sigma_\Gamma} \Delta_{AB}^{\text{intra}} \tag{5.93}$$

where

$$K = \frac{\sigma_0}{\sigma_\Gamma} \sum_{P(\Gamma)=(\gamma, M \geq 2)} (-1)^M (M-2)! \prod_\gamma \hat{\sigma}_\gamma \tag{5.94}$$

and $\Delta_{AB}^{\text{inter}}$ and $\Delta_{AB}^{\text{intra}} = \Delta_{AB}^{\text{inter}} W_m$ are the inter- and intramolecular association strengths respectively.

Equations (5.93) and (5.94) can be written in terms of $X_\gamma = \sigma_{\Gamma-\gamma}/\sigma_\Gamma$ ($\sigma_\Gamma = N/V$:

$$\frac{A^{\text{assoc}}}{NkT} = \ln X_0 + 1 + K - \sum_A X_A - \frac{N}{2V} \sum_A \sum_B X_A X_B \Delta_{AB}^{\text{inter}}$$
$$- \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.95}$$

and

$$K = X_0 \sum_{P(\Gamma)=(\gamma, M \geq 2)} (-1)^M (M-2)! \prod_\gamma \frac{X_{\Gamma-\gamma}}{X_0} \tag{5.96}$$

At equilibrium the energy of the system will be at a minimum with respect to any bonding state, and the expression for the Helmholtz free energy in (5.95) therefore has the property that the derivative with respect to any bonding state is zero, that is the derivatives with respect to X_0, X_A, X_B, X_{AB} and so on are all zero. We can use this to find an expression for the Helmholtz free energy at the stationary point. (This is similar to what is done in the paper by Michelsen and Hendriks [40] for intermolecular association, and in the paper by Sear and Jackson [10] for a chain with two sites, which associate inter- and intramolecularly. The latter was discussed in section 5.4.2.)

Since K depends on the number of sites (5.95) cannot be differentiated generally with respect to all bonding states (which of course also depends on the total number of sites), but it can be shown for any specific number of sites that

$$K = -1 + \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} + \sum_A X_A \left[1 + \frac{N}{V} \sum_B X_B \Delta_{AB}^{\text{inter}} \right] \qquad (5.97)$$

and

$$K = -1 + n(\Gamma) - \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} \qquad (5.98)$$

It is shown for 3 and 4 sites later in this section.

If we add (5.97) and (5.98) we get:

$$K = -1 + \frac{1}{2} (X_A + 1) + \frac{1}{2 V_m} \sum_A \sum_B X_A X_B \Delta_{AB}^{\text{inter}} \qquad (5.99)$$

We can then insert the expression in equation (5.99) in (5.95) to find an expression for the Helmholtz free energy at equilibrium (the stationary point):

$$\tilde{a}_{\text{sp}}^{\text{assoc}} = \ln X_0 - \sum_A (X_A - 1) - \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} \qquad (5.100)$$

We can equate the two expressions for K in (5.97) and (5.98) to find:

$$n(\Gamma) - \sum_A X_A \left[1 + \frac{N}{V} \sum_B X_{B_j} \Delta_{AB}^{\text{inter}} \right] - \sum_A \sum_{B \neq B} X_{AB} \Delta_{AB}^{\text{intra}} = 0$$

$$\Rightarrow \sum_A \left(1 - X_A \left[1 + \frac{N}{V} \sum_B X_{B_j} \Delta_{AB}^{\text{inter}} \right] - \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \right) = 0 \qquad (5.101)$$

3 sites

As mentioned the expressions for K in (5.97) and (5.98) can be derived for any specific number of sites. For 3 sites we have:

$$K = \sum_A \frac{X_A X_{\Gamma-A}}{X_0} - \frac{X_{\Gamma-A} X_{\Gamma-B} X_{\Gamma-C}}{X_0^2} \qquad (5.102)$$

The derivatives of Q with respect to different X_γ's are given below

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_A} = -1 + \frac{X_{\Gamma-A}}{X_0} - \frac{N}{V}\sum_B X_B \Delta_{AB}^{\text{inter}} = 0$$

$$\Rightarrow \sum_A X_A \left[1 + \frac{N}{V}\sum_B X_B \Delta_{AB}^{\text{inter}} \right] = \sum_A \frac{X_A X_{\Gamma-A}}{X_0} \tag{5.103}$$

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}} = \frac{X_A}{X_0} - \frac{X_{\Gamma-B}X_{\Gamma-C}}{X_0^2} - \Delta_{\Gamma-A}^{\text{intra}} = 0 \tag{5.104}$$

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} = \frac{1}{X_0} - \sum_A \frac{X_A X_{\Gamma-A}}{X_0^2} + \frac{2X_{\Gamma-A}X_{\Gamma-B}X_{\Gamma-C}}{X_0^3} = 0 \tag{5.105}$$

$$X_0 \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} + \sum_A X_{\Gamma-A}\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}} = 1 - \frac{X_{\Gamma-A}X_{\Gamma-B}X_{\Gamma-C}}{X_0^2} - \sum_A X_{\Gamma-A}\Delta_{\Gamma-A}^{\text{intra}} = 0 \tag{5.106}$$

The last term on the right hand side can be written in a more familiar form:

$$\sum_A X_{\Gamma-A}\Delta_{\Gamma-A}^{\text{intra}} = \frac{1}{2}\sum_A \sum_B X_{AB}\Delta_{AB}^{\text{intra}} \tag{5.107}$$

From equations (5.102), (5.103) and (5.106) we then find:

$$K = -1 + \frac{1}{2}\sum_A \sum_B X_{AB}\Delta_{AB}^{\text{intra}} + \sum_A X_A \left[1 + \frac{N}{V}\sum_B X_{B_j}\Delta_{AB}^{\text{inter}} \right] \tag{5.108}$$

which was the first term we were looking for.

The second expression is found from a different combination of $\partial \tilde{a}^{\text{assoc}}/\partial X_0$ and $\partial \tilde{a}^{\text{assoc}}/\partial X_{\Gamma-A}$:

$$2X_0 \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} + \sum_A X_{\Gamma-A}\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}}$$

$$= 2 - \sum_A \frac{2X_A X_{\Gamma-A}}{X_0} + \frac{4X_{\Gamma-A}X_{\Gamma-B}X_{\Gamma-C}X_{\Gamma-D}}{X_0^2} + \sum_A \frac{X_A X_{\Gamma-A}}{X_0}$$

$$- \frac{3X_{\Gamma-A}X_{\Gamma-B}X_{\Gamma-C}X_{\Gamma-D}}{X_0^2} - \frac{1}{2}\sum_A \sum_B X_{AB}\Delta_{AB}^{\text{intra}}$$

$$= n\left[2 - K - \frac{1}{2}\sum_A \sum_B X_{AB}\Delta_{AB}^{\text{intra}} \right] = 0 \tag{5.109}$$

$$\Rightarrow K = -1 + n(\Gamma) - \frac{1}{2}\sum_A \sum_B X_{AB}\Delta_{AB}^{\text{intra}} \tag{5.110}$$

4 sites

For 4 sites we have:

$$K = \sum_A \frac{X_A X_{\Gamma-A}}{X_0} + \frac{1}{4} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-AB}}{X_0} - \frac{1}{2} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-A} X_{\Gamma-B}}{X_0^2}$$
$$+2 \frac{X_{\Gamma-A} X_{\Gamma-B} X_{\Gamma-C} X_{\Gamma-D}}{X_0^3} \tag{5.111}$$

The derivatives of $\tilde{a}^{\text{assoc}}$ with respect to different X_γ's are given below

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_A} = -1 + \frac{X_{\Gamma-A}}{X_0} - \frac{N}{V} \sum_B X_B \Delta_{AB}^{\text{inter}} = 0$$

$$\Rightarrow \sum_A X_A \left[1 + \frac{N}{V} \sum_B X_B \Delta_{AB}^{\text{inter}} \right] = \sum_A \frac{X_A X_{\Gamma-A}}{X_0} \tag{5.112}$$

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} = \frac{1}{X_0} - \sum_A \frac{X_A X_{\Gamma-A}}{X_0^2} - \frac{1}{4} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-AB}}{X_0^2}$$

$$+ \sum_A \sum_B \frac{X_{AB} X_{\Gamma-A} X_{\Gamma-B}}{X_0^3} - 6 \frac{X_{\Gamma-A} X_{\Gamma-B} X_{\Gamma-C} X_{\Gamma-D}}{X_0^4} = 0 \tag{5.113}$$

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}} = \frac{X_A}{X_0} - \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-B}}{X_0^2} + 2 \frac{X_{\Gamma-B} X_{\Gamma-C} X_{\Gamma-D}}{X_0^2} = 0 \tag{5.114}$$

$$\frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{AB}} = \frac{X_{\Gamma-AB}}{X_0} - \frac{X_{\Gamma-A} X_{\Gamma-B}}{X_0^2} - \Delta_{AB}^{\text{intra}} = 0 \tag{5.115}$$

The last three expressions are combined

$$X_0 \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} + \sum_A X_{\Gamma-A} \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}} + \frac{1}{2} \sum_A \sum_B X_{AB} \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{AB}}$$

$$= 1 - \frac{1}{4} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-AB}}{X_0} - \frac{1}{2} \sum_A \sum_B \frac{X_{AB} X_{\Gamma-A} X_{\Gamma-B}}{X_0^2}$$

$$+2 \frac{X_{\Gamma-A} X_{\Gamma-B} X_{\Gamma-C} X_{\Gamma-D}}{X_0^3} - \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} = 0 \tag{5.116}$$

By insertion of (5.112) and (5.116) in (5.111) we then find:

$$K = -1 + \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} + \sum_A X_A \left[1 + \frac{N}{V} \sum_B X_B \Delta_{AB}^{\text{inter}} \right] \tag{5.117}$$

which is identical to (5.97), the first equation that was postulated.

As for three sites we can make a different combination of $\partial \tilde{a}^{\text{assoc}}/\partial X_0$, $\partial \tilde{a}^{\text{assoc}}/\partial X_{\Gamma-A}$ and $\partial \tilde{a}^{\text{assoc}}/\partial X_{AB}$ to find the expression in (5.98):

$$
3X_0 \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_0} + 2 \sum_A X_{\Gamma-A} \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{\Gamma-A}} + \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \frac{\partial \tilde{a}^{\text{assoc}}}{\partial X_{AB}}
$$

$$
= \; 3 - \sum_A \frac{X_A X_{\Gamma-A}}{X_0} - \frac{1}{4} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-AB}}{X_0} + \frac{1}{2} \sum_A \sum_{B \neq A} \frac{X_{AB} X_{\Gamma-A} X_{\Gamma-B}}{X_0^2}
$$

$$
+ 2 \frac{X_{\Gamma-A} X_{\Gamma-B} X_{\Gamma-C} X_{\Gamma-D}}{X_0^3} - \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}}
$$

$$
= \; 3 - K - \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} = 0 \tag{5.118}
$$

$$
\Rightarrow K = -1 + n(\Gamma) - \frac{1}{2} \sum_A \sum_B X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.119}
$$

The more sites we include the more complex the derivation gets, but it can in principal be done for any number of sites.

5.5.3   Recap of the new theory

As we did for the expressions for chains with two sites, derived by the two groups at Imperial College and Rice University, we will now compare the resulting equations with the two approaches that were just presented. The derivations were done for pure components, but the corresponding expressions for mixtures will also be presented in this section.

From approach #1 we have an expression for the Helmholtz free energy and the fraction of sites not bonded:

$$
\tilde{a}^{\text{assoc}} = \frac{A^{\text{assoc}}}{NkT} = \ln X_0 + \frac{1}{2} \sum_{A \in \Gamma} (1 - X_A) - \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.120}
$$

and

$$
1 = X_A \left[1 + \rho \sum_B X_B \Delta_{AB}^{\text{inter}} \right] + \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.121}
$$

We also have an expression for the fraction of sites not bonded intermolecularly given that they are not bonded intramolecularly:

$$X_A^{\text{inter'}} \equiv \frac{X_A}{X_A^{\text{intra}}} = \frac{1}{1 + \rho \sum\limits_{B \in \Gamma} X_B \Delta_{AB}^{\text{inter}}} \tag{5.122}$$

and the monomer fraction given by

$$X_0 = X_0^{\text{intra}} \prod_{A \in \Gamma} X_A^{\text{inter'}} \tag{5.123}$$

An expression for the fraction of molecules not bonded intramolecularly, X_0^{intra}, was however only determined for certain cases. For the cases with 2 and 3 sites that can bond intramolecularly, where one site (e.g. A) is the limiting "species", $X_0^{\text{intra}} = X_A^{\text{intra}}$, which is given by:

$$X_A^{\text{intra}} = \frac{X_A}{1 + \rho \sum\limits_{B} X_B \Delta_{AB}^{\text{inter}}} \tag{5.124}$$

For the same special cases X_{AB} was found to be given by

$$X_{AB} = X_A X_B^{\text{inter'}} = \frac{X_A}{1 + \rho \sum\limits_{C} X_C \Delta_{BC}^{\text{inter}}} \tag{5.125}$$

For approach #2 we have two expressions for the Helmholtz free energy; one general, and one at equilibrium:

$$\tilde{a}^{\text{assoc}} = \ln X_0 + 1 + K - \sum_A X_A - \frac{1}{2V_m} \sum_A \sum_B X_A X_B \Delta_{AB}^{\text{inter}} - \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.126}$$

with

$$K = X_0 \sum_{P(\Gamma) = (\gamma, M \geq 2)} (-1)^M (M-2)! \prod_\gamma \frac{X_{\Gamma - \gamma}}{X_0} \tag{5.127}$$

and

$$\tilde{a}_{\text{sp}}^{\text{assoc}} = \ln X_0 - \frac{1}{2} \sum_A (X_A - 1) - \frac{1}{2} \sum_A \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \tag{5.128}$$

and the following expression was found for the fraction of unbonded sites:

$$\sum_A \left(1 - X_A \left[1 + \frac{N}{V} \sum_B X_{B_j} \Delta_{AB}^{\text{inter}} \right] - \sum_{B \neq A} X_{AB} \Delta_{AB}^{\text{intra}} \right) = 0 \tag{5.129}$$

It is clear that the expressions for the Helmholtz free energy from the two approaches are identical ($\rho = N/V$) (the derivation of the Helmholtz energy with approach #1 was done at equilibrium, and the expression therefore corresponds to the equilibrium expression from approach #2, $\tilde{a}_{\text{sp}}^{\text{assoc}}$).

The two expressions for the fraction of sites not bonded are not identical, and while we can easily go from (5.121) to (5.129) by adding a summation over sites, it is not clear from (5.129) that the expression in (5.121) is true.

The first approach thus gives us all the expressions we need to calculate the Helmholtz free energy at equilibrium (which approach #2 does not), while the second approach gives us an expression for the Helmholtz free energy with the property that the derivative with respect to any bonding state is zero, which is very useful when calculating the derivatives, as will be shown in the next section.

The expression for the Helmholtz free energy (from association) for a mixture is:

$$\tilde{a}_{\text{sp}}^{\text{assoc}} = \sum_i x_i \left[\ln X_{0_i} - \sum_{A_i} (X_{A_i} - 1) \right] - \frac{1}{2} \sum_i x_i \sum_A \sum_{B \neq A} X_{A_i B_i} \Delta_{A_i B_i}^{\text{intra}} \quad (5.130)$$

and the fraction of unbonded sites in a mixture is:

$$-1 + X_{A_i} \left[1 + \frac{N}{V} \sum_j x_j \sum_{B_j} X_{B_j} \Delta_{A_i B_j}^{\text{inter}} \right] + \sum_{B_i \neq A_i} X_{A_i B_i} \Delta_{A_i B_i}^{\text{intra}} = 0 \quad (5.131)$$

The intermolecular association strength was given in equation (2.24) in section 2.2.4:

$$\Delta_{A_i B_j}^{\text{inter}} = \frac{\pi}{6} \sigma_{ij}^3 g^{\text{HS}}(d) \kappa^{A_i B_j} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT} \right) - 1 \right] \quad (5.132)$$

and we use the following expression for the intramolecular association strength:

$$\Delta_{A_i B_i}^{\text{intra}} = W_m \Delta_{A_i B_i}^{\text{inter}} = W_m \frac{\pi}{6} \sigma_{ij}^3 g^{\text{HS}}(d) \kappa^{A_i B_i} \left[\exp\left(\frac{\varepsilon^{A_i B_i}}{kT} \right) - 1 \right] \quad (5.133)$$

where

$$W_m = \frac{m(m-1)}{\sigma^3 8\pi} \sum_{j=0}^{l} \frac{(-1)^j}{j!(m-j)!} \left[\frac{m-1-2j}{2} \right]^{m-2} \quad (5.134)$$

and l is the smallest integer satisfying

$$l \geq \frac{m-1}{2} - 1$$

5.5.4   Derivatives of the Helmholtz free energy

In the paper by Michelsen and Hendriks from 2001 [40] they present a simple way to calculate the derivatives needed to calculate properties like pressure and chemical potential when an expression for the Helmholtz free energy contribution from association is given (as for SAFT). In that paper the derivation is shown when only intermolecular association is considered, but the approach has in this work been applied for the theory where also intramolecular association is considered. The derivatives are given for the case where only two sites on a molecule can associate intramolecularly.

A nomenclature similar to the one used in the program has been chosen to ease comparison between theory and program. In this nomenclature all sites in the system is listed after each other, starting with the sites on component 1, followed by the sites on component 2 and so on. Sites are referred to by the number in the list. This is very convenient computationally, because it reduces the number of sums in the equations significantly. Thus instead of using X_{A_i} for the fraction of sites A on component i that are unbonded we use XA_i which is the fraction of sites i that are unbonded. The information of which component site i belongs to is "saved" elsewhere, and is not relevant for the equations. The only exception is for intramolecular association, where sums over j are implicitly understood only to be a sum over sites on the same molecule as site i, since the two sites involved in an intramolecular bond must belong to the same molecule. Otherwise, if nothing else is stated, a sum over sites are over all sites in the system.

Moreover the intermolecular association strength (Δ^{inter}) in the program is per mole instead of per molecule, and the association strength is therefore corrected with Avogadro's number. W_m is also corrected so that Δ^{intra} remains dimensionless.

k and l will be used to refer to components and i, j, m and n to sites, meaning that x_k is the molefraction of component k and x_i is the molefraction of site i. If site i is on component k then $x_i = x_k$.

