5-2006

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Recommended Citation

Octavio, Leah M., "Numerical Aspects of the SAFT Equation of State" (2006). *Senior Honors Projects.* Paper 13.
https://digitalcommons.uri.edu/srhonorsprog/13

Numerical Aspects of the SAFT Equation of State

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May 2, 2006

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Abstract

Equations of states are used to model fluid behavior. At a given temperature and pressure, for example, a mixture of water and alcohol might form a liquid and vapor phase, with the vapor phase being richer in alcohol and the liquid phase richer in water. In many industrial processes, such as distillation or extraction where mixtures of different compounds need to be separated, knowing how the fluid mixture will behave at various conditions helps make the operations more efficient and economical.

While many equations of state exist, they differ in their accuracy in modeling systems and in their mathematical complexity. In particular, the Statistical Association Fluid Theory (SAFT) equation is a model that holds great promise as a predictive model because of its basis in statistical mechanics. Unlike many other equations of state, it is able to account for non-spherical shaped molecules, attraction and repulsion between molecules and site-site interactions. But while it has been able to successfully model a wide range of fluid systems where other models have failed, the SAFT equation is also mathematically complicated. This work focuses on the numerical difficulties and issues that arise in using the SAFT equation, and how they can be resolved.

Numerical difficulties encountered in calculation of compressibility roots, mole fraction of unbonded sites, partial derivatives of the association term, and phase equilibria are addressed. Implications of simplifying assumptions about association strengths on different sites are also discussed. From the work done, it has been found that strategies making use of physically sound quantities in the SAFT model were successful in overcoming computational difficulties, which supports the predictive capabilities of the model. Current work is thus aimed at using the SAFT equation to model more complicated fluids, such as self-assembling surfactant systems, where it is expected that correct use of the sound physical basis of the model will lead to accurate results.

Keywords: SAFT, unbonded sites, compressibility roots, surfactant

Introduction

While the successful predictive capabilities of the Statistical Associating Fluid Theory (SAFT) equation of state have been well established (see, for example, Chapman et al, 1990: Huang and Radosz, 1991), few studies have revealed the numerical issues involved with using this equation. This report outlines the details of the numerical challenges encountered in calculating the monomer fraction (X^{Ai}), compressibility roots, and partial derivatives of the association term, with explanations of the strategies that are used to resolve these issues.

As the SAFT equation of state is capable of modeling various sized molecules with sites that can associate with other sites, future work includes testing the ability of the SAFT equation to model self-assembling systems, such as micelles and lamellae. To prepare for this, the use of unequal association strengths, which has not been reported in previous SAFT literature, is explored in detail with two numerical experiments.

We begin with a brief introduction of the SAFT equation.

Simplified SAFT Equation of State

Statistical Associating Fluid Theory, or SAFT, is an equation of state, which assumes fluid molecules are composed of spherical segments that can interact to form chains and associate at specific bonding sites. The equation of state is given in terms of residual Helmholtz energy as a function of molar density, with contributions from 1) Hard sphere effects, 2) Dispersion effects, 3) Chain formation, and 4) Association. The compressibility factor, Z, and the residual chemical potential may be derived by differentiation of $A^{\mathbf{res}}$ with respect to molar density and mole number, respectively.

SAFT has an advantage over other equations of state (like the Van der Waals EOS) because it takes into account the possible chain-like shape and size differences in the fluid molecules, and the effects of any association between molecules such as hydrogen bonding. It also has a solid basis in statistical fluid theory, with the hard sphere and dispersion terms analogous to the van der Waals molecular co-volume and attraction terms, and the chain formation and association terms based on Wertheim's theory (see Wertheim, 1985). SAFT has thus been successful in modeling behavior of many real fluids, pure components and mixtures alike.