The starting point in the paper by Michelsen and Hendriks is an objective function Q, which is said to be equal to the Helmholtz free energy from association in the stationary point with respect to the site fractions X (this Q function is not the same as the Q function from Wertheim in section 2.4.1).

The Helmholtz free energy was given in equation (5.95) in section 5.5.2 for a pure

component. The corresponding equation for a mixture is:

$$Q/n = \tilde{a}^{\text{assoc}} = \sum_k^{\text{NC}} x_k \left(\ln X0_k + K_k + 1 - \sum_i^{\text{NS}_k} XA_i \right)$$

$$- \frac{1}{2V_m} \sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}^{\text{inter}}$$

$$- \frac{1}{2} \sum_i \sum_{j \neq i} x_i XAB_{ij} \Delta_{ij}^{\text{intra}} \tag{5.135}$$

with

$$K_k = X0_k \sum_{P(\Gamma_k)=\gamma, M \geq 2} (-1)^M (M-2)! \prod \frac{X_{\Gamma_k - \gamma_k}}{X0_k} \tag{5.136}$$

here Γ_k is the total amount of sites on component k, α_k is a subset of the sites on component k, X_α is the fraction of molecules on which the sites in the subset α are unbonded, XA_i is (as mentioned) the fraction of sites of type i that are unbonded and XAB_{ij} is the fraction of molecules containing both a site i and a site j on which both sites are unbonded. $X0_k$ is the monomer fraction for component k, NS_k is the number of sites on component k and NC is the number of components.

An expression for XA_i was given in equation (5.131) section 5.5.3, which in the nomenclature used here is:

$$-1 + XA_i \left[1 + \frac{1}{V_m} \sum_j x_j XA_j \Delta_{ij}^{\text{inter}} \right] + \sum_{j \neq i} XAB_{ij} \Delta_{ij}^{\text{intra}} = 0 \tag{5.137}$$

From this expression we define the function f_i, which we will use to determine the value of XA_i at equilibrium:

$$\Rightarrow f_i = (XA_i - 1) \frac{x_i V_m}{XA_i g} + x_i \sum_j x_j XA_j \frac{\Delta_{ij}^{\text{inter}}}{g} + \sum_{j \neq i} x_i V_m \frac{XAB_{ij}}{XA_i} \frac{\Delta_{ij}^{\text{intra}}}{g} = 0 \tag{5.138}$$

(We define f_i in this way because it is convenient for the calculations).

An expression for XAB_{ij} was given in equation (5.84) in section 5.5.1:

$$XAB_{ij} = \frac{XA_i}{1 + \frac{1}{V_m} \sum_n x_n XA_n \Delta_{jn}} = \frac{XA_i x_j \dfrac{V_m}{g}}{x_j \dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}} \tag{5.139}$$

$$\Rightarrow f_i = (XA_i - 1)\frac{x_i V_m}{XA_i g} + x_i \sum_j x_j XA_j \frac{\Delta_{ij}^{\text{inter}}}{g} + \sum_{j\neq i} \frac{x_i x_j \frac{V_m^2}{g} \frac{\Delta_{ij}^{\text{intra}}}{g}}{x_j \frac{V_m}{g} + x_j \sum_n x_n XA_n \frac{\Delta_{jn}}{g}} \tag{5.140}$$

The intramolecular association strength is given by (see section 5.5.3):

$$\Delta_{ij}^{\text{intra}} = W_{ij}\Delta_{ij}^{\text{inter}} \tag{5.141}$$

where W_{ij} is an end-to-end distribution function for the chain between sites i and j. If there for example is 4 links (bonds) between the sites i and j, then $W_{ij} = W_4$.

For associating components that cannot form intramolecular bonds, the monomer fraction, $X0$ is given in the same way as in the normal association theory:

$$X0_k = \prod_i^{\text{NS}_k} XA_i \tag{5.142}$$

while for components that can form intramolecular bonds the monomer fraction is given by

$$X0_k = XAB_{nm} \prod_{i\neq n,m}^{\text{NS}_k} XA_i \tag{5.143}$$

where n and m are the two sites that can form an intramolecular bond.

The Q function in (5.135) has the property that all derivatives with respect to any bonding state, X_α, is zero (as mentioned in section 2.4.1), which is very convenient when we need the derivatives of the Helmholtz free energy.

$$\frac{\partial Q}{\partial X_\alpha} = 0 \tag{5.144}$$

If we for example wish to calculate the contribution to the pressure from association we need the volume derivative of the Helmholtz free energy at equilibrium:

$$\frac{P^{\text{assoc}}}{RT} = -\frac{\partial Q_{\text{sp}}}{\partial V} \tag{5.145}$$

where the derivative of Q is calculated using the chain rule [40]

$$\frac{\partial Q_{\text{sp}}}{\partial V} = \left(\frac{\partial Q}{\partial V}\right)_X + \sum_k \sum_{\alpha\subset\Gamma_k} \frac{\partial Q}{\partial X_\alpha}\frac{\partial X_\alpha}{\partial V} = \left(\frac{\partial Q}{\partial V}\right)_X \tag{5.146}$$

where the last equality sign is true because of (5.144), and $\mathbf{X}$ refer to any (or all) bonding states. It is therefore only necessary to calculate the derivative of Q at constant $\mathbf{X}$. This is utilized in the derivation of the derivatives of Q and f_i with respect to volume, temperature and composition. All derivatives are listed in Appendix C.

5.6 Comparison of SAFT and LFHB

A general theory has now been developed for modeling intramolecular association with SAFT, though the monomer fraction has so far only been expressed for certain cases. It is not stated anywhere that the lattice fluid theory for intramolecular association [75] is limited to certain cases, but it has only been published for and applied to glycol ethers, and it is apparent from the derivation that they take advantage of the fact that there is only one proton-donor site on the molecule (similarly to what is done in this work in section 5.5.2).

The hydrogen-bonding contribution to the chemical potential for the associating component 1 for polyethoxyalcohol from LFHB is given by (see section 5.3):

$$
\begin{aligned}
\frac{G_{\mathrm{H}}}{kT} = \frac{N_1 \mu_{\mathrm{H},1}}{kT} &= N_{\mathrm{H}} + N_1 \ln\left(1 - \frac{N_{\mathrm{H}} + B}{N_1}\right) + N_1 \ln\left(1 - \frac{N_{11}}{N_1}\right) \\
&\quad + x N_1 \ln\left(1 - \frac{N_{12}}{x N_1 - B}\right)
\end{aligned}
\tag{5.147}
$$

To compare the SAFT and LFHB equations for inter- and intramolecular association we will look at the case of 3 sites; one proton-donor site of type 1 = site A, one proton-acceptor of type 1 = site B and one proton-acceptor of type 2 = site C (a glycol ether like 2-methoxyethanol). This corresponds to $x = 1$ in (5.147). In order to compare the equations we will introduce the nomenclature of SAFT in (5.147). The expressions in the parentheses are recognised to be:

The fraction of A sites not bonded (1 - the number of bonds involving a site A/number of A sites):

$$
1 - \frac{N_{\mathrm{H}} + B}{N_1} = X_{A_1}
\tag{5.148}
$$

the fraction of B sites not bonded (1 - the number of bonds involving a site B/number of B sites):

$$
1 - \frac{N_{11}}{N_1} = X_{B_1}
\tag{5.149}
$$

and the fraction of C sites not bonded intermolecularly given that they are not bonded intramolecularly (1 - number of C sites bonded intermolecularly/number of C sites not bonded intramolecularly):

$$1 - \frac{N_{12}}{N_1 - B} = X_{C_1}^{\text{inter'}} \tag{5.150}$$

The number of intermolecular bonds, N_{H} can be expressed in different ways with the SAFT nomenclature, for example as

$$N_{\text{H}}/N_1 = \frac{1}{2} \sum_{A \in \Gamma_1} \left(1 - X_{A_1}^{\text{inter}}\right) \tag{5.151}$$

This is inserted in (5.147) and we divide through with N_1:

$$\frac{G_{\text{H}}}{N_1 kT} = \frac{\mu_{\text{H},1}}{kT} = \frac{1}{2} \sum_{A_1 \in \Gamma_1} \left(1 - X_{A_1}^{\text{inter}}\right) + \ln\left(X_{A_1} X_{B_1} X_{C_1}^{\text{inter'}}\right) \tag{5.152}$$

B sites can only form intermolecular bonds, and therefore $X_{B_1} = X_{B_1}^{\text{inter'}}$. For site A we use that according to (5.71) $X_{A_1} = X_{A_1}^{\text{inter'}} X_{A_1}^{\text{intra}} = X_{A_1}^{\text{inter'}} X_{0_1}^{\text{intra}}$, where the last equality sign follows from (5.82).

From (5.80) and (5.81) we have

$$X_0^{\text{intra}} \prod_{A \in \Gamma} X_A^{\text{inter'}} = X_0 \tag{5.153}$$

which we can use to simplify (5.152)

$$\frac{G_{\text{H}}}{N_1 kT} = \frac{\mu_{\text{H},1}}{kT} = \frac{1}{2} \sum_{A_1 \in \Gamma_1} \left(1 - X_{A_1}^{\text{inter}}\right) + \ln\left(X_{0_1}\right) \tag{5.154}$$

Under the assumption that G_{H}/N_1 and A^{assoc}/N_1 are independent of composition, equation(5.154) is identical to the expression for SAFT in (5.69). This assumption is implicit in LFHB because of the equality of $G_{\text{H}} = N_1\mu_{\text{H},1}$ in (5.147).

There is no assumption of composition independency in the SAFT equations for inter- and intramolecular association presented here, and it is not required because it, when using the approach from Michelsen and Hendriks [40], is straight forward to obtain all the derivatives (though the equations in the case of both inter- and intramolecular association are rather extensive).

The same comparison can be done for the chemical equilibrium constants in the two theories. From Missopolinou et al. [75] we have

$$\frac{B(xN_1 - B)}{(xN_1 - B - N_{12})N_{10}x} = c\exp\left(-\frac{G_B^0}{kT}\right) = K_B \tag{5.155}$$

$$\frac{N_{11}}{(N_1 - N_{11})N_{10}} = \frac{\tilde{\rho}}{rN}\exp\left(-\frac{G_{11}^0}{kT}\right) = \frac{K_{11}}{N} \tag{5.156}$$

$$\frac{N_{12}}{((xN_1 - B - N_{12})N_{10}} = \frac{\tilde{\rho}}{rN}\exp\left(-\frac{G_{12}^0}{kT}\right) = \frac{K_{12}}{N} \tag{5.157}$$

where K_{11} is the equilibrium constant for intermolecular association between two hydroxyl groups, K_{12} is for intermolecular association between a hydroxyl group and an ether oxygen, and K_B is for intramolecular association.

If the SAFT nomenclature is introduced in (5.155) we get

$$K_B = \frac{(1 - X_0^{\text{intra}})X_0^{\text{intra}}}{X_C X_A} \quad \Rightarrow \quad X_0^{\text{intra}} = 1 - K_B\frac{X_A X_C}{X_0^{\text{intra}}} = 1 - K_B X_{AC} \tag{5.158}$$

which is identical to (5.75) for a system of this type if $K_B = \Delta_{AC}^{\text{intra}}$.

Similarly for (5.156)

$$K_{11} = \frac{1 - X_B}{X_B X_A} \quad \Rightarrow \quad X_B = \frac{1}{1 + X_A K_{11}} \tag{5.159}$$

This is identical to (5.71) for B if $K_{11} = \rho\Delta_{BA}^{\text{inter}}$ since $X_B = X_B^{\text{inter'}}$ in this case.

From (5.157) we get:

$$K_{12} = \frac{1 - X_C^{\text{inter}}}{X_C X_A} = \frac{X_C^{\text{intra}} - X_C}{X_C X_A} \quad \Rightarrow \quad X_C^{\text{intra}} - X_C = K_{12} X_C X_A$$

$$\Rightarrow \quad \frac{X_C}{X_C^{\text{intra}}} = X_C^{\text{inter'}} = \frac{1}{1 + X_A K_{12}} \tag{5.160}$$

which is the corresponding equation of (5.71) for site C if $K_{12} = \rho\Delta_{CA}^{\text{inter}}$.

It is not surprising that identical results are obtained for Approach #1 with SAFT and LFHB since while the SAFT approach counts sites, the LFHB approach counts bonds, and this should give the same result. The two models however use different pure component parameters.

5.7 Chapter summary

This chapter has presented previous work on intramolecular association as well as the derivation of a new general theory.

Experimental data was presented for two cases to illustrate the importance of intramolecular association; dilute solutions of glycol ether in a non-associating solvent, and telechelic polymers. Spectroscopy data was shown for a glycol ether in n-hexane, and the data showed that large amounts of intramolecular hydrogen bonds are present at low glycol ether concentrations. The data also showed that while the amount of intermolecular association decreases with decreasing glycol ether concentration, the amount of intramolecular association increases. Cloud-point pressure curves for three telechelic polymers (blank, monohydroxy and dihydroxy polyisobutylene (PIB)) in polar and non-polar solvents were discussed, and it was argued that the results for dihydroxy PIB in polar solvents can only be explained by the formation of intramolecular hydrogen bonds.

The previous work by Sear and Jackson and by Ghonasgi, Perez and Chapman on modeling intramolecular association of chains with two associating sites with SAFT has been presented and discussed, and a comparison showed that the resulting equations from the two approaches are equivalent.

The theory for modeling intramolecular association with a lattice theory was also presented. While the SAFT theory so far has been limited to chains with two sites, the lattice theory can be applied to polyethoxyalcohols with one hydroxyl group and one or more ether oxygens.

A general theory for inter- and intramolecular association in the frame of SAFT was developed based on the previous work, though the monomer fraction has so far only been derived for certain cases. The theory was derived using two approaches similar to the ones used in the previous work. It was found that both methods have advantages, and each method provides expressions not available with the other method. The first approach gave all the expressions needed for calculating the contribution from association to the Helmholtz free energy at equilibrium, and the second approach gave an expression for the Helmholtz free energy with the property that the derivatives with respect to any bonding state is zero, which is very useful for the calculation of the derivatives of the Helmholtz free energy.

The lattice theory and the new SAFT theory for intramolecular association were

then compared, and shown to give identical expressions for the contribution from association to the chemical potential of an intramolecularly associating compound (a glycol ether), under the assumption that the Gibbs energy is proportional to the content of the associating compound (at equilibrium).

With the new SAFT theory for intramolecular association both lattice theories and SAFT can be used for glycol ethers (or polyethoxyalcohols).

CHAPTER 6

Glycol ethers

6.1 Introduction

Glycol ethers are non-ionic surfactants with a variety of industrial applications, including a number of applications in the petroleum industry. Glycol ethers contain one hydroxyl group and one or more ether oxygens, and they are the simplest real compounds which can form intramolecular hydrogen bonds. Glycol ethers are therefore interesting candidates for testing the new intramolecular theory for SAFT type equations of state presented in the previous chapter.

As mentioned in section 5.3 lattice theory has been applied to model polyethoxyalcohols, including glycol ethers, with explicit treatment of inter- as well as intramolecular association [75, 76, 85, 86], similarly to the new theory. CPA was applied for glycol ethers by Garrido et al. [89], but only the intermolecular association was accounted for in that work. No work has been done for these compounds with sPC-SAFT, so in order to evaluate the performance of the new intramolecular theory it was necessary to apply "regular" sPC-SAFT (sPC-SAFT without intramolecular association) as well for comparison.

Three glycol ethers are considered in this work: 2-methoxyethanol (C_1E_1), 2-ethoxy-ethanol (C_2E_1) and 2-butoxyethanol (C_4E_1). The structures of the three glycol ethers are shown in Figure 6.1. The multifunctionality of glycol ethers gives the option of several association schemes. Different association schemes

have been used for modeling glycol ethers with SAFT type theories; Garrido et al. [89] applied both the 2 (1:1) and 3 (2:1) schemes, while Garcia-Lisbona et al. [90] used a complex scheme with three sites for each ether oxygen and three sites for the hydroxyl group, where some sites are only allowed to cross-associate, while others can self- as well as cross-associate. The 3 (2:1) scheme (two sites for the hydroxyl group and one site for the ether oxygen) is the simplest reasonable scheme for which intramolecular association is possible, and only this scheme will be used in this work. A similar definition of the associating sites is used in the work with lattice theories for polyethoxyalcohols [75, 76, 85, 86].
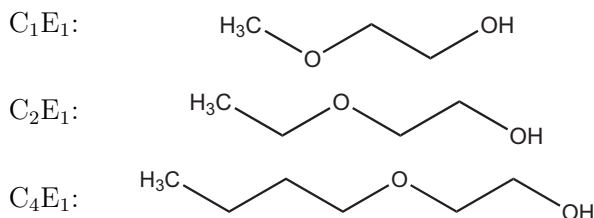
Figure 6.1: Structures of C_1E_1, C_2E_1 and C_4E_1.

This chapter will present parameters for the glycol ethers and phase equilibrium results for glycol ether mixtures with sPC-SAFT with and without inclusion of intramolecular association.

6.2   Parameters

Two parameter sets have been estimated for each of the three glycol ethers; one set for regular sPC-SAFT, and one for sPC-SAFT plus intramolecular association. sPC-SAFT plus intramolecular association means that the new association term from chapter 5, where intramolecular association is included, is used instead of the usual association term from sPC-SAFT, while the remaining terms are the same for the two models. Both models have the same five adjustable pure component parameters, but intramolecularly associating compounds have an additional parameter, W_m (an end-to-end distribution function for the chain), in the association term. The W_m parameter is in this work not considered to be an adjustable parameter, but is determined from equation (5.134). W_m depends on the number of links (bonds), m (not identical to the number of segments) between the intramolecularly associating sites and on the segment diameter. The number of bonds between the ether oxygen and the hydroxyl hydrogen in the three glycol ethers considered in this work is 4, giving the following value of the end-to-end

distribution function:

$$W_4 = 0.0248/\sigma^3$$

This value of W_m is used in all calculations with intramolecular association in this chapter.

The pure component sPC-SAFT parameters were obtained by fitting DIPPR [51] correlations of pure component vapor pressure and liquid density. The parameters for the three glycol ethers are listed in Table 6.1. 3inter indicates parameter sets for sPC-SAFT without intramolecular association with the 3 (2:1) scheme for the glycol ether. 3intra indicates sets for sPC-SAFT plus intramolecular association also with the 3 (2:1) association scheme for the glycol ether.