Parameters that need to be determined for each fluid component modeled are $\mathbf{v^{00}}$, the molar volume of a segment at T=0 K, $\boldsymbol{\mu}$, the potential well depth, and **m**, the number of segments in the molecule. If the fluid molecules associate, two additional parameters are required: $\boldsymbol{\varepsilon}^{\mathbf{AB}}$, the energy at the interaction site, and $\boldsymbol{\kappa}^{\mathbf{AB}}$, the volume of the interaction site. These parameters can be obtained by fitting experimental liquid density and vapor pressure data to the SAFT model.

The SAFT equation is as follows; each term is discussed in more detail below. Symbols used are defined in the appendix.

$$\mathbf{A^{res} = A^{hs} + A^{disp} + A^{chain} + A^{assoc}}$$

Eq. 1

1) Residual Helmholtz energy from ***hard sphere*** effect for a mixture

$$6\,\frac{R\,T\left(\frac{\zeta_2^{\,3}+3\,\zeta_1\,\zeta_2\,\zeta_3-3\,\zeta_1\,\zeta_2\,\zeta_3^{\,3}}{\zeta_3\,(1-\zeta_3)^2}-\left(\zeta_0-\frac{\zeta_2^{\,3}}{\zeta_3^{\,2}}\right)\ln(1-\zeta_3)\right)}{\pi\,N_{av}\,\rho}$$

where

$$\zeta_k=\frac{1}{6}\,\pi\,N_{av}\,\rho\,\Sigma\,x_i\,m_i\left(6^{(1/3)}\left(\frac{v00_i\,\tau\left(1-C\,\mathbf{e}^{\left(-3\,\frac{\mu_i}{k\,T}\right)}\right)^3}{\pi\,N_{av}}\right)^{(1/3)}\right)^k$$

for k = 0,1,2,3

Eq. 2

For a pure component:

$$\mathbf{A^{hs}} = \frac{m\,R\,T\,(4\,\eta-3\,\eta^2)}{(1-\eta)^2}$$

Eq. 3

where

$$\eta=\frac{1}{6}\,\pi\,N_{av}\,m\,\rho\,6^{(1/3)}\left(\frac{v00\,\tau\left(1-C\,\mathbf{e}^{\left(-3\,\frac{\mu}{k\,T}\right)}\right)^3}{\pi\,N_{av}}\right)^{(1/3)}$$

Eq. 4

The residual Helmholtz energy from hard sphere effects takes the spherical shape of the molecule segments into account. This term assumes fluids are made of spheres that occupy a non-zero volume and that will bump off each other during collision (repulsion).

In the equations above, Eq. 2 is the hard sphere equation for mixtures derived by Mansoori et al[2]. Equation 3, which applies to pure component hard spheres, is an equation derived by Carnahan and Starling[1], obtained by writing the virial coefficients in closed form series. Virial coefficients for hard spheres are based on statistical mechanics, where a partition function for hard spheres (which is a function of the pair potential between the particles) is integrated over all the pairs of particles in the system.

In the expression for η, Eq. 4, the first term [(1/6) π Nav ρ] is simply the packing fraction of the molecule segments, which is the ratio of space occupied by the spherical segments to the total space available. The terms that follow the first in Eq. 4, which represent the effective hard sphere diameter, come from the pair potential equation used. In this case, the potential between hard spheres is modeled by a square well potential.

2) Residual Helmholtz energy from ***dispersion*** effects for a mixture

$$\mathbf{A^{disp}} = R\,T\,m\,Z_m \ln\left(\frac{v_s}{v_s + v\,Y}\right)$$

Eq. 5

where

$$v\,Y = \frac{N_{av}\,\Sigma_i\,\Sigma_j\,x_i\,x_j\,m_i\,m_j\left(\mathbf{e}^{\left(\frac{\mu\,T}{k}\right)} - 1\right)[.7072135785\,d_{ij}^{\,3}]}{\Sigma_i\,\Sigma_j\,x_i\,x_j\,m_i\,m_j}$$

$$v_s = \frac{1}{\rho\,m}$$

$$d_{ii} = 6^{(1/3)}\left(\frac{v00_i\,\tau\left(1 - C\,\mathbf{e}^{\left(-3\,\frac{\mu_i}{k\,T}\right)}\right)^3}{\pi\,N_{av}}\right)^{(1/3)}$$