Table 6.1: Pure component sPC-SAFT parameters for glycol ethers, temperature interval used in the estimation and absolute relative deviations (ARD%) between sPC-SAFT and DIPPR correlations in the temperature range of the estimations.

	σ [Å]	ε [K]	m	ε^{AB} [K]	κ^{AB}	T [K]	ARD% P^{sat}	ρ^L
C_1E_1 3inter	2.958	187.69	3.956	1698.3	0.4975	282-508	2.31	0.21
C_1E_1 3intra	2.779	187.97	4.768	1546.9	0.5603	310-508	1.71	0.30
C_2E_1 3inter	2.999	189.56	4.693	1289.2	0.9179	285-512	2.28	0.24
C_2E_1 3intra	2.921	187.95	5.055	1465.7	0.6375	313-512	1.74	0.28
C_4E_1 3inter	3.518	257.63	4.194	1206.7	0.0446	317-571	0.39	0.23
C_4E_1 3intra	3.525	258.10	4.173	1239.4	0.0405	317-571	0.38	0.24
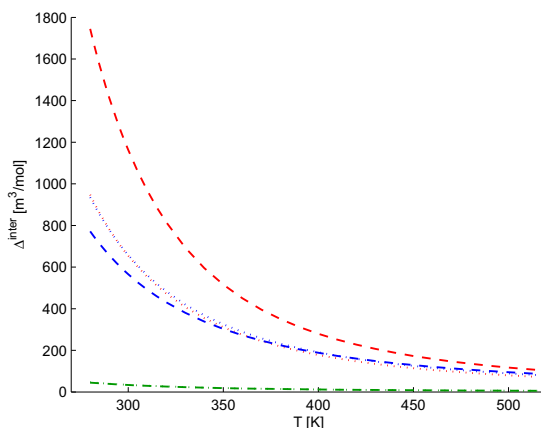
Figure 6.2: Intermolecular association strength for C_1E_1, C_2E_1 and C_4E_1. Dashed lines are with the inter sets and dotted lines are with the intra sets. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.

The simplest way of comparing different association parameters is to compare the

association strength. Figures 6.2 and 6.3 show the intermolecular and intramolecular association strength respectively versus temperature for the six glycol ether parameter sets shown in Table 6.1. For simplicity the association strengths are calculated for the radial distribution function, $g = 1$, and the intermolecular association strength is per mole.
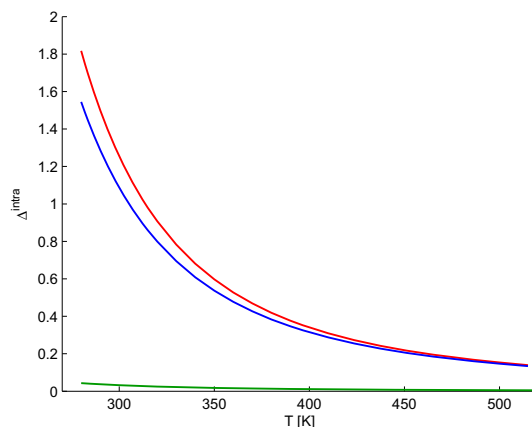
Figure 6.3: Intramolecular association strength for C_1E_1, C_2E_1 and C_4E_1. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.

As seen from Figure 6.2 while the intermolecular association strengths for C_1E_1 and C_2E_1 with the inter sets are rather different, the intermolecular association strengths with the intra sets for the two compounds are very similar, and lies in between the inter curves. The intramolecular association strengths of the two compounds are also very similar as seen from Figure 6.3. It is clear from the figures that the association strengths for C_4E_1 are much smaller than for the other compounds, and the intermolecular association strengths for that compound are for clarity shown alone in Figure 6.4.

The two parameter sets for C_4E_1 are very similar, and the intermolecular association strengths for the two sets are also very similar. Because of the small association strengths, association will not have as big an influence on the phase equilibrium results for this glycol ether, compared to C_1E_1 and C_2E_1, and the inclusion of intramolecular association is therefore not expected to influence the results for C_4E_1 significantly.
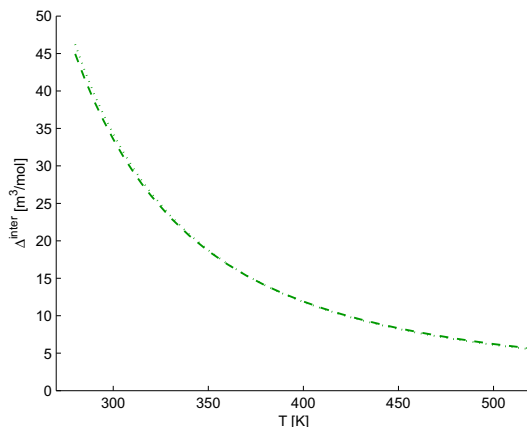
Figure 6.4: Intermolecular association strength for C_4E_1. The dashed line is with the inter set and the dotted line is with the intra set.

6.3 Extent of hydrogen bonding

Another way of comparing the association of the three compounds, and of the 3inter versus 3intra sets, is to calculate the amount of inter- and intramolecular hydrogen bonds in a mixture of a glycol ether with a non-associating compound. Figure 6.5 shows the results with sPC-SAFT at $T = 300$ K and $P = 1$ atm for C_xE_1 - hexane with each of the parameter sets at low glycol ether concentrations, while Figure 6.6 shows the results in the entire concentration range. As we will see in section 6.4, C_1E_1 - hexane is not completely miscible at this temperature and pressure, but since this is a qualitative comparison of the sets the LLE has not been taken into account. The results are for a single liquid phase at the specified conditions.

The results with 3intra for C_1E_1 and C_2E_1 are again very similar. The amount of intermolecular bonds predicted with the 3inter parameters for C_1E_1 is larger than for C_2E_1, but the same trends are observed for the two compounds. There is a big difference in the amount of intermolecular bonds between 3inter and 3intra at low glycol ether concentrations for the two compounds, but as the glycol ether concentration increases the amount of intermolecular bonds predicted with the 3intra parameters approaches the amount of bonds predicted with the 3inter parameters. There is a large amount of intramolecular bonds at low glycol ether concentrations, where there is little competition from intermolecular interactions, because of the large distance between glycol ether molecules. As the concentration

increases the probability of being within bonding range of another glycol ether molecule increases, and so does the amount of intermolecular association, while the amount of intramolecular association decreases.
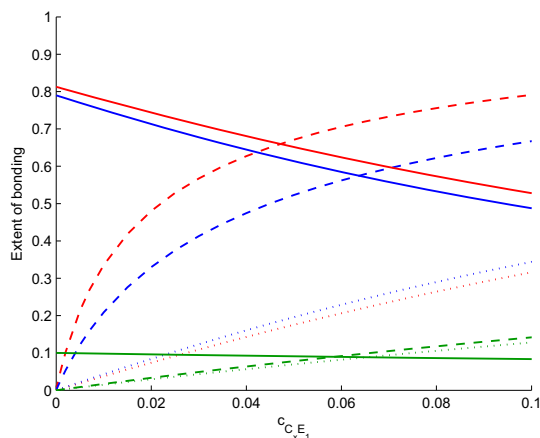
Figure 6.5: Amount of inter and intramolecular bonds in C_xE_1 - hexane, low C_xE_1 concentrations. Dashed lines are intermolecular association strength with the inter sets. Dotted lines are intermolecular association strength with the intra sets. Full lines are intramolecular association strength with the intra sets. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.
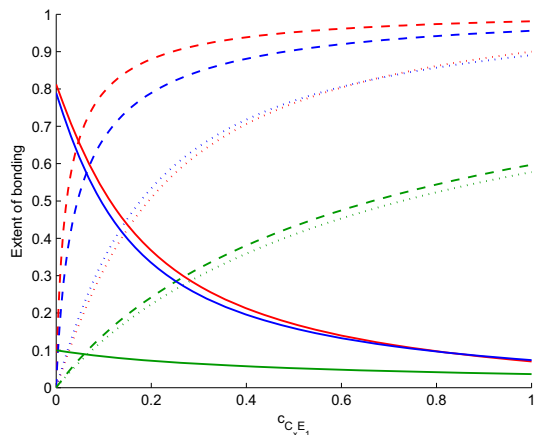
Figure 6.6: Amount of inter and intramolecular bonds in C_xE_1 - hexane. Dashed lines are intermolecular association strength with the inter sets. Dotted lines are intermolecular association strength with the intra sets. Full lines are intramolecular association strength with the intra sets. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.

There is only a small difference between the amount of intermolecular bonds predicted with 3inter and 3intra for C_4E_1, and the amount of bonds for C_4E_1 is in general significantly smaller than for C_1E_1 and C_2E_1. Because of the smaller amounts of intermolecular association, the amount of intramolecular association

is not effected as significantly by the concentration for C_4E_1 as for the other two glycol ethers.

6.4 Phase equilibrium results

This section presents phase equilibrium results for glycol ethers in self-associating and cross-associating mixtures with sPC-SAFT, with and without accounting for intramolecular association. Additional results are shown in Appendix B. The parameters for other compounds considered in this chapter are listed in Appendix A.

6.4.1 Self-associating mixtures

We will first consider binary mixtures of a glycol ether and an inert (non-associating) compound. Figures 6.7 and 6.8 show VLE and LLE results for C_1E_1 - hexane.
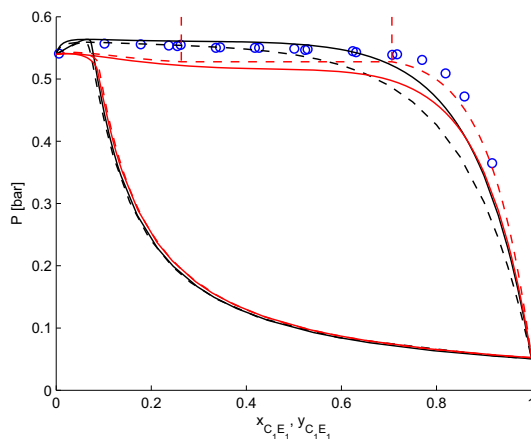
Figure 6.7: C_1E_1 - hexane VLE at $T = 323.15$ K. Black lines are sPC-SAFT with 3inter for C_1E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = 0.007$. Red lines are sPC-SAFT with 3intra for C_1E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.0054$. Experimental data: Dolch et al. [91]

The 3inter parameters do not predict LLE for this system, whereas 3intra predicts a too high upper critical solution temperature (UCST). It is not possible with either set to correlate the very flat upper part of the immiscibility area. If an interaction parameter is fitted to match the UCST, the estimated immiscibility area becomes too small (narrow) with both sets. The results with 3intra deviate

similarly for the two phases, while the results with 3inter are shifted to lower glycol ether concentrations. The VLE and LLE are very close in temperature, and since the 3intra parameters overestimate the UCST they predict VLLE at $T = 323.15$ K.
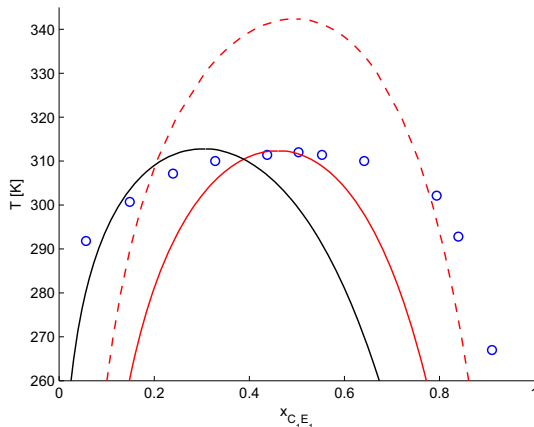
Figure 6.8: C_1E_1 - hexane LLE at $P = 1.013$ bar. The black line is sPC-SAFT with 3inter for C_1E_1 with $k_{ij} = 0.007$. Red lines are sPC-SAFT with 3intra for C_1E_1; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.0054$. Experimental data: Bijl et al. [92]

The same k_{ij} values are used for VLE and LLE for C_1E_1 - hexane, but it is not possible to match all the VLE data points with either parameter set even with a k_{ij} optimized for VLE. 3inter can only match the data points at medium and low glycol ether concentrations, while 3intra matches the glycol ether rich part well, but is disturbed by the VLLE estimation. Similar results are obtained for C_1E_1 - heptane (figures are shown in Appendix B).
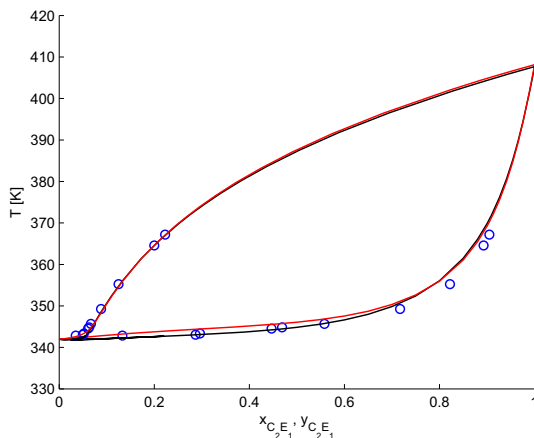
Figure 6.9: C_2E_1 - hexane VLE at $P = 1.013$ bar. Black lines are sPC-SAFT with 3inter for C_2E_1 and $k_{ij} = 0$. Red lines are sPC-SAFT with 3intra for C_2E_1 and $k_{ij} = 0$. Experimental data: Suryanarayana and Van Winkle [93].

Contrary to C_1E_1, C_2E_1 is miscible with hexane. Figure 6.9 shows predicted VLE results with sPC-SAFT for that mixture. As seen from the figure, sPC-SAFT with both parameter sets gives very satisfactory predictions for this system, and no k_{ij} is needed to correlate the data.

VLE results are shown for C_2E_1 - octane in Figure 6.10. Both parameter sets predict the azeotrope of this mixture, though both sets predict an azeotrope temperature a few degrees lower than the experimental value. The error with 3inter is twice the error with 3intra. It is possible with both sets to correlate the data including the azeotrope satisfactorily by fitting a k_{ij}, though slightly better results are obtained with 3intra than with 3inter.
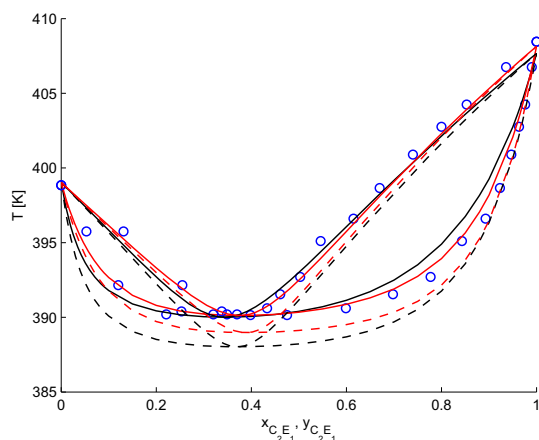
Figure 6.10: VLE calculations of C_2E_1 - octane. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.013$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.007$. Experimental data: Murti and Van Winkle [94].

LLE data is available for C_2E_1 - dodecane/tetradecane/hexadecane. Figure 6.11 shows the results for C_2E_1 - dodecane, while results for the tetradecane and hexadecane mixtures are shown in Appendix B. As seen in Figure 6.11 both sets predict LLE for this system, and both overestimate the UCST. The results with an interaction parameter fitted to match the UCST are similar to the results for C_1E_1 - hexane. The estimated immiscibility areas are too narrow, and the 3inter results are shifted towards lower glycol ether concentrations compared to the 3intra results, which lie in the center of the experimental immiscibility area. Similar results are obtained for C_2E_1 - tetradecane/hexadecane.
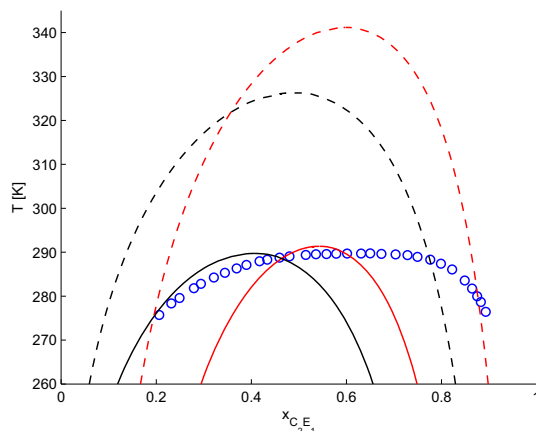
Figure 6.11: LLE calculations of C_2E_1 - dodecane. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.0037$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed line: $k_{ij} = 0$, full line: $k_{ij} = -0.0052$. Experimental data: Rubio et al. [95]

The results with sPC-SAFT for C_4E_1 - octane are nearly identical with the two parameter sets, and almost indistinguishable. Figure 6.12 shows the results with both sets. As seen from Figure 6.12 the predicted results are not very good for this system, but sPC-SAFT correlates the data reasonably well with an optimal k_{ij}.
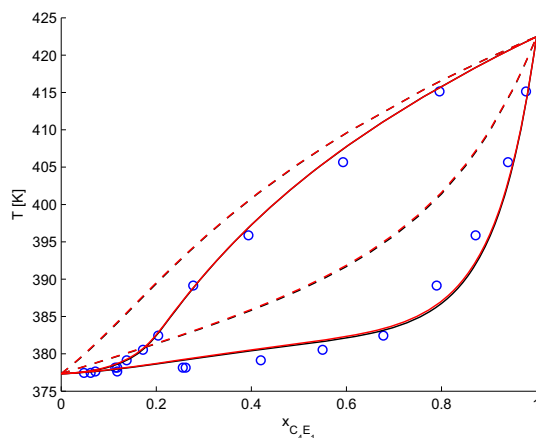
Figure 6.12: VLE calculations of C_4E_1 - octane at $P = 0.533$ bar. Black lines are sPC-SAFT with 3inter for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = 0.037$. Red lines are sPC-SAFT with 3intra for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = 0.037$. Experimental data: Komatsu et al. [96]

6.4.2 Cross-associating mixtures

Because of the high density of association sites in cross-associating mixtures, there is not expected to be a large amount of intramolecular bonds. This section will investigate how the different parameter sets perform for this type of systems. The ECR combining rule was used for all systems.
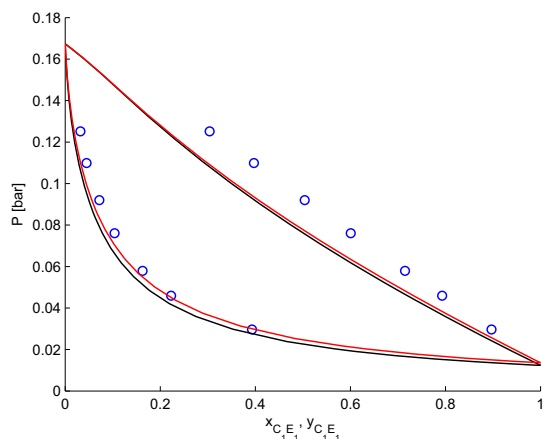
Figure 6.13: VLE calculations of C_1E_1 - methanol at $T = 298.15$ K. Lines are sPC-SAFT with $k_{ij} = 0$ and the parameters for methanol from this work. Black lines are with 3inter for C_1E_1 and red lines are with 3intra for C_1E_1. Experimental data: Martin et al. [97]
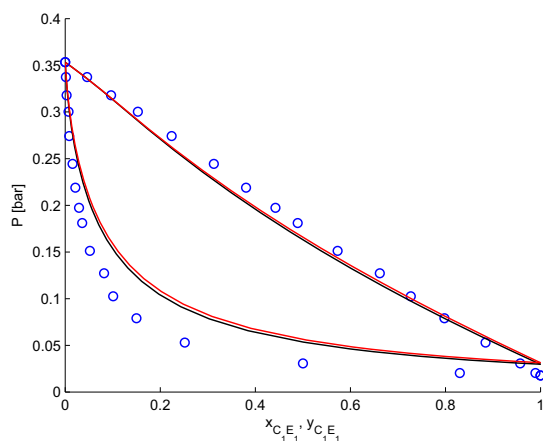
Figure 6.14: VLE calculations of C_1E_1 - methanol at $T = 313.15$ K. Lines are sPC-SAFT with $k_{ij} = 0$ and the parameters for methanol from this work. Black lines are with 3inter for C_1E_1 and red lines are with 3intra for C_1E_1. Experimental data: Antosik et al. [98]

Data is available for C_1E_1 and C_2E_1 with methanol, but there seems to be some discrepancy in the data. Figures 6.13 and 6.14 show the results for C_1E_1 - methanol with sPC-SAFT with the methanol parameters from this work (Chapter 3), and 3inter and 3intra for C_1E_1, at two different temperatures. The methanol parame-

ters were given in section 3.2. Both figures are with $k_{ij} = 0$. The data is from two different papers [97, 98], and since data is not available at the same temperature from the two papers, the data cannot be compared directly, but the sPC-SAFT results implicitly show a big disagreement between the data. There is little difference between the results with 3inter and 3intra for C_1E_1. To investigate the influence of the parameters for the other associating compound Figure 6.15 shows the results at $T = 313.15$ K with the parameters for methanol from Gross and Sadowski [21].
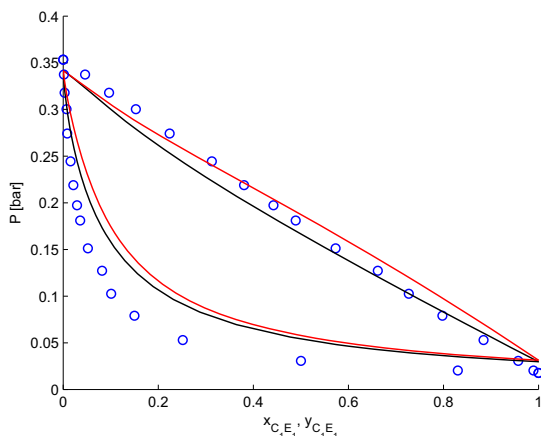
Figure 6.15: VLE calculations of C_1E_1 - methanol at $T = 313.15$ K. Lines are sPC-SAFT with $k_{ij} = 0$ and the parameters for methanol from Gross and Sadowski [48]. Black lines are with 3inter for C_1E_1 and red lines are with 3intra for C_1E_1. Experimental data: Antosik et al. [98]

A comparison between Figures 6.14 and 6.15 shows that there is a much bigger difference between the 3inter and 3intra parameters for C_1E_1, when the parameters from Gross and Sadowski [48] are used for methanol compared to the parameters from this work. Thus, the choice of parameters for the other associating compound in a cross-associating mixture seems to have as big an influence on the results as including intramolecular association for this kind of systems.

Data is also available for C_1E_1 - ethanol and C_1E_1 - propanol. The results for the propanol system are shown in Figures 6.16 and 6.17 and the results for the ethanol system are shown in Appendix B. The generalized alkanol parameters from Grenner et al. [22] are used for ethanol and propanol.

Figure 6.16 shows the results for C_1E_1 - propanol with $k_{ij} = 0$, and as seen from this figure, the 3intra set gives a better prediction for this mixture than 3inter. Both sets, however, overestimate the cross-attractions between the two compounds, and need a small positive k_{ij} to match the data points. Figure 6.17

shows the results with an optimal k_{ij}, and as seen from the figure both sets correlate the system very satisfactorily. 3inter needs a larger k_{ij} than 3intra because of the larger error in the predictions.
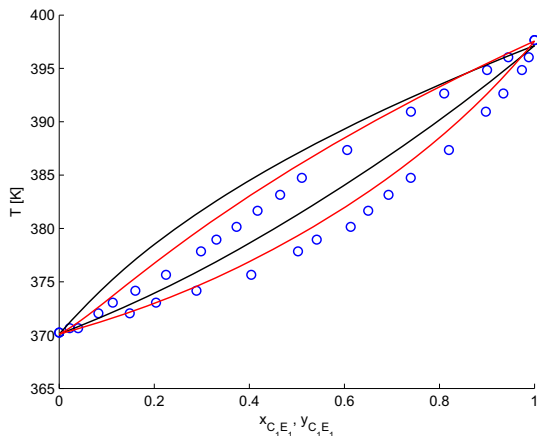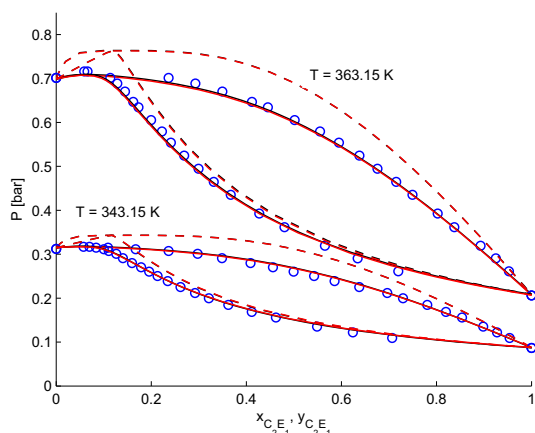

Figure 6.16: VLE calculations of C_1E_1 - propanol. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = 0$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = 0$. Experimental data: Chandak et al. [99].
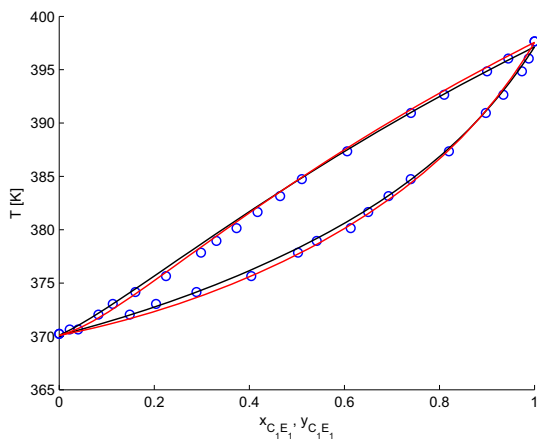

Figure 6.17: VLE calculations of C_1E_1 - propanol. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = 0.025$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = 0.012$. Experimental data: Chandak et al. [99].

Figures 6.18 and 6.19 show the results for C_1E_1 - water with $k_{ij} = 0$ and fitted k_{ij} respectively at $T = 343.15$ K and $T = 363.15$ K. The 4 (2:2) parameters from Grenner et al. [100] were used for water. sPC-SAFT performs satisfactorily for this system, and the 3inter and 3intra sets perform similarly. Both sets match the experimental data well with a small negative temperature independent interaction parameter. The 3inter set gives slightly better results with $k_{ij} = 0$ than

3intra, whereas the results with 3intra with a fitted k_{ij} are slightly better than with 3inter.
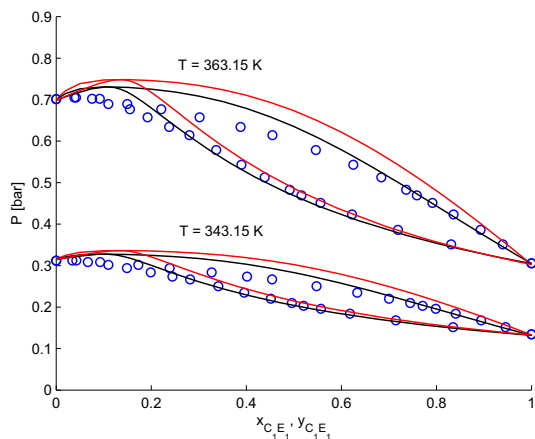
Figure 6.18: VLE calculations of C_1E_1 - water. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = 0$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = 0$. Experimental data: Chiavone-Filho et al. [101]

The sPC-SAFT results for C_2E_1 - water are shown in Figures 6.20 and 6.21. The figures show the results with both 3inter and 3intra for C_2E_1, but the results with the two sets are indistinguishable. As seen from the figures, sPC-SAFT very satisfactorily models this system, and a single k_{ij} is sufficient to match the experimental data, including the azeotrope, at all temperatures and pressures investigated here.
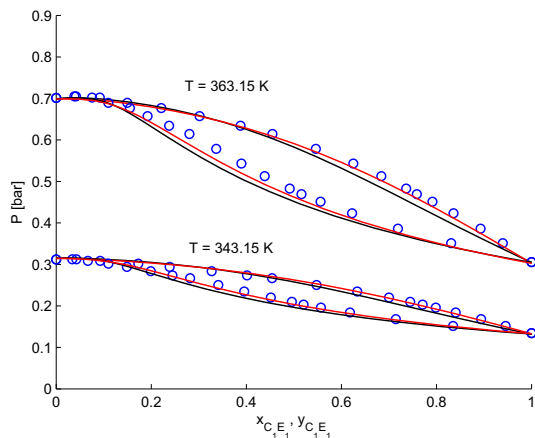
Figure 6.19: VLE calculations of C_1E_1 - water. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = -0.025$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = -0.035$. Experimental data: Chiavone-Filho et al. [101]

Figure 6.20: VLE calculations of C_2E_1 - water. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.035$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.035$. Experimental data: Chiavone-Filho et al. [101].
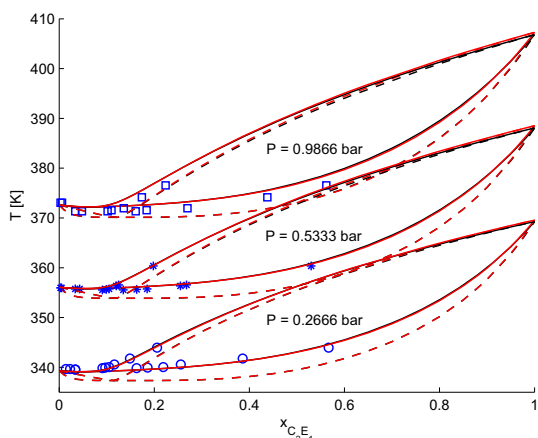
Figure 6.21: VLE calculations of C_2E_1 - water. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.035$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.035$. Experimental data: Boublik and Kuchynka [102].

The last cross-associating mixture with a glycol ether to be considered here is C_4E_1 - water. This is a very interesting mixture, both because of its industrial applications and because it exhibits closed-loop LLE. The closed-loop LLE is a result of the competition between energetic and entropic effects. At temperatures above UCST the system will minimize its free energy by maximizing its compositional and orientational entropy. At intermediate temperatures the entropy is less important, and the system will consequently try to minimize the enthalpy. The system will therefore split into two immiscible liquid phases because of the weak van der Waals forces between unlike molecules. At temperatures below

the lower critical solution temperature (LCST) cross-association becomes strong enough to overcome the unfavorable enthalpy and orientational entropy and to keep the mixture in one miscible phase [90]. Since the entropic effects are essential for the formation of closed-loop LLE, the highly anisotropic hydrogen bonds must be treated in the theory in order to describe the phase behavior. An EoS like sPC-SAFT is therefore capable of modeling closed-loop LLE.
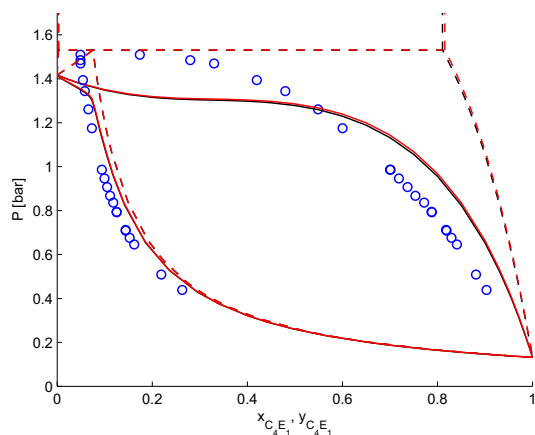
Figure 6.22: VLE calculations of C_4E_1 - water at $T = 383.15$ K. Black lines are sPC-SAFT with 3inter for C_4E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.1$. Red lines are sPC-SAFT with 3intra for C_4E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.1$. Experimental data: Schneider and Wilhelm [103].
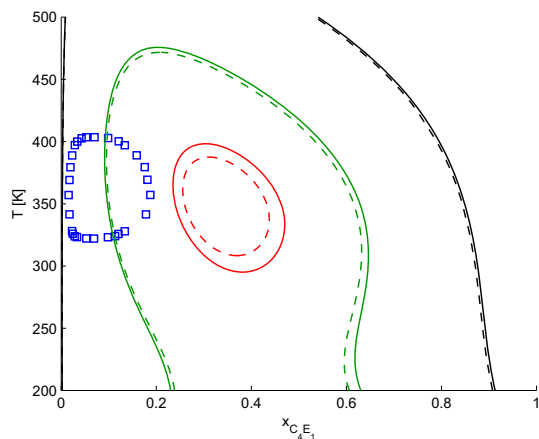
Figure 6.23: LLE calculations of C_4E_1 - water at $P = 10.13$ bar. Dashed lines are sPC-SAFT with 3inter for C_4E_1. Full lines are sPC-SAFT with 3intra for C_4E_1. Black lines are with $k_{ij} = 0$, green lines are with $k_{ij} = -0.07$ and red lines are with $k_{ij} = -0.092$. Experimental data: Schneider [104], taken from Knudsen et al. [105]

Figure 6.22 shows the VLE results and Figure 6.23 the LLE results with sPC-SAFT for this mixture. The VLE results with the 3inter and 3intra sets are

indistinguishable, but the LLE results differ somewhat, when the same k_{ij} is used for both sets. The $k_{ij} = -0.092$ for LLE was fitted to give an immiscibility area of approximately the same size as the experimental data shows.

It is clear from Figures 6.22 and 6.23 that sPC-SAFT with the 3inter and 3intra parameters are incapable of correlating the data points for this mixture. The VLE results are very poor, and the use of an interaction parameter does not improve the results (for either parameter set). The experimental data shows VLLE at $T = 383.15$ K at low glycol ether concentrations but sPC-SAFT with both sets predicts a much wider VLLE area. Figure 6.23 shows that both sets significantly overestimate the immiscibility area both in temperature and composition, and fitting an interaction parameter is not enough to match the experimental data points. It is however possible to get a good match to the UCST and LCST with the same k_{ij}. The fact that both sets predict a significantly larger immiscibility area than what the experimental data shows could be a result of the small association parameters for C_4E_1 estimated in this work. More cross-association will presumably increase the miscibility between C_4E_1 and water.

Among the applications of glycol ethers in the petroleum industry is enhanced oil recovery (EOR) by chemical flooding of the oil reservoirs. Since the reservoir pressures are usually significantly higher than atmospheric pressure, it is important to know how the efficiency of the flooding depends on pressure. As a step in that investigation it is also of importance to know how the miscibility of C_4E_1 and water is influenced by pressure. Schneider [104] has presented extrapolated LLE data for this mixture at different pressures. Figure 6.24 shows the results with sPC-SAFT with 3intra at $P = 10$ atm, $P = 200$ atm and $P = 600$ atm.

As seen from Figure 6.24 sPC-SAFT with the 3intra parameters predicts qualitatively the correct pressure dependency, but the experimental data shows a stronger pressure dependency than the one predicted with sPC-SAFT. Moreover the predicted LLE area shifts towards lower temperatures as the pressure increases, compared to the experimental data.

The results presented in this section showed that a significant improvement is obtained in the predicted LLE results for C_1E_1 - alkane mixtures, when intramolecular association is included. The same improvement is not seen for C_2E_1, where the predicted results are more similar with and without intramolecular association than for C_1E_1. Neither of the models are capable of matching the data points with a single binary interaction parameter. The VLE results of the immiscible

mixtures are generally disturbed by VLLE predictions. Good results are obtained
with both theories for VLE of completely miscible self-associating mixtures, ei-
ther with $k_{ij} = 0$ or a small k_{ij} value. The results with intramolecular association
are slightly better than the results without intramolecular association for these
mixtures.
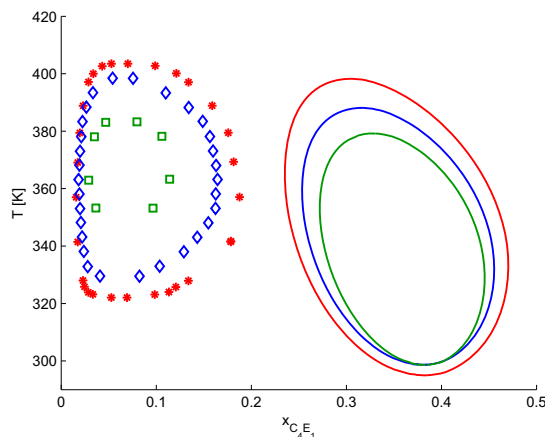
Figure 6.24: LLE calculations of C_4E_1 - water. Lines are sPC-SAFT with 3intra for C_4E_1
with $k_{ij} = -0.092$. Red lines are $P = 10$ atm, blue lines are $P = 200$ atm and green lines are
$P = 600$ atm. Experimental data: Schneider [104], taken from Knudsen et al. [105]; 10 atm ($*$),
200 atm ($\diamond$) and 600 atm ($\square$).