The following mixing rules are used:

$$m = \Sigma_i\, x_i\, m_i$$

$$d_{ij} = \frac{1}{2} d_{ii} + \frac{1}{2} d_{jj}$$

$$\mu_{ij} = (1 - k_{ij}) \sqrt{\mu_i\, \mu_j}$$

For a pure component these equations reduce to:

$$\mathbf{A}^{\mathbf{disp}} = R\, T\, m\, Z_m \ln\left(\frac{v_s}{v_s + v\, Y} \right)$$

Eq. 6

Where

$$v\, Y = .7071067814\, N_{av}\, d^3 \left(\mathbf{e}^{\left(1/2 \frac{\mu \left(1 + \frac{e}{k\, T} \right)}{k\, T} \right)} - 1 \right)$$

In the Simplified SAFT Equation proposed by Fu and Sandler (1995), the only difference from the original equation was the dispersion term used. Equations for the dispersion term are generally obtained by fitting a power series to molecular dynamics data for square-well fluids, and in the Simplified SAFT model, the dispersion term was from Lee et al. (1985), which was a simpler equation than other dispersion terms available.

3) Residual Helmholtz energy from ***chain*** effects for a mixture

$$\mathbf{A}^{\mathbf{chain}} = R\, T\, \Sigma_i\, x_i\, (1 - m_i) \ln(g_{ii}^{hs}\, [\, d_{ii}\,])$$

Eq. 7

where

$$g_{ii}^{hs}[d_{ii}] = \frac{1}{1-\zeta_3} + \frac{\frac{3}{2} d_{ii} \zeta_2}{(1-\zeta_3)^2} + \frac{\frac{1}{2} d_{ii}^{\;2} \zeta_2^{\;2}}{(1-\zeta_3)^3} \quad \text{where}$$

$$\zeta_k = \frac{1}{6} \pi N_{av} \rho \Sigma x_i m_i \left(6^{(1/3)} \left(\frac{v00_i \tau \left(1 - C \mathbf{e}^{\left(-3 \frac{\mu_i}{k T}\right)} \right)^3}{\pi N_{av}} \right)^{(1/3)} \right)^k$$

for k = 0,1,2,3

For a pure component:

$$\mathbf{A}^{\mathbf{chain}} = \qquad R\, T\, (1-m) \ln\left(\frac{1 - .5\, \eta}{(1-\eta)^3} \right)$$

Eq. 8

Where

$$\eta = \frac{1}{6} \pi N_{av}\, m\, \rho\, 6^{(1/3)} \left(\frac{v00\, \tau \left(1 - C \mathbf{e}^{\left(-3 \frac{\mu}{k T}\right)} \right)^3}{\pi N_{av}} \right)^{(1/3)}$$

4) Residual Helmholtz energy from ***association*** effects for a mixture

$$\mathbf{A}^{\mathbf{assoc}} = \qquad R\, T\, \Sigma_i\, x_i\, (\Sigma_{\mathrm{Ai}}\, (\ln(X^{\mathrm{Ai}}) - .5\, X^{\mathrm{Ai}}) + .5\, M_i)$$

Eq. 9

Where

$$X^{\mathrm{Ai}} = \frac{1}{1 + N_{av}\, \Sigma_j\, \Sigma_{Bj}\, \rho_j\, X^{Bj}\, \Delta^{AiBj}}$$

$$\Delta^{AiBj} = g_{ij}^{\;hs}\;\{d_{ij}\}\;\mathbf{e}^{\left(\frac{\varepsilon^{AiBj}\;T}{k}\right)}\;d_{ij}^{\;3}\;\kappa^{AiBj}$$

$$g_{ij}^{\;hs}\;\{d_{ij}\} = \frac{1}{1-\zeta_3} + \frac{3\;d_{ii}\,d_{jj}\,\zeta_2}{(d_{ii}+d_{jj})\,(1-\zeta_3)^{2}} + \frac{2\;d_{ii}^{\;2}\;d_{jj}^{\;2}\;\zeta_2^{\;2}}{(d_{ii}+d_{jj})^{2}\,(1-\zeta_3)^{3}}$$