Little difference was seen between sPC-SAFT with and without intramolecular
association for cross-associating mixtures of C_1E_1, while indistinguishable results
were obtained for C_2E_1. The results for C_4E_1 are in all cases similar with and
without intramolecular association because of the very similar parameters, and
weak association.

In general sPC-SAFT (with or without intramolecular association) gives satis-
factory VLE results for miscible mixtures, while poorer results are obtained for
immiscible mixtures. sPC-SAFT is not capable of modeling the mixture of C_4E_1
- water, with the parameters presented in section 6.2.

6.5   Comparison with other SAFT type theories

As mentioned in the beginning of this chapter, Garrido et al. [89] applied the CPA
EoS to model glycol ether mixtures. This section will present a comparison be-
tween the results with CPA and sPC-SAFT (without intramolecular association)
for four mixtures. The figures with CPA results shown in this section were taken

from Garrido [106]. For CPA the choice of combining rule for cross-associating systems has a significant influence on the phase equilibrium results. Garrido et al. [89] applied both the ECR and CR-1, but ECR gave better results in most cases, and only results with ECR will therefore be shown here. Garrido et al. [89] moreover applied both the 2 (1:1) scheme and the 3 (2:1) scheme. Results are shown for both schemes or the scheme which gives better results.

Figure 6.25 shows the results with CPA for C_1E_1 - hexane. By comparing the red line in Figure 6.25 with the black line in Figure 6.8 we can see that CPA and sPC-SAFT perform similar for this system. Neither model is capable of correlating the whole LLE area, but it is possible with both models with a fitted k_{ij} to match the UCST and the composition of the hexane rich phase.
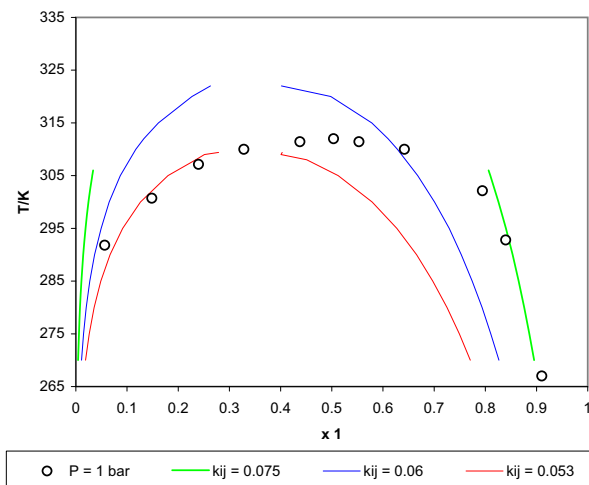

Figure 6.25: LLE calculations of C_1E_1 - hexane at $P = 1.013$ bar. Lines are CPA with the 2 (1:1) scheme for C_1E_1. Experimental data: Bijl et al. [92]
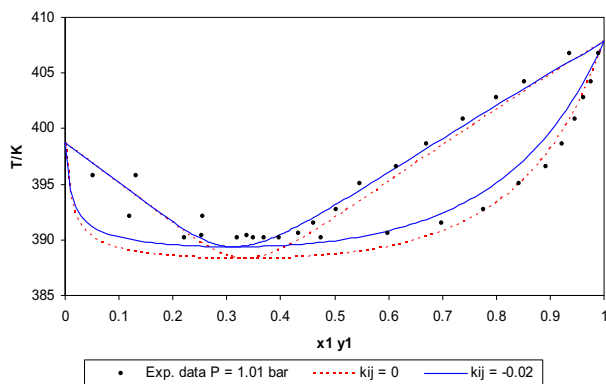
Figure 6.26: VLE calculations of C_2E_1 - octane at $P = 1.013$ bar. Lines are CPA with the 2 (1:1) or 3 (2:1) scheme for C_2E_1 (the lines coincide). Experimental data: Murti et al. [94]

Figure 6.26 shows the CPA results for C_2E_1 - octane. A comparison with Figure 6.10 shows that sPC-SAFT gives better results for this mixture than CPA. The predicted results are similar, but sPC-SAFT gives a better correlation of the data points. The biggest difference between the models is seen at low glycol ether concentration.

Figures 6.27 and 6.28 show the CPA results for C_1E_1 - water with the 2 (1:1) and 3 (2:1) schemes for C_1E_1 respectively. The results with sPC-SAFT were shown in Figures 6.18 and 6.19. The 2 (1:1) scheme clearly works better than the 3 (2:1) scheme for CPA for this mixture. The CPA results with the 3 (2:1) scheme are significantly worse than the sPC-SAFT results with the same scheme, but CPA with the 2 (1:1) scheme and sPC-SAFT with the 3 (2:1) scheme give more or less equally good results with fitted k_{ij}, but a single temperature independent k_{ij} is sufficient for sPC-SAFT, while slightly different values of k_{ij} are used for CPA at the two different temperatures examined here.
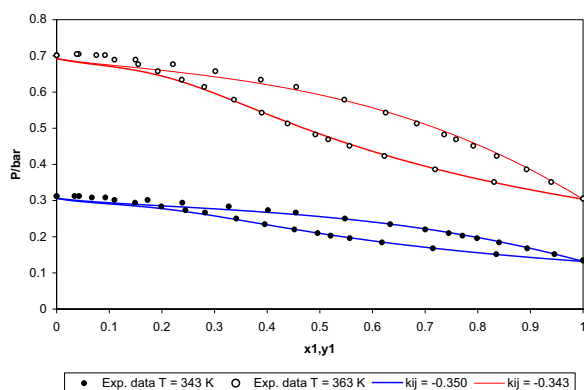
Figure 6.27: VLE calculations of C_1E_1 - water at $T = 383.15$ K. Lines are CPA with the 2 (1:1) scheme for C_1E_1. Experimental data: Chiavone-Filho et al. [101]
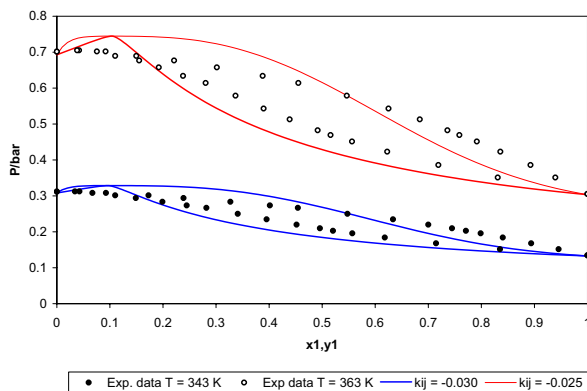
Figure 6.28: VLE calculations of C_1E_1 - water at $T = 383.15$ K. Lines are CPA with the 3 (2:1) scheme for C_1E_1. Experimental data: Chiavone-Filho et al. [101]

Figures 6.29 and 6.30 show the CPA results for C_4E_1 - water. The VLE results are with the 2 (1:1) scheme and the LLE with the 3 (2:1) scheme. The VLE results for this system with sPC-SAFT were very poor, but CPA with the 2 (1:1) scheme models it reasonably well with a temperature dependent interaction parameter. Satisfactory LLE results are obtained with the 3 (2:1) scheme with CPA. This scheme however performed poorly for all other glycol ether systems, including the VLE of C_4E_1 - water.
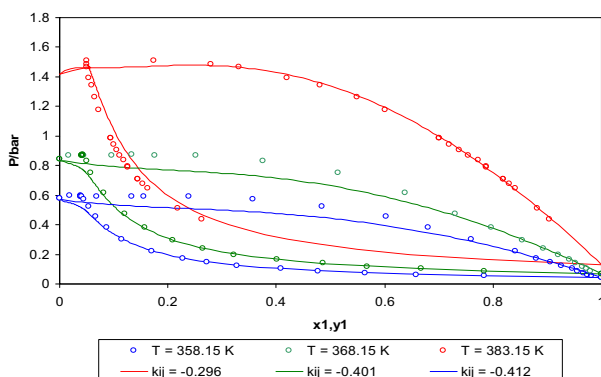
Figure 6.29: VLE calculations of C_4E_1 - water at $T = 383.15$ K. Lines are CPA with the 2 (1:1) scheme for C_4E_1. Experimental data: Chiavone-Filho et al. [101] ($T = 358.15$ K and $T = 368.15$ K) and Schneider and Wilhelm [103] ($T = 383.15$ K).
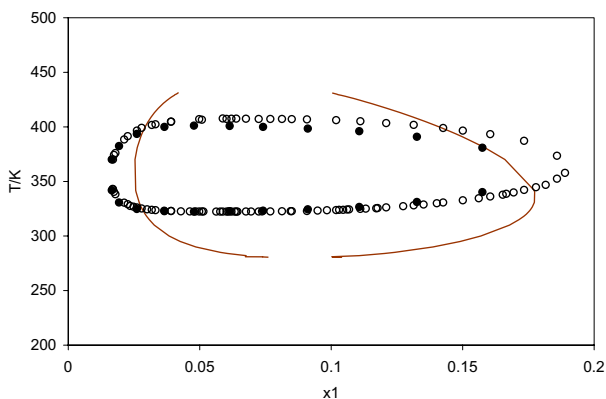
Figure 6.30: LLE calculations of C_4E_1 - water. Lines are CPA with the 3 (2:1) scheme for C_4E_1. Experimental data: Closed circles are from Aizpiri et al. [107] and open circles are from Schneider [104].

CPA with the 2 (1:1) scheme and sPC-SAFT with the 3 (2:1) scheme thus perform similar for glycol ether containing systems, the only exception being C_4E_1 - water. sPC-SAFT with the 3 (2:1) scheme is however significantly better than CPA with the 3 (2:1) scheme. It has not been investigated how the 2 (1:1) scheme performs for sPC-SAFT. For C_4E_1 - water CPA with the 2 (1:1) scheme gives satisfactory

results for the VLE but not for LLE (no results were presented by Garrido [106]), while CPA with the 3 (2:1) scheme is capable of modeling the LLE but not the VLE (or any other glycol ether containing mixture). sPC-SAFT with the 3inter and 3intra parameters are incapable of modeling the VLE and can only give good correlations of the UCST and LCST, but not for the composition of the liquid phases for the LLE.

Garcia-Lisbona et al. [90] modeled the C_4E_1 - water mixture with SAFT-HS. They used a complex association scheme for C_4E_1, with a total of 6 sites, with restrictions on which sites can self-associate and which can cross-associate. The scheme was adjusted to give the best results for this mixture. The authors moreover use different parameters for the unlike interactions between water and the different types of sites on C_4E_1, which were fitted to the coexistence compositions. The results are shown in Figures 6.31 and 6.32. Reasonable results are obtained for both VLE and LLE with SAFT-HS.
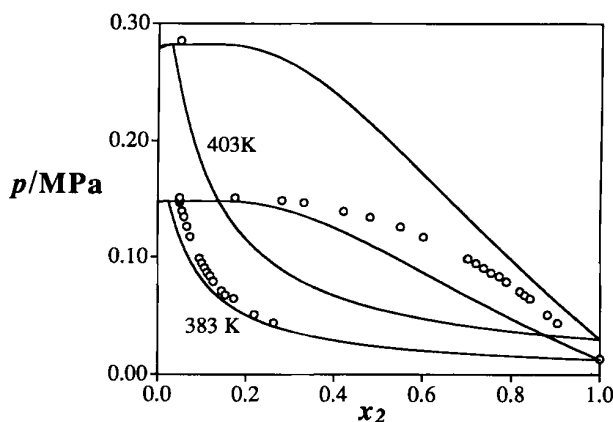
Figure 6.31: VLE calculations of C_4E_1 - water at $T = 383.15$ K. Lines are SAFT-HS. Experimental data: Schneider and Wilhelm [103].

The association scheme used by Garcia-Lisbona et al. is actually a simple way of accounting for intramolecular association, because sites are "removed" in pure C_4E_1 or self-associating mixtures, where some sites cannot associate, to account for the formation of intramolecular bonds, while a larger number of sites is available for cross-association with for example water, where we do not expect intramolecular bonds. It is, however, not possible to model the competition between inter- and intramolecular association in this way, or to account for the different density dependencies of the two types of bonds. Moreover, 3 sites for each of the two lone pairs on the ether oxygen does not seem physically correct.
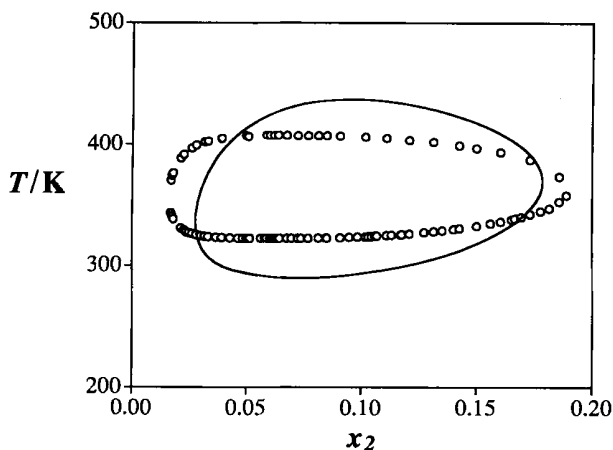
Figure 6.32: LLE calculations of C$_4$E$_1$ - water. Lines are SAFT-HS. Experimental data: Aizpiri et al. [107].

The LLE results with SAFT-HS are similar to the ones obtained by Garrido et al. [89] with CPA with the 3 (2:1) scheme. It is clear from the results with CPA and SAFT-HS, that it is difficult to find parameters and an association scheme that can model equally well both the VLE and LLE of this mixture.
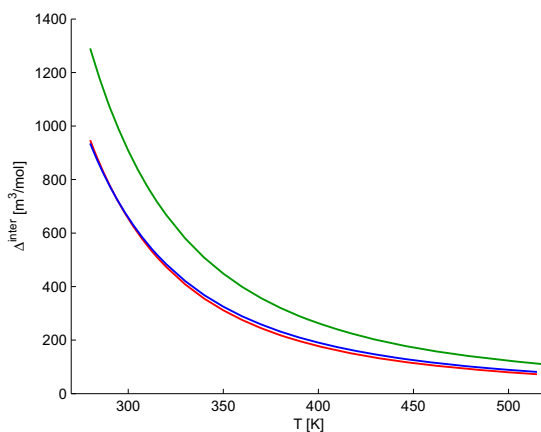
6.6 New intra parameters for C$_4$E$_1$

As seen previously in this chapter, the association strengths with the estimated parameters for C$_4$E$_1$ are significantly smaller than those for C$_1$E$_1$ and C$_2$E$_1$, and a smaller amount of hydrogen bonds is predicted. It was moreover reasonable to assume that part of the reason for the poor results for C$_4$E$_1$ - water was the small amount of cross-association, or at least it was argued that more association for C$_4$E$_1$ will improve the (LLE) results. We have also seen that the 3intra parameters for C$_1$E$_1$ and C$_2$E$_1$ give very similar association, and since the associating part of the three glycol ethers are identical, it seems reasonable to use the same association parameters for all three glycol ethers. As a test of this concept a new intra parameter set has been estimated for C$_4$E$_1$, with the association parameters from C$_2$E$_1$. The three remaining parameters were fitted in the same way as the 3intra parameters. The new parameter set, 3intra2 is shown in Table 6.2 together with the 3intra parameters. It should be noted that the new parameter set gives a significantly larger error in pure component vapor pressure compared to 3intra, while almost identical deviations are obtained for the liquid density.

Table 6.2: sPC-SAFT + intra parameters for C_4E_1, temperature interval used in the estimation and absolute relative deviations (ARD%) between sPC-SAFT and DIPPR correlations in the temperature range of the estimations.

	σ [Å]	ε [K]	m	ε^{AB} [K]	κ^{AB}	T [K]	ARD% P^{sat}	ARD% ρ^L
C_4E_1 3intra	3.525	258.10	4.173	1239.4	0.0405	317-571	0.38	0.24
C_4E_1 3intra2	3.252	203.41	5.127	1465.7	0.6375	317-571	4.18	0.18

Figures 6.33 and 6.34 show the inter- and intramolecular association strengths respectively for the three glycol ethers with sPC-SAFT plus intramolecular association, where the new parameter set is used for C_4E_1.

Figure 6.33: Intermolecular association strength for C_1E_1, C_2E_1 and C_4E_1 with the 3intra sets for the C_1E_1 and C_2E_1, and the new 3intra2 parameters for C_4E_1. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.
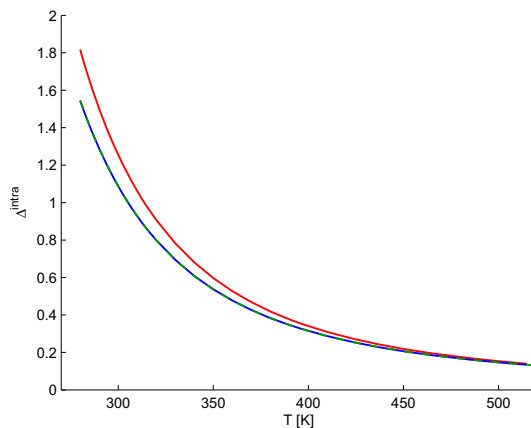
Figure 6.34: Intramolecular association strength for C_1E_1, C_2E_1 and C_4E_1 with the 3intra sets for the C_1E_1 and C_2E_1, and the new 3intra2 parameters for C_4E_1. Red is C_1E_1, blue is C_2E_1 and green is C_4E_1.

As seen from the figures the new parameters for C$_4$E$_1$ give an intramolecular association strength identical to that of C$_2$E$_1$, whereas the new intermolecular association strength for C$_4$E$_1$ is somewhat higher than that for the other two glycol ethers, despite the use of the association parameters from C$_2$E$_1$ for C$_4$E$_1$. This is because of the different σ values for C$_2$E$_1$ and C$_4$E$_1$, which appears in the intermolecular association strength but not in the intramolecular association strength. In order to obtain similar intermolecular association strengths for the three glycol ethers the parameters must be estimated differently. Two possible procedures are to fit the parameters for all three glycol ethers simultaneously and use identical σ, ε^{AB} and κ^{AB} values for the three compounds, or to use the same ε^{AB} and $\sigma^3\kappa^{AB}$ value for the three glycol ethers. The second procedure will give identical intermolecular association strengths for the glycol ethers, but different intramolecular association strengths. The investigation of these new procedures for parameter estimation will not be included in this work, but is left as a suggestion for future work. Despite the disagreement between the intermolecular association strengths for C$_4$E$_1$ and C$_1$E$_1$ and C$_2$E$_1$ this section will present phase equilibrium results with the new parameter set for C$_4$E$_1$, in order to investigate whether introducing stronger cross-association can solve some of the problems for the C$_4$E$_1$ - water mixture.
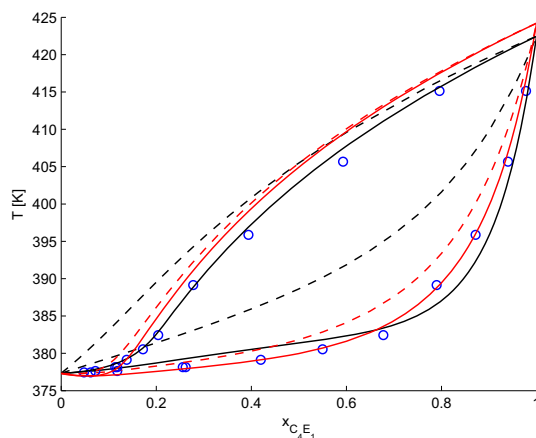
Figure 6.35: VLE calculations of C$_4$E$_1$ - octane at $P = 0.533$ bar. Black lines are sPC-SAFT with 3intra for C$_4$E$_1$; dashed line: $k_{ij} = 0$, full line: $k_{ij} = 0.037$. Red lines are sPC-SAFT with 3intra2 for C$_4$E$_1$; dashed line: $k_{ij} = 0$, full line: $k_{ij} = 0.01$. Experimental data: Komatsu et al. [96]

The results for C$_4$E$_1$ - octane with sPC-SAFT with the new parameter set as well as with the 3intra set for C$_4$E$_1$ are shown in Figure 6.35. The figure shows that the 3intra2 set gives significantly better results for $k_{ij} = 0$, and a better match to the liquid curve with an optimal k_{ij} than the 3intra set. The 3intra set correlates

the vapor curve slightly better than the 3intra2 set, which is a result of the error in vapor pressure for pure C_4E_1 with 3intra2.

Figure 6.36 shows the VLE results for C_4E_1 - water with sPC-SAFT with the two intra parameter sets for C_4E_1. The figure shows that the new parameter set for C_4E_1 gives significantly better results for this system than the 3intra parameters. The predicted VLLE area is however still larger than the experimental data suggests, which disturbs the results for the liquid curve. It is not possible to fit a k_{ij} to match the entire liquid curve.
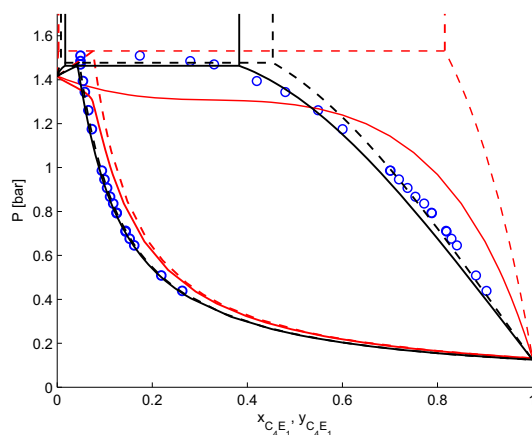
Figure 6.36: VLE calculations of C_4E_1 - water at $T = 383.15$ K. Red lines are sPC-SAFT with 3intra for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.1$. Black lines are sPC-SAFT with 3intra2 for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.015$. Experimental data: Schneider and Wilhelm [103].
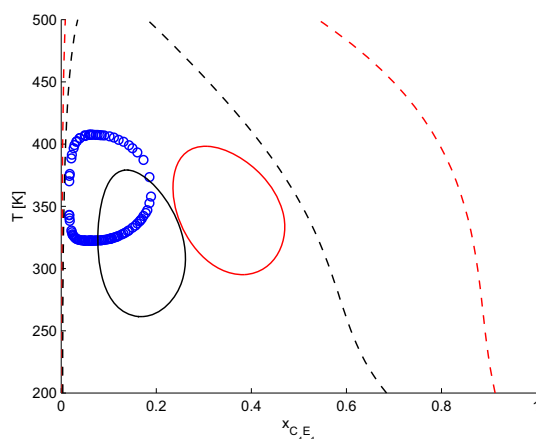
Figure 6.37: LLE calculations of C_4E_1 - water at $P = 10.13$ bar. Red lines are sPC-SAFT with 3intra for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.092$. Black lines are sPC-SAFT with 3intra2 for C_4E_1; dashed lines: $k_{ij} = 0$, full lines: $k_{ij} = -0.041$. Experimental data: Aizpiri et al. [107]

The LLE results for C_4E_1 - water with both intra sets for C_4E_1 are shown in Figure 6.37. The 3intra2 set gives a significantly better correlation of the compositions, though still not satisfactorily, but UCST and LCST are not as well matched as with the 3intra set.

Figure 6.38 shows the results for C_4E_1 - water with sPC-SAFT with the 3intra2 set for C_4E_1 at different pressures. A comparison of Figures 6.24 and 6.38 shows that the 3intra2 set gives a better prediction of the pressure dependency than the 3intra set. The 3intra set gives a weaker pressure dependency than the experimental data shows, whereas the pressure dependency of sPC-SAFT with 3intra2 for C_4E_1 is very similar to the experimental pressure dependency.
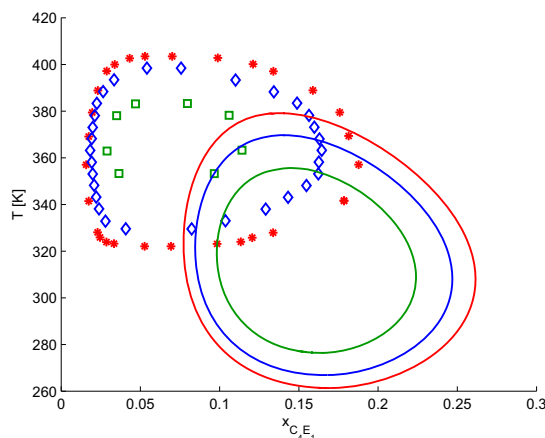
Figure 6.38: LLE calculations of C_4E_1 - water. Lines are sPC-SAFT with 3intra2 for C_4E_1 with $k_{ij} = -0.041$. Red line is $P = 10$ atm, blue line is $P = 200$ atm and green line is $P = 600$ atm. Experimental data: Schneider [104], taken from Knudsen et al. [105]; 10 atm ($*$), 200 atm ($\diamond$) and 600 atm ($\square$).

The results presented in this section show that the performance of sPC-SAFT (plus intramolecular association) is significantly improved for C_4E_1 - water when the new parameter set is used for C_4E_1 instead of the 3intra set. The results for C_4E_1 - octane with the new set are also better than the results with 3intra, even though the results for that mixture are affected negatively by the large error in vapor pressure for pure C_4E_1.

6.7 Chapter summary

This chapter has presented results for glycol ether containing mixtures with sPC-SAFT with and without the new theory for intramolecular association. Parame-

ters were initially estimated by fitting pure component vapor pressure and liquid density. The parameters for C_1E_1 and C_2E_1 with intramolecular association were found to give very similar association strength, whereas the parameters for C_4E_1 gave significantly weaker association than for the other glycol ethers. The phase equilibrium results showed that the predicted results in most cases were better when intramolecular association was included, especially for LLE. sPC-SAFT was in general found to give good results for miscible mixtures and reasonably good results for immiscible mixtures, except for the mixture of C_4E_1 - water, for which very poor results were obtained. Based on the very similar association strength for C_1E_1 and C_2E_1 with the sets for sPC-SAFT plus intramolecular association, a new parameter set was estimated for C_4E_1 with the association parameters from C_2E_1. The new parameter set was found to give significantly better VLE results for C_4E_1 - water, as well as better LLE results.

The results with sPC-SAFT (without intramolecular association) were also compared to results with CPA, and it was found that the results with sPC-SAFT with the 3 (2:1) scheme and CPA with the 2 (1:1) scheme are similar, and significantly better than the results for CPA with the 3 (2:1) scheme.

Chapter 7

Conclusion and future work

7.1   Conclusion

Different limitations and problems in the use of SAFT type theories have been investigated in the Ph.D. project. The influence of parameter estimation and association scheme on phase equilibrium and monomer fraction/amount of hydrogen bonds calculations has been investigated for different hydrogen bonding compounds of interest to the petroleum industry, and a general theory for intramolecular association in the framework of SAFT has been developed and applied for glycol ether containing mixtures.

Methanol parameters from the literature have been compared to a new parameter set estimated solely to pure component vapor pressure and liquid density. It was found that the new parameter set gives better predictive results for phase equilibrium of binary mixtures than the parameter set from Gross and Sadowski [48], which on the other hand correlates the data significantly better than the new set. The new parameters give more accurate monomer fraction results than the parameters from Gross and Sadowski, and it was thus found that the parameters which perform best for monomer fraction calculations may not necessarily be the best for phase equilibrium calculations. It is therefore necessary to be cautious when using monomer fraction data in the parameter estimation. Since the different parameter sets give so different results it is important to know on what conditions a parameter set was estimated, and what information was included in the estimation

if different association schemes or thermodynamic models are compared.

CPA has previously been applied to model mixtures of alkanolamines [38]. The results from that work showed that the 4 (2:2) scheme was superior to the 2 (1:1) scheme for monoethanolamine (MEA), and that the 4 (2:2) scheme also give good results for diethanolamine (DEA) and methyl diethanolamine (MDEA). As a continuation of that work, it was in this project investigated for MEA whether identical or different association parameters should be used for the hydroxyl and amine groups, corresponding to the 4 (2:2) and 4 (1:1,1:1) schemes. The results presented in the thesis show that the more complex association scheme does not improve the performance of CPA for MEA, and it is therefore recommended to use the more simple 4 (2:2) scheme for MEA. Based on these results it was decided not to investigate the effect of differentiating the association parameters for DEA or MDEA. For DEA it was instead investigated whether the CPA results are improved by using an association scheme with more sites; the 6 (3:3) scheme. It was found that the 4 (2:2) and 6 (3:3) schemes give equally good results for DEA. The correlated results are very similar, but different values are needed for the interaction parameter for the two schemes. Based on this, it is found that the 4 (2:2) scheme is adequate for DEA.

Spectroscopy data shows that intramolecular association is predominant compared to intermolecular association in dilute solutions of glycol ether in a non-associating solvent, but the association term in SAFT theories does not consider intramolecular association. The previous work on modeling intramolecular association with SAFT and lattice theory is presented and discussed in the thesis, and a new general theory for inter- and intramolecular association in the frame of SAFT is presented. An expression for the Helmholtz free energy is given, which enables us to calculate derivatives of the free energy using the approach of Michelsen and Hendriks [40]. The new theory was compared to the corresponding equations from lattice theory, and the two models were found to give equivalent expressions for the contribution from association to the chemical potential of an intramolecularly associating compound (a glycolether), under the assumption that the Gibbs energy is proportional to the content of the associating compound (at equilibrium). The new theory for intramolecular association only influences the association term of SAFT, and was derived consistently with the original Wertheim theory, which is used in most SAFT models. The theory for intramolecular association presented in the thesis can therefore easily be applied in connection with other SAFT models, without making new derivations.

Finally the new theory was applied to binary mixtures of glycol ethers. Calculations were made with sPC-SAFT with and without inclusion of intramolecular association. sPC-SAFT was in general found to give very good results for miscible mixtures, and reasonably good results for immiscible mixtures. The predictive performance of sPC-SAFT is increased when intramolecular association is included, but for most systems there is not a big difference in the results with and without inclusion of intramolecular association. More consistent (association) parameters are, however, obtained when intramolecular association is included, and it is therefore realistic to obtain general association parameters for glycol ethers. The concept is tested by fitting new intra parameters for C_4E_1 using the association parameters for C_2E_1. The new parameters give significantly better results for C_4E_1 - water compared to using the original parameters.

The overall conclusions of the project are that parameter estimation is at least as important as the shortcomings of the theory. Inclusion of mixture data in the parameter estimation influences the results of CPA and sPC-SAFT more than the inclusion of intramolecular association in the theory (for sPC-SAFT). Improvement of the theory, however, improves the predictive performance of the model, and more consistent parameters are obtained in the parameter estimation.

7.2 Future work

There are many remaining issues to be considered regarding the SAFT EoS, some of which were mentioned in the Introduction chapter of this thesis. Some specific suggestions for future work related to the work done in the Ph.D. project are given here.

In order to confirm the conclusions for the new theory for intramolecular association, the theory must be applied to a larger number of mixtures, including other intramolecularly associating compounds. A general theory for intramolecular association was developed in the project, except for the monomer fraction, where only expressions for specific cases were obtained (it is for the fraction of molecules not bonded intramolecularly that a general expression has not been obtained). To extend the applicability of the model it is desirable to derive a general expression for the monomer fraction as well.

The parameter estimation is a time-consuming step in the process of applying an

EoS like sPC-SAFT or CPA to new compounds, but it was found in the project that the parameter estimation is as important as improving the theory, and emphasis must be put on that area as well. It is still necessary to investigate what information is most useful to include in the parameter estimation. For glycol ethers it would be interesting to include LLE of one mixture in the parameter estimation and see how the new parameters would perform for other mixtures. If a parameter set could be obtained for 2-butoxyethanol which can correlate the experimental LLE data at low pressure, and predict the correct pressure dependency of the LLE, then the resulting model would be an important tool in reservoir engineering.

Because of the theoretical basis of the theory it must be possible to develop a group-contribution approach for associating compounds with sPC-SAFT, preferably as an extension to the already available group-contribution approach for non-associating compounds [14]. A first step could be to extent the approach of generalized association parameters for alkanols and glycols by Grenner et al. [22, 23] to other associating groups. Suggestions for how to obtain generalized parameters for glycol ethers were presented in Chapter 6.

If the theory for intramolecular association is to be applied for (telechelic) polymers or other large compounds it will be necessary to include somehow the effect of the solvent on the structure of the compound. As mentioned in section 5.2.2 a polymer with a hydrocarbon backbone will behave very differently in polar and non-polar solvents, which significantly influences the amount of intramolecular association in the system. The different structural behavior cannot be accounted for with the new theory in the present form.

Nomenclature

Symbol	Description	SI Units
a_0	Parameter in the energy term (a) in CPA	Pa m^6 mol^{-2}
$\bar{a}$	Reduced Helmholtz free energy	
A	Helmholtz free energy	J
A_i	Site A on molecule i	
b	Co-volume parameter	m^3 mol^{-1}
B_j	Site B on molecule j	
c_1	Parameter in the energy term (a) in CPA	
$c^{(0)}$	Sum of graphs	
d	Temperature-dependent segment diameter	m
D	Fraction of molecules in bonding orientation in reference system	
f_{AB}	Mayer f-function	
g	Radial distribution function	
k	Boltzmann constant	J K^{-1}
k_{ij}	Binary interaction parameter	
m	Segment number per molecule	
$\bar{m}$	Mean segment number per molecule	
n	Number of moles	mol
N	Number of molecules	
P	Pressure	Pa
P_c	Critical pressure	Pa
P_r	Reduced pressure (P/P_c)	
P^{sat}	Saturated vapor pressure	Pa
R	Gas constant	J mol^{-1} K^{-1}

Symbol	Description	SI Units
T	Temperature	K
T_c	Critical temperature	K
T_r	Reduced Temperature (T/T_c)	
V	Volume	m^3
V_m	Molar volume	m^3 mol^{-1}
W_m	End-to-end distribution function for a chain with m links	m^{-3}
x	Mole fraction	
X_A	Fraction of molecules, not bonded at site A	
XA_i	Fraction of sites of type i not bonded	
X_0	Monomer fraction	
y	Vapor mole fraction	
y	Cavity distribution function	
Z	Compressibility factor	

β^{AB}	Association volume parameter in sPC-SAFT	
Γ	Set of sites	
Δ_{AB}	Association strength in CPA	m^3 mol^{-1}
Δ_{AB}	Association strength in sPC-SAFT	m^3
$\Delta_{AB}^{\text{inter}}$	Intermolecular association strength in sPC-SAFT	m^3
$\Delta_{AB}^{\text{intra}}$	Intramolecular association strength in sPC-SAFT	
ε	Energy parameter in sPC-SAFT	m^3 mol^{-1}
ε^{AB}	Association energy parameter in sPC-SAFT	Pa m^3
ε^{AB}	Association energy parameter in CPA	Pa m^3 mol^{-1}
ζ	Partial volume fraction	
η	Reduced density	
κ^{AB}	Association volume parameter in sPC-SAFT	
Λ	De Broglie wavelength	
ρ	Number density	m^{-3}
ρ^L	Saturated liquid density	mol m^{-3}
σ	Segment diameter	m
σ	Combined number density	m^{-3}
ϕ_{AB}	Site-site potential (Wertheim)	Pa m^3
ω	Acentric factor	

Commonly used abbreviations

ARD%	Absolute Relative Deviation. For a property x:

$$ARD\% = \frac{1}{NP} \sum_{k=1}^{NP} \left| \frac{x_k^{\text{exp}} - x_k^{\text{calc}}}{x_k^{\text{exp}}} \right| \times 100\%$$

AAD	Absolute Average Deviation. For a property x:

$$AAD = \frac{1}{NP} \sum_{k=1}^{NP} \left| x_k^{\text{exp}} - x_k^{\text{calc}} \right|$$

assoc	Association
calc	Calculated value
CPA	Cubic Plus Association
CR-1	Combining Rule 1
DEA	Diethanolamine
DIPPR	Design Institute for Physical Properties
EoS	Equation of State
exp	Experimental value
hc	Hard chain
hs	Hard sphere
inter	Intermolecular
intra	Intramolecular
LFHB	Lattice-fluid/hydrogen-bonding theory
LLE	Liquid-Liquid Equilibrium
mCR-1	Modified CR-1
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
mono	Monomer
NC	Number of components
NP	Number of data points
NS	Number of sites
PC-SAFT	Perturbed Chain Statistical Associating Fluid Theory
ref	Reference fluid
seg	Segment
sPC-SAFT	Simplified PC-SAFT
SRK	Soave-Redlich-Kwong EoS
VLE	Vapor-Liquid Equilibrium

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APPENDIX A

Additional pure component parameters

A.1 sPC-SAFT parameters

The pure component sPC-SAFT parameters for other compounds considered in this work were taken from three different papers; the water parameters were taken from Grenner et al., 2006 [100], the alkanol parameters (except for the methanol parameters, for which different parameter sets were investigated in Chapter 3) are generalized parameters from Grenner et al., 2007 [22], where the same association parameters are used for all alkanols and the alkane parameters were taken from the original PC-SAFT paper by Gross and Sadowski, 2001 [21]. The κ values are for sPC-SAFT.