For a pure component:

$\mathbf{A}^{\mathbf{assoc}}$ = $R\;T\;(\Sigma_A\;(\ln(X^A)-.5\;X^A)+.5\;M)$

Eq. 10

Where

$$X^A = \frac{1}{1+N_{av}\;\Sigma_B\;\rho\;X^B\;\Delta^{AB}}$$

$$\Delta^{AB} = \frac{(1-.5\;\eta)\;\mathbf{e}^{\left(\frac{\varepsilon^{AB}\;T}{k}\right)}\;d^3\;\kappa^{AB}}{(1-\eta)^3}$$

Finally, the chain and association terms of the SAFT equation were derived by Chapman et. al. (1990), using Wertheim's theory. The chain term was derived essentially by extending the association to "infinite" association, thereby replacing association bonds with covalent, chain-forming bonds. This work largely focuses on the computational complexity that results from association.

I. Calculation of X^{Ai}, Mole fraction of Unbonded Sites

When performing root-finding calculations to obtain compressibility roots for a system with a mixture of associating components, the mole fractions of unbonded sites, X^{Ai}, must be computed at each iteration. Except for cases with only a single association site, values of X^{Ai} are obtained by solving a system of nonlinear equations, shown below.

$$X^{\mathrm{Ai}} = \frac{1}{1 + N_{av}\, \Sigma_j\, \Sigma_{Bj}\, \rho_j\, X^{Bj}\, \Delta^{AiBj}} \qquad \text{Eq. 11}$$

Since X^{Ai} is a function of the density (or compressibility, Z), the solutions to the nonlinear equations change at each value of Z during the root-finding calculations. This poses a problem since any initial guess for X^{Ai} must be sufficiently close to the correct solution~~s~~ to converge to a physically meaningful value. Otherwise, the calculations would converge to an incorrect value outside the range [0,1].

To overcome this problem and provide a good initial guess, the values of X^{Ai} were initialized using explicit expressions for X^{Ai} from Huang and Radosz[3], which were obtained by making a few simplifying assumptions about the association strengths at the different sites. For pure components, these expressions provide the actual X^{Ai} values while for mixtures, close approximations to the actual solution are obtained. Table 1 shows a comparison between the approximate mole fractions of unbonded sites using the explicit equations and the actual mole fractions from solving the system of equations, at various values of Z and compositions of a binary mixture of water and acetic acid. Note that for the most part, the approximate and actual values of X^{Ai} are very close, except at compositions close to either pure water or pure acetic acid. Despite this disparity, no root-finding compressibility calculations or phase equilibrium calculations performed have ever failed because of convergence to an incorrect set of X^{Ai} values when using this initialization strategy. This demonstrates that initializing X^{Ai} using the approximate explicit expressions from Huang and Radosz provides a reliable way to ensure convergence to the correct solution.

Table 1: Mole Fraction of Unbonded Sites for Acetic Acid (1) and Water (2) at T = 300K, p = 1.013 bar. Site 1 corresponds to –COOH site in acetic acid, and sites 2, 3 and 4 correspond to –H, -H and –O sites in water respectively. Tolerance = 1e-10.