Table A.1: Additional pure component sPC-SAFT parameters

Compound	Ref.	Scheme	σ [Å]	ε [K]	m	ε^{AB} [K]	κ^{AB}
water	[100]	4 (2:2)	2.627	180.30	1.500	1804.2	0.1799
ethanol	[22]	2 (1:1)	4.106	316.91	1.231	2811.0	0.00633
propanol	[22]	2 (1:1)	3.904	292.11	1.800	2811.0	0.00633
1-butanol	[22]	2 (1:1)	3.785	276.90	2.398	2811.0	0.00633
n-hexane	[21]		3.798	236.77	3.058		
n-heptane	[21]		3.805	238.40	3.483		
n-octane	[21]		3.837	242.78	3.818		
n-dodecane	[21]		3.896	249.21	5.306		
n-tetradecane	[21]		3.940	254.21	5.900		
n-hexadecane	[21]		3.955	254.70	6.649		
cyclohexane	[21]		3.850	278.11	2.530		

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A.2   CPA parameters

The additional CPA parameters were taken from five different papers; Yakoumis et al., 1997 [108], Kontogeorgis et al., 1999 [41], Folas et al., 2005 [36], Garrido et al. [89] and Avlund, 2007 [46].

**Table A.2:** Additional pure component CPA parameters

| Compound	Ref.	Scheme	b (L/mol)	Γ (K)	c_1	ε/R (K)	$\beta \times 10^3$
Water	[41]	4 (2:2)	0.01452	1017.3	0.6766	2003.2	69.2
Ethanol	[36]	2 (1:1)	0.04911	2123.8	0.7369	2589.8	8.00
C_1E_1	[89]	2 (1:1)	0.06459	1492.2	1.051	2745.1	0.07
C_1E_1	[89]	3 (2:1)	0.06491	1298.0	1.425	2411.5	0.05
C_2E_1	[89]	2 (1:1)	0.07785	1509.5	0.780	3324.3	0.02
C_2E_1	[89]	3 (2:1)	0.07986	1347.5	1.314	2705.1	0.03
C_4E_1	[89]	2 (1:1)	0.11531	1870.6	1.438	2245.1	0.13
C_4E_1	[89]	3 (2:1)	0.11526	1636.2	1.748	1953.3	0.10
n-Hexane	[108]		0.12535	2800	0.9137		
n-Heptane	[36]		0.12535	2800	0.9137		
n-Octane	[108]		0.12535	2800	0.9137		
Benzene	[108]		0.07499	2867	0.7576		
Hexadecane	[46]		0.29458	3846	1.3753		

Additional VLE and LLE results for glycolethers

sPC-SAFT was applied to modeling mixtures of glycol ethers in Chapter 6. Additional results are given here.
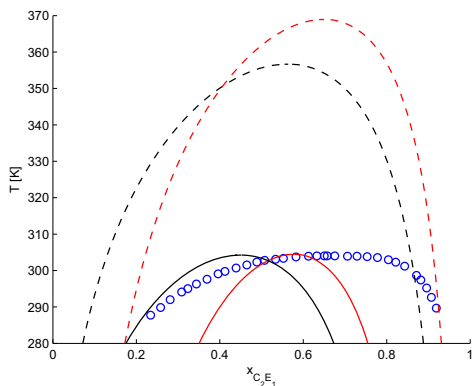
B.1 Self-associating mixtures
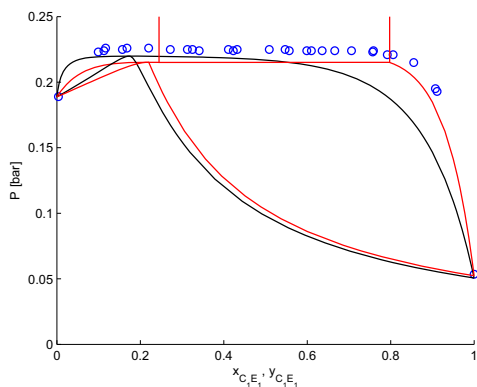
Figure B.1: VLE calculations of C_1E_1 - heptane. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = 0$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = 0$. Experimental data: Dolch et al. [91]
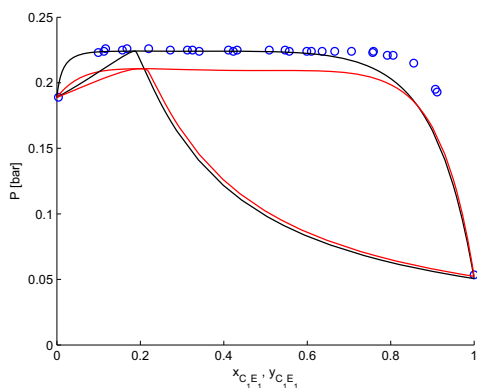
Figure B.2: VLE calculations of C_1E_1 - heptane. Black lines are sPC-SAFT with 3inter for C_1E_1 and $k_{ij} = 0.0065$. Red lines are sPC-SAFT with 3intra for C_1E_1 and $k_{ij} = -0.0055$. Experimental data: Dolch et al. [91]
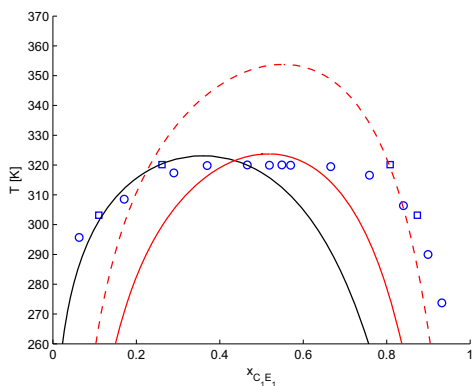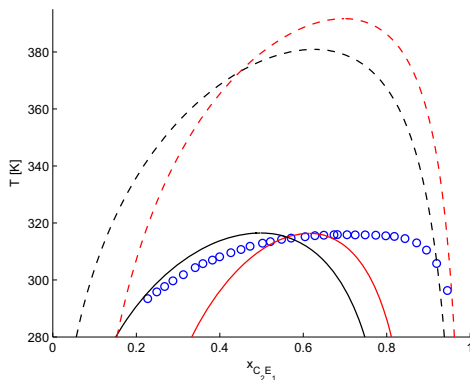

Figure B.3: LLE calculations of C_1E_1 - heptane. Black lines are sPC-SAFT with 3inter for C_1E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = 0.0065$. Red lines are sPC-SAFT with 3intra for C_1E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.0055$. Experimental data: Bijl et al. [92] ($\circ$) and DECHEMA (smoothed data) [58] ($\square$).

Figure B.4: LLE calculations of C_2E_1 - tetradecane. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.0065$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.0075$. Experimental data: Rubio et al. [95]
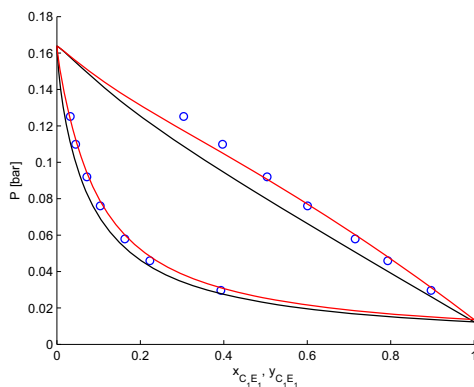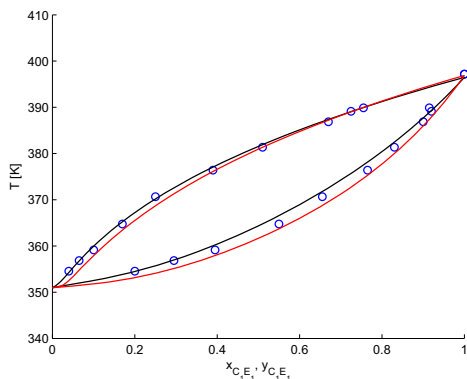
Figure B.5: LLE calculations of C_2E_1 - hexadecane. Black lines are sPC-SAFT with 3inter for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.0085$. Red lines are sPC-SAFT with 3intra for C_2E_1; dashed lines: $k_{ij} = 0$, full line: $k_{ij} = -0.0097$. Experimental data: Rubio et al. [95]
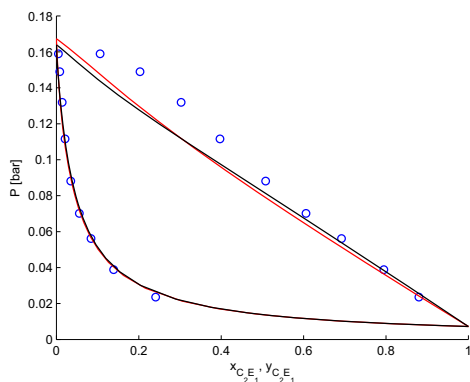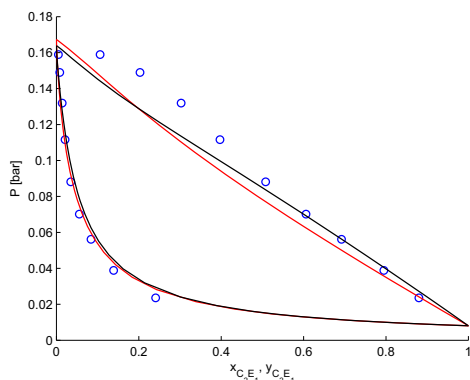
B.2   Cross-associating mixtures

Figure B.6: VLE calculations of C_1E_1 - methanol at $T = 298.15$ K. Lines are sPC-SAFT with $k_{ij} = 0$. Methanol parameters are from Gross and Sadowski [48]. Black lines are with 3inter for C_1E_1 and red lines are with 3intra for C_1E_1. Experimental data: Martin et al. [97]

Figure B.7: VLE calculations of C_1E_1 - ethanol. Black lines are sPC-SAFT with 3inter for C_2E_1 and $k_{ij} = 0$. Red lines are sPC-SAFT with 3intra for C_2E_1 and $k_{ij} = 0$. Experimental data: Sporzynski and Gregorowicz [109].

Figure B.8: VLE calculations of C_2E_1 - methanol at $T = 298.15$ K. Lines are sPC-SAFT with 3inter for C_2E_1 and $k_{ij} = 0$. Black lines are with methanol parameters from Gross and Sadowski [48], and red lines are with methanol parameters from this work. Experimental data: Martin et al. [97].

Figure B.9: VLE calculations of C_2E_1 - methanol at $T = 298.15$ K. Lines are sPC-SAFT with 3intra for C_2E_1 and $k_{ij} = 0$. Black lines are with methanol parameters from Gross and Sadowski [48], and red lines are with methanol parameters from this work. Experimental data: Martin et al. [97].

Derivatives of the Helmoltz free energy

A new theory for intramolecular association in the framework of SAFT was presented in Chapter 5. The derivatives of the contribution to the Helmholtz free energy from association, for the new theory, which are needed to do phase equilibrium calculations analytically are given in this appendix. Various other derivatives needed for the calculations are also given.

In this appendix $\Delta = \Delta^{\text{inter}}$ and $\Delta_{ij}^{\text{intra}} = W_{ij} \Delta^{\text{inter}}$.

C.1 Derivatives of Q

The Q function is the unstable Helmholtz free energy, and was given in equation (5.135), with XAB_{ij} as defined in equation (5.139).

Derivative of Q with respect to V

$$
\begin{aligned}
\frac{\partial Q}{\partial V} &= \left(\frac{\partial Q}{\partial V}\right)_X + \sum_k \sum_{\alpha \subset \Gamma_k} \frac{\partial Q}{\partial X_\alpha}\frac{\partial X_\alpha}{\partial V} = \left(\frac{\partial Q}{\partial V}\right)_X \\
&= \frac{-n^2}{2V}\left(-\frac{1}{V}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij} + \sum_i \sum_j x_i x_j XA_i XA_j \frac{\partial \Delta_{ij}}{\partial V}\right) \\
&\quad - \frac{n}{2}\sum_i \sum_j x_i XAB_{ij}\frac{\partial \Delta_{ij}^{\mathrm{intra}}}{\partial V}
\end{aligned}
\tag{C.1}
$$

Δ only depends on volume (and composition) through the radial distribution function g. The volume derivative of Δ is:

$$
\frac{\partial \Delta}{\partial V} = \frac{\Delta}{g}\frac{\partial g}{\partial V} = \Delta\frac{\partial \ln g}{\partial V}
\tag{C.2}
$$

Using this and (5.137) we can simplify the expression in (C.1):

$$
\begin{aligned}
\frac{\partial Q}{\partial V} &= \frac{n^2}{2V^2}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij} \\
&\quad - \left[\frac{n^2}{2V}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij} + \frac{n}{2}\sum_i \sum_j x_i XAB_{ij}\Delta_{ij}W_{ij}\right] \times \frac{\partial \ln g}{\partial V} \\
&= \frac{n^2}{2V^2}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij} - \frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial \ln g}{\partial V}
\end{aligned}
\tag{C.3}
$$

Since Δ as mentioned only depends on volume and composition through g, we will separate Δ into two parts; g and Δ/g, where g depends on volume, temperature and composition and Δ/g only depends on temperature:

$$
\frac{\partial Q}{\partial V} = \frac{n^2 g}{2V^2}\sum_i \sum_j x_i x_j XA_i XA_j \frac{\Delta_{ij}}{g} - \frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial \ln g}{\partial V}
\tag{C.4}
$$

Derivatives of $\partial Q/\partial V$ with respect to V, XA and T

For the second derivative of Q with respect to volume we need to take the derivative of $\partial Q/\partial V$ with respect to volume at constant **XA** as well as with respect to

XA_i since

$$\frac{\partial^2 Q}{\partial V^2} = \left(\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial V}\right)\right)_{XA} + \sum_i \frac{\partial}{\partial XA_i}\left(\frac{\partial Q}{\partial V}\right)\frac{\partial XA_i}{\partial V} \tag{C.5}$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial V}\right)\right)_X = \frac{n^2}{V^2}\sum_i\sum_j x_i x_j XA_i XA_j \frac{\Delta_{ij}}{g}\left[-\frac{g}{V} + \frac{1}{2}\frac{\partial g}{\partial V}\right]$$
$$-\frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial^2 \ln g}{\partial V^2} \tag{C.6}$$

$$\frac{\partial}{\partial XA_i}\left(\frac{\partial Q}{\partial V}\right) = \frac{n^2 g}{V^2}x_i\sum_j x_j XA_j\frac{\Delta_{ij}}{g} + \frac{n}{2}x_i\frac{\partial \ln g}{\partial V} \tag{C.7}$$

How $\partial XA_i/\partial V$ is determined is explained in section C.2

For the derivative of $\partial Q/\partial V$ with respect to temperature we need the derivative with respect to temperature at constant **XA** and the derivative with respect to XA_i which we just found.

$$\frac{\partial^2 Q}{\partial V \partial T} = \left(\frac{\partial}{\partial T}\left(\frac{\partial Q}{\partial V}\right)\right)_{XA} + \sum_i \frac{\partial}{\partial XA_i}\left(\frac{\partial Q}{\partial V}\right)\frac{\partial XA_i}{\partial T} \tag{C.8}$$

where

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial Q}{\partial V}\right)\right)_X = \frac{n^2}{2V^2}\sum_i\sum_j x_i x_j XA_i XA_j \frac{\Delta_{ij}}{g}\frac{\partial g}{\partial T}$$
$$+\frac{n^2 g}{2V^2}\sum_i\sum_j x_i x_j XA_i XA_j\frac{\partial \Delta_{ij}/g}{\partial T}$$
$$-\frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial^2 \ln g}{\partial V \partial T} \tag{C.9}$$

The determination of $\partial XA_i/\partial T$ will be explained in section C.2.