Z = 0.5

Mole fraction of component (1)	***approx* site 1**	***actual* site 1**	***approx* site 2**	***actual* site 2**	***approx* site 3**	***actual* site 3**	***approx* Site 4**	***actual* site 4**
0.5	9.92E-3	1.40e-2	0.99887	0.99870	0.99887	0.99870	0.99773	0.99813
0.7	9.91E-3	1.18E-2	0.99886	0.99879	0.99886	0.99879	0.99773	0.99845
0.999	9.91E-3	9.92E-3	0.99886	0.99895	0.99886	0.99895	0.99773	0.99895

Z = 0.005

Mole fraction of component (1)	***approx* site 1**	***actual* site 1**	***approx* site 2**	***actual* site 2**	***approx* site 3**	***actual* site 3**	***approx* site 4**	***actual* site 4**
0.3	8.70E-4	1.56E-3	0.89739	0.91669	0.89739	0.91669	0.79479	0.83966
0.5	8.50E-4	1.19E-3	0.89422	0.93132	0.89422	0.93132	0.78844	0.87098
0.7	8.30E-4	9.86E-4	0.89090	0.94970	0.89090	0.94970	0.78180	0.90952

II. Calculation of Partial Derivatives of Association Term

To search for compressibility roots within the feasible region, the terrain method of Lucia and co-workers (Lucia and Yang, 2003) was used. This method requires function values, as well as first and second derivatives with respect to the molar density. For associating systems, the derivatives of the mole fraction of unbonded sites, X^{Ai}, with respect to density needed to be calculated. Since the functionality of X^{Ai} with respect to molar density is not explicitly calculated, many previous studies have used numerical methods requiring iterative computations to find X^{Ai} and its first and second derivatives[8].

In this study, however, iterative computations during compressibility root finding calculations were minimized by using the implicit function theorem to calculate first and second partial derivatives of X^{Ai} with respect to density. By doing so, only X^{Ai} needed to be computed iteratively and the derivatives could be calculated explicitly. Details of the derivative expressions are given in the appendix.

Once all roots in the feasible region were obtained, the lowest Z value was assigned as the liquid compressibility and the highest Z was the vapor compressibility.

III. Compressibility

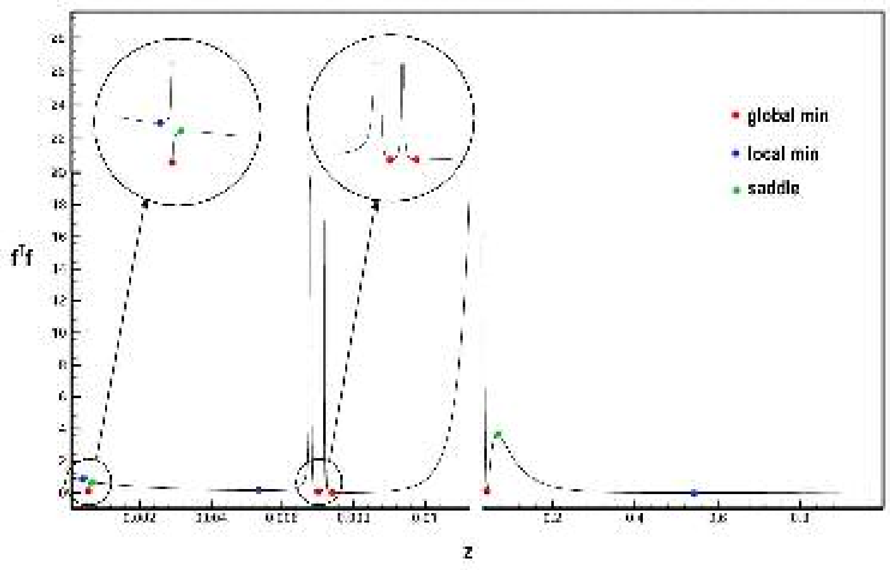
Nature of SAFT curve used for Root-finding calculations

For non-associating pure components, the SAFT equation of state is a seventh-order polynomial. With mixtures and associating components, the order increases. Finding and determining the correct compressibility roots, therefore, become much more challenging with the SAFT equation compared to simpler models, such as cubic equations of state.

To begin the search for roots, a lower bound for the compressibility is calculated using the minimum molar volume physically possible (mv^{00}). From numerous simulations performed, we have found that above this lower bound, the SAFT equation behaves much like a smooth, cubic equation, with three roots. Below the lower bound, the SAFT curve has several asymptotes and roots extremely close to each other, making root finding extremely difficult. Figure 1 gives an illustration of this.

As the figure shows, the portion of the curve after the first asymptote from the right-hand side (near $Z = 0.01$) is a smooth and well-behaved curve. The lower bound of Z always occurs to the left of the first asymptote in the curve. Moreover, the existence of this first asymptote, as well as others, is the result of the denominator in the hard sphere term, $(1-\zeta_3)$, approaching zero as ζ_3 becomes close to one. It can be easily shown, however, that at the suggested physical lower bound of Z, the function *always* has a value of ζ_3 less than one, so it is never at the asymptote (see justification in the appendix).

Figure 1: Compressibility roots for Pentane and Ethane mixture at T=240 K, p=10 bar



Compressibility Roots for the SAFT Equation for Non-Associating Binary Mixture

Importance of Setting a Lower Bound for Z

The key to success in compressibility root and phase equilibria calculation is limiting the search for Z to within the physically meaningful region and using knowledge that the SAFT curve is well behaved in this region. Below the lower bound, the erratic behavior of the curve might be attributed to certain quantities becoming physically meaningless. For example, at some values of Z below the lower bound, the radial distribution function g becomes negative. In associating systems, this negative value can cause monomer fraction calculations to fail. In the SAFT model, the numerical features of the function appear to support the physical significance of quantities within the model. Our experience shows that whenever difficulties were encountered during the calculations, the reason was the result of physically meaningless quantities being present in the model (e.g., negative values of the radial distribution function). In our opinion, one of the desirable features of the SAFT equation is that it holds great promise as a predictive model because of its sound physical foundations, as opposed to correlative models with no real physical basis. Thus we are interested in exploiting physically sound strategies, like using physically meaningful lower bound and trapping negative values of the radial distribution function, in order to preserve the capabilities of SAFT.

IV. Use of Unequal Association Strength at Different Sites

The association term in the SAFT equation of state was developed by Chapman et. al. using Wertheim's first order theory, which gives an important relationship between monomer density (or mole fraction of unbonded sites) and the residual Helmholtz energy from which other thermodynamic quantities, including compressibility and chemical potentials, can be derived. Key to calculating monomer density is the characterization of the association strength between different sites on the molecules.

While the theory does not allow ring like cluster formation, simultaneous bonding of one site to two different sites, or double bonding between two molecules, no constraints are imposed on the number and strength of association sites on a molecule[4]. In many previous simulations of associating mixtures performed using the SAFT equation of state, however, simplifying assumptions about the association strengths of different sites were made (see Huang and Radosz, 1991) and still used. For example, a carboxylic acid group is considered a single association site, and the two hydrogen atoms on a given water molecule are assumed to have equal association strengths.

In our opinion, these assumptions do not account for steric hindrance and, whether valid or not, have been incorporated for the specific purpose of simplifying the calculations to obtain X^{Ai} and also to reduce the number of association parameters required. To see this note that each site is characterized by two parameters: an association energy (ε^{AB}) and an association volume (κ^{AB}). Thus a molecule with three sites, for example, would have a total of six association parameters. Moreover, if the sites were assumed to have equivalent association strengths, then all sites would all have equal values of ε^{AB} and κ^{AB}. As a result, only two parameters are required for the molecule. For certain systems, especially ones with simple self-associating molecules, the assumptions might not introduce much error in the subsequent calculations. However, it is unknown-how the same assumptions might affect compressibility and phase equilibria calculations in more complicated systems, such as a self-assembling surfactant in solution. To investigate the validity of these simplifying assumptions, the following numerical experiments were performed.