Derivative of Q with respect to T

When taking the temperature derivative of Q we can again utilize that $\frac{\partial Q}{\partial X_\alpha} = 0$, and only calculate the temperature derivative at constant **X**:

$$
\frac{\partial Q}{\partial T} = \left(\frac{\partial Q}{\partial T} \right)_X + \sum_k \sum_{\alpha \subset \Gamma_k} \frac{\partial Q}{X_\alpha} \frac{\partial X_\alpha}{\partial T} = \left(\frac{\partial Q}{\partial T} \right)_X
$$

$$
= -\frac{n^2}{2V} \sum_i \sum_j x_i x_j X A_i X A_j \left[\frac{\Delta_{ij}}{g} \frac{\partial g}{\partial T} + g \frac{\partial \Delta_{ij}/g}{\partial T} \right]
$$

$$
-\frac{n}{2} \sum_i \sum_{j \neq i} x_i X A B_{ij} W_{ij} \left[\frac{\Delta_{ij}}{g} \frac{\partial g}{\partial T} + g \frac{\partial \Delta_{ij}/g}{\partial T} \right] \qquad \text{(C.10)}
$$

Derivative of $\partial Q/\partial T$ with respect to T

To calculate the second temperature derivative of Q we need the temperature derivative of $\partial Q/\partial T$ at constant **XA** and the derivative of $\partial Q/\partial T$ with respect to XA_i:

$$
\frac{\partial^2 Q}{\partial T^2} = \left(\frac{\partial}{\partial T} \left(\frac{\partial Q}{\partial T} \right) \right)_{XA} + \sum_m \frac{\partial}{\partial X A_m} \left(\frac{\partial Q}{\partial T} \right) \frac{\partial X A_m}{\partial T} \qquad \text{(C.11)}
$$

$$
\left(\frac{\partial}{\partial T} \left(\frac{\partial Q}{\partial T} \right) \right)_{XA} = -\frac{n^2}{2V} \sum_i \sum_j x_i x_j X A_i X A_j
$$

$$
\times \left[\frac{\partial \Delta_{ij}/g}{\partial T} \frac{\partial g}{\partial T} + \frac{\Delta_{ij}}{g} \frac{\partial^2 g}{\partial T^2} + \frac{\partial g}{\partial T} \frac{\partial \Delta_{ij}/g}{\partial T} + g \frac{\partial^2 \Delta_{ij}/g}{\partial T^2} \right]
$$

$$
-\frac{n}{2} \sum_i \sum_{j \neq i} x_i X A B_{ij} W_{ij}
$$

$$
\times \left[\frac{\partial \Delta_{ij}/g}{\partial T} \frac{\partial g}{\partial T} + \frac{\Delta_{ij}}{g} \frac{\partial^2 g}{\partial T^2} + \frac{\partial g}{\partial T} \frac{\partial \Delta_{ij}/g}{\partial T} + g \frac{\partial^2 \Delta_{ij}/g}{\partial T^2} \right]
$$

$$
-\frac{n}{2} \sum_i \sum_{j \neq i} x_i \left(\frac{\partial X A B_{ij}}{\partial T} \right)_{XA} W_{ij} \left[\frac{\Delta_{ij}}{g} \frac{\partial g}{\partial T} + g \frac{\partial \Delta_{ij}/g}{\partial T} \right] \text{(C.12)}
$$

$$\left(\frac{\partial XAB_{ij}}{\partial T}\right)_{XA} = \frac{\partial}{\partial T}\left(\frac{XA_i x_j \frac{V_m}{g}}{x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}}\right)_{XA}$$

$$= \left[-XAB_{ij} + \frac{XA_i x_j^2\frac{V_m^2}{g^2}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2}\right] \times \frac{\partial \ln g}{\partial T}$$

$$- \frac{XA_i x_j^2\frac{V_m}{g}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2}\sum_n x_n XA_n\frac{\partial\Delta_{jn}/g}{\partial T} \quad \text{(C.13)}$$

$$\frac{\partial}{\partial XA_m}\left(\frac{\partial Q}{\partial T}\right) = -\frac{n^2}{V}x_m\sum_j x_j XA_j \times \left[\frac{\Delta_{mj}}{g}\frac{\partial g}{\partial T} + g\frac{\partial\Delta_{mj}/g}{\partial T}\right]$$

$$- \frac{n}{2}x_i\sum_i\sum_{j\neq i}\frac{\partial XAB_{ij}}{\partial XA_m}W_{ij} \times \left[\frac{\Delta_{ij}}{g}\frac{\partial g}{\partial T} + g\frac{\partial\Delta_{ij}/g}{\partial T}\right] \quad \text{(C.14)}$$

where for the last term in the first bracket we utilize the assumption that the molefraction must be the same for the two sites that associate intramolecularly $(x_i = x_j)$.

$$\frac{\partial XAB_{ij}}{\partial XA_m} = \frac{x_j\frac{V_m}{g}}{x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}} - \frac{XA_i x_j^2 x_m\frac{\Delta_{jm}}{g}\frac{V_m}{g}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2} \quad \text{(C.15)}$$

$$\Rightarrow \sum_i\sum_{j\neq i}\frac{\partial XAB_{ij}}{\partial XA_m} = \sum_{j\neq m}\frac{x_j\frac{V_m}{g}}{x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}}$$

$$- \sum_i\sum_{j\neq i}\frac{XA_i x_j^2 x_m\frac{\Delta_{jm}}{g}\frac{V_m}{g}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2} \quad \text{(C.16)}$$

where the blue term only is for $m = i$.

Derivative of Q with respect to n_l

$$\frac{\partial Q}{\partial n_l} = \left(\frac{\partial Q}{\partial n_l}\right)_X + \sum_k \sum_{\alpha \subset \Gamma_k} \frac{\partial Q}{\partial X_\alpha} \frac{\partial X_\alpha}{\partial n_l} = \left(\frac{\partial Q}{\partial n_l}\right)_X \tag{C.17}$$

We have to distinguish between associating and non-associating components. For non-associating components we find

$$
\begin{aligned}
\frac{\partial Q}{\partial n_l} &= -\left(\frac{n^2}{2V}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij} + \frac{n}{2}\sum_i \sum_{j\neq i} x_i XAB_{ij}\Delta_{ij}^{\text{intra}}\right)\frac{\partial \ln g}{\partial n_l} \\
&= -\frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial \ln g}{\partial n_l} \tag{C.18}
\end{aligned}
$$

and for associating components we have

$$
\begin{aligned}
\frac{\partial Q}{\partial n_l} &= \ln X0_l + \left[1 + K_l - \sum_i^{\text{NS}_l} XA_i - \frac{n}{V}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}\right. \\
&\quad \left. -\frac{1}{2}\sum_i \sum_{j\neq i} x_i XAB_{ij}\Delta_{ij}^{\text{intra}}\right] - \left(\frac{n^2}{2V}\sum_i \sum_j x_i x_j XA_i XA_j \Delta_{ij}\right. \\
&\quad \left. +\frac{n}{2}\sum_i \sum_{j\neq i} x_i XAB_{ij}\Delta_{ij}^{\text{intra}}\right)\frac{\partial \ln g}{\partial n_l} \\
&= \ln X0_l - \frac{n}{2}\sum_i x_i(1 - XA_i)\frac{\partial \ln g}{\partial n_l} \tag{C.19}
\end{aligned}
$$

The terms in the square bracket sums to zero according to (5.97), and the red term is the only difference between the derivative for associating and non-associating compounds.

Derivatives of $\partial Q/\partial n_l$ with respect to n_k, V and T

The derivatives of $\partial Q/\partial n_k$ are given by:

$$
\begin{aligned}
\frac{\partial}{\partial n_k}\left(\frac{\partial Q}{\partial n_l}\right) &= \frac{1}{X0_l}\frac{\partial X0_l}{\partial n_k} - \frac{1}{2}\sum_i^{\text{NS}_k}(1 - XA_i)\frac{\partial \ln g}{\partial n_l} + \frac{1}{2}\sum_i x_i \frac{\partial \ln g}{\partial n_l}\frac{\partial XA_i}{\partial n_k} \\
&\quad -\frac{1}{2}\sum_i x_i(1 - XA_i)\frac{\partial^2 \ln g}{\partial n_l \partial n_k} \tag{C.20}
\end{aligned}
$$

$$\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial n_l}\right) = \frac{1}{X0_l}\frac{\partial X0_l}{\partial V} + \frac{1}{2}\sum_i x_i \frac{\partial \ln g}{\partial n_l}\frac{\partial XA_i}{\partial V} - \frac{1}{2}\sum_i x_i(1-XA_i)\frac{\partial^2 \ln g}{\partial n_l \partial V} \quad \text{(C.21)}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial Q}{\partial n_l}\right) = \frac{1}{X0_l}\frac{\partial X0_l}{\partial T} + \frac{1}{2}\sum_i x_i \frac{\partial \ln g}{\partial n_l}\frac{\partial XA_i}{\partial T} - \frac{1}{2}\sum_i x_i(1-XA_i)\frac{\partial^2 \ln g}{\partial n_l \partial T} \quad \text{(C.22)}$$

The red terms are only included if component l is associating and the blue term is only included if component k is associating.

How to determine the derivative of XA_i with respect to n_k is explained in section C.2.

The red terms in (C.20), (C.21) and (C.22) can for the components that only form intermolecular bonds be calculates as

$$\frac{1}{X0_l}\frac{\partial X0_l}{\partial y} = \sum_n^{\text{NS}_l} \frac{1}{XA_n}\frac{\partial XA_n}{\partial y} \quad \text{(C.23)}$$

where $y = n_k$, V and T.

For the component that also form intramolecular bonds the same term is calculated as

$$\frac{1}{X0_l}\frac{\partial X0_l}{\partial y} = \frac{1}{XAB_{ij}}\frac{\partial XAB_{ij}}{\partial y} + \sum_{m\neq i,j}^{\text{NS}_l} \frac{1}{XA_m}\frac{\partial XA_m}{\partial y} \quad \text{(C.24)}$$

The composition derivative of XAB_{ij} is given by:

$$\frac{\partial XAB_{ij}}{\partial n_k} = \left(\frac{\partial XAB_{ij}}{\partial n_k}\right)_{XA} + \sum_m \frac{\partial XAB_{ij}}{\partial XA_m}\frac{\partial XA_m}{\partial n_k} \quad \text{(C.25)}$$

where:

$$\left(\frac{\partial XAB_{ij}}{\partial n_k}\right)_{XA} = \left[XAB_{ij} + \frac{XA_i x_j^2 \frac{V_m^2}{g^2}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2}\right]\frac{\partial \ln g}{\partial n_k}$$
$$- \frac{XA_i x_j^2 \frac{V_m}{g}}{\left(x_j\frac{V_m}{g} + x_j\sum_n x_n XA_n\frac{\Delta_{jn}}{g}\right)^2}\sum_n^{NS_k} XA_n\frac{\Delta_{jn}}{g} \quad \text{(C.26)}$$

The blue term is only for associating components.

$\partial X AB_{ij}/\partial X A_m$ was given in equation (C.15).

The temperature derivative is similarly given by:

$$\frac{\partial X AB_{ij}}{\partial T} = \left(\frac{\partial X AB_{ij}}{\partial T}\right)_{XA} + \sum_m \frac{\partial X AB_{ij}}{\partial X A_m}\frac{\partial X A_m}{\partial T} \tag{C.27}$$

where $(\partial X AB_{ij}/\partial T)_{XA}$ was given in equation (C.13).

Finally the volume derivative of $X AB_{ij}$ is given by:

$$\frac{\partial X AB_{ij}}{\partial V} = \left(\frac{\partial X AB_{ij}}{\partial V}\right)_{XA} + \sum_m \frac{\partial X AB_{ij}}{\partial X A_m}\frac{\partial X A_m}{\partial V} \tag{C.28}$$

where:

$$
\begin{aligned}
\left(\frac{\partial X AB_{ij}}{\partial V}\right)_{XA} &= \frac{X A_i x_j \dfrac{1}{g}}{x_j \dfrac{V_m}{g} + x_j \sum_n x_n X A_n \dfrac{\Delta_{jn}}{g}} - \frac{X A_i x_j \dfrac{V_m}{g^2}}{x_j \dfrac{V_m}{g} + x_j \sum_n x_n X A_n \dfrac{\Delta_{jn}}{g}}\frac{\partial g}{\partial V} \\[2em]
&\quad - \frac{X A_i x_j^2 \dfrac{V_m}{g^2}}{\left(x_j \dfrac{V_m}{g} + x_j \sum_n x_n X A_n \dfrac{\Delta_{jn}}{g}\right)^2} \\[2em]
&\quad + \frac{X A_i x_j^2 \dfrac{V_m^2}{g^3}}{\left(x_j \dfrac{V_m}{g} + x_j \sum_n x_n X A_n \dfrac{\Delta_{jn}}{g}\right)^2}\frac{\partial g}{\partial V} \\[2em]
&= \frac{X AB_{ij}}{V} - X AB \frac{\partial \ln g}{\partial V} \\[2em]
&\quad + \frac{X A_i x_j^2 \dfrac{V_m}{g^2}}{\left(x_j \dfrac{V_m}{g} + x_j \sum_n x_n X A_n \dfrac{\Delta_{jn}}{g}\right)^2}\left[-1 + V_m\frac{\partial \ln g}{\partial V}\right] \tag{C.29}
\end{aligned}
$$

C.2   Derivatives of f_i and XA_i

The f function is used to determine XA, and was given in equation (5.138)

Determination of XA

To determine **XA** so that $\mathbf{f} = \mathbf{0}$ we need $\partial f_i / \partial XA_m$.

For $m \neq i$:

$$
\frac{\partial f_i}{\partial XA_m} = x_i x_m \frac{\Delta_{im}}{g} - \sum_j \frac{\dfrac{V_m^2}{g} x_i x_j \dfrac{\Delta_{ij}}{g} W_{ij} x_j x_m \dfrac{\Delta_{jm}}{g}}{\left(x_j \dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g} \right)^2} \tag{C.30}
$$

and for $m = i$:

$$
\frac{\partial f_i}{\partial XA_i} = \frac{x_i V_m}{XA_i^2 g} + x_i x_i \frac{\Delta_{ii}}{g} - \sum_j \frac{\dfrac{V_m^2}{g} \left(x_i x_j \dfrac{\Delta_{ij}}{g} \right)^2 W_{ij}}{\left(x_j \dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g} \right)^2} \tag{C.31}
$$

We then find **XA** by solving $\mathbf{DF} \times \boldsymbol{\Delta} - \mathbf{f} = \mathbf{0}$ ($DF_{im} = \partial f_i / \partial XA_m$) for $\boldsymbol{\Delta}$ and setting $\mathbf{XA} = \mathbf{XA} + \boldsymbol{\Delta}$ and iterate until convergence.

Derivative of f_i and XA_i with respect to V

In order to determine $\partial XA_i / \partial V$ we first need to find the volume derivative of f_i at constant **XA**:

$$
\left(\frac{\partial f_i}{\partial V}\right)_{XA} = (XA_i - 1)\frac{x_i}{XA_i g} - (XA_i - 1)\frac{x_i V_m}{XA_i g^2}\frac{\partial g}{\partial V}
$$

$$
+ \sum_j \frac{2\dfrac{V_m}{g}x_i x_j \dfrac{\Delta_{jn}}{g}W_{ij}}{x_j\dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}
$$

$$
- \sum_j \frac{\dfrac{V_m^2}{g^2}x_i x_j \dfrac{\Delta_{ij}}{g}W_{ij}}{x_j\dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}\frac{\partial g}{\partial V}
$$

$$
- \sum_j \frac{\dfrac{V_m^2}{g^2}x_i x_j^2 \dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}
$$

$$
+ \sum_j \frac{\dfrac{V_m^3}{g^3}x_i x_j^2 \dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j \sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\frac{\partial g}{\partial V} \qquad \text{(C.32)}
$$

We can then solve

$$
\frac{\partial f_i}{\partial V} = \left(\frac{\partial f_i}{\partial V}\right)_{XA} + \sum_j \frac{\partial f_i}{\partial XA_j}\frac{\partial XA_j}{\partial V} = 0 \qquad \text{(C.33)}
$$

to find $\partial XA_j / \partial V$.

Derivative of f_i and XA_i with respect to T

Similarly for $\partial XA_m/\partial T$ we first calculate

$$\left(\frac{\partial f_i}{\partial T}\right)_{XA} = -(XA_i - 1)\frac{x_i V_m}{XA_i g^2}\frac{\partial g}{\partial T} + x_i \sum_j x_j XA_j \frac{\partial \Delta_{ij}/g}{\partial T}$$

$$- \sum_j \frac{\dfrac{V_m^2}{g^2}x_i x_j \dfrac{\Delta_{ij}}{g}W_{ij}}{x_j \dfrac{V_m}{g} + x_j \displaystyle\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}\frac{\partial g}{\partial T}$$

$$+ \sum_j \frac{\dfrac{V_m^2}{g}x_i x_j W_{ij}}{x_j \dfrac{V_m}{g} + x_j \displaystyle\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}\frac{\partial \Delta_{ij}/g}{\partial T}$$

$$+ \sum_j \frac{\dfrac{V_m^3}{g^3}x_i x_j^2 \dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j \dfrac{V_m}{g} + x_j \displaystyle\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\frac{\partial g}{\partial T}$$

$$- \sum_j \left[\frac{\dfrac{V_m^2}{g}x_i x_j^2 \dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j \dfrac{V_m}{g} + x_j \displaystyle\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\sum_n x_n XA_n \frac{\partial \Delta_{jn}/g}{\partial T}\right] \quad \text{(C.34)}$$

and then determine $\partial XA_j/\partial T$ by solving

$$\frac{\partial f_i}{\partial T} = \left(\frac{\partial f_i}{\partial T}\right)_{XA} + \sum_j \frac{\partial f_i}{\partial XA_j}\frac{\partial XA_j}{\partial T} = 0 \quad \text{(C.35)}$$

Derivative of f_i and XA_i with respect to n_l

The same approach is used to determine $\partial XA_j/\partial n_l$, but when taking the composition derivative we again need to differentiate between associating and non-associating components.

$$
\left(\frac{\partial f_i}{n_l}\right)_{XA} = (XA_i - 1)\frac{V_m}{XA_i g} - (XA_i - 1)\frac{x_i V_m}{XA_i g^2}\frac{\partial g}{\partial n_l} + x_i \sum_j^{NS_l} XA_j \frac{\Delta_{ij}}{g}
$$

$$
+ \sum_j x_j XA_j \frac{\Delta_{ij}}{g} + \sum_{j \neq i} \frac{\dfrac{V_m^2}{g}x_j\dfrac{\Delta_{ij}}{g}W_{ij}}{x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}
$$

$$
- \sum_{j \neq i} \frac{\dfrac{V_m^2}{g^2}x_i x_j\dfrac{\Delta_{ij}}{g}W_{ij}}{x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}\frac{\partial g}{\partial n_l}
$$

$$
+ \sum_{j \neq i} \frac{\dfrac{V_m^3}{g^3}x_i x_j^2\dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\frac{\partial g}{\partial n_l}
$$

$$
- \sum_{j \neq i} \frac{\dfrac{V_m^2}{g}x_i x_j^2\dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\sum_n^{NS_l} XA_n \frac{\Delta_{jn}}{g}
$$

$$
= -(XA_i - 1)\frac{x_i V_m}{XA_i g^2}\frac{\partial g}{\partial n_l} + x_i \sum_j^{NS_l} XA_j \frac{\Delta_{ij}}{g}
$$

$$
- \sum_{j \neq i} \frac{\dfrac{V_m^2}{g^2}x_i x_j\dfrac{\Delta_{ij}}{g}W_{ij}}{x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}}\frac{\partial g}{\partial n_l}
$$

$$
+ \sum_{j \neq i} \frac{\dfrac{V_m^3}{g^3}x_i x_j^2\dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\frac{\partial g}{\partial n_l}
$$

$$
- \sum_{j \neq i} \frac{\dfrac{V_m^2}{g}x_i x_j^2\dfrac{\Delta_{ij}}{g}W_{ij}}{\left(x_j\dfrac{V_m}{g} + x_j\sum_n x_n XA_n \dfrac{\Delta_{jn}}{g}\right)^2}\sum_n^{NS_l} XA_n \frac{\Delta_{jn}}{g} \tag{C.36}
$$

The terms in green are only included if site i is on component l, and they sum to f_i/x_i which is equal to zero, and are therefore canceled out. The red terms are only for associating components, while the black terms are common for associating

and non-associating components.

$\partial XA_j/\partial n_l$ is then found by solving

$$\frac{\partial f_i}{\partial n_l} = \left(\frac{\partial f_i}{\partial n_l}\right)_{XA} + \sum_j \frac{\partial f_i}{\partial XA_j}\frac{\partial XA_j}{\partial n_l} = 0 \tag{C.37}$$