Ethanol and water in a mixture are known to form hydrogen bonds: a hydrogen bond can form between the oxygen atom of ethanol and the hydrogen atom of water, or it can form between the hydrogen atom of ethanol and the oxygen atom of water. Let these hydrogen bonds be called WE and EW respectively. Under simplifying assumptions and cross-association mixing rules used in previous studies[3,5], these hydrogen bonds were considered to have equal association strengths. But in reality, this is not true. Relative binding energies calculations by Fileti et al. have shown that the EW hydrogen bond has a binding energy roughly 20% greater and a bond distance about 4% shorter than the WE hydrogen bond[6].

To determine whether the SAFT association term predicts the same 20% difference in the hydrogen bond strengths with the simplifying assumptions made, the following analysis was done. Fraction contributions of each site-site interaction to the mole fraction of bonded sites were first computed, by rearranging Eq. 11 as follows:

$$1- X^{Ai} = Nav \sum\sum (\rho\, x_j X^{Ai} X^{Bj} \Delta^{AiBj})$$

Then, the fraction contributions of the mole fraction of unbonded sites to the total Helmholtz association energy was computed. From these, the fraction contributions of each site-site interaction to the total Helmholtz association energy could then be determined. For example, to determine the fraction contribution of the interaction of site 1-5 to the total Helmholtz association energy, then the individual fraction contributions of the following bolded terms below would calculated and then multiplied together.

$$\begin{aligned} 1- X^1 = Nav(&\rho\, x_E X^1 X^1 \Delta^{11} + \rho\, x_E X^1 X^2 \Delta^{12} + \rho\, x_W X^1 X^3 \Delta^{13} \\ &+ \rho\, x_W X^1 X^4 \Delta^{14} + \boldsymbol{\rho\, x_W X^1 X^5 \Delta^{15}}) \end{aligned}$$

$$\begin{aligned} A^{assoc} = x_E\, (&\mathbf{\ln X^1 - 0.5X^1} + \ln X^2 - 0.5X^2) + x_W\, (\ln X^3 - 0.5X^3 + \\ &\ln X^4 - 0.5X^4 + \ln X^5 - 0.5X^5) + 0.5M_E + 0.5\, M_W \end{aligned}$$

Table 2 shows the results of the analysis for the Ethanol (1) and Water (2) mixture, using equal association strengths for the WE and EW bonds. From the result, it turns out that the SAFT equation predicts a fraction contribution of 0.078 for the WE bond, and a fraction contribution of 0.104 for the EW bond to the total Helmholtz association energy. Note that the Helmholtz energy of the WE bond is predicted to be slightly *lower* than the EW bond energy, which is *contrary* to the ab-initio calculation predictions.

Next, the association strengths of the EW and WE bonds were set unequal to each other and adjusted so that there would be the correct 20% difference in the fraction contributions of each bond. Then compressibility root calculations were done, with the results shown in Table 3.

Table 2: Fraction Contributions of Each Site-Site Interaction to Helmholtz Association Energy for Ethanol (1) and Water (2) at T=283.15 K, p=1.013 bar. Mole fraction of ethanol = 0.21, sites 1 and 2 correspond to –H and –O on ethanol respectively, and sites 3, 4 and 5 correspond to sites –H, –H, and –O on water respectively.

	X1		X2		X3		X4		X5
1-1	0	2-1	0.321619	3-1	0	4-1	0	5-1	**0.038622**
1-2	0.246213	2-2	0	3-2	**0.027618**	4-2	0.027618	5-2	0
1-3	0	2-3	**0.050097**	3-3	0	4-3	0	5-3	0.038753
1-4	0	2-4	0.050097	3-4	0	4-4	0	5-4	0.038753
1-5	**0.065685**	2-5	0	3-5	0.047462	4-5	0.047462	5-5	0

Table 3: Liquid Compressibility Factor, Z, for Ethanol (1) and Water (2) at T=283.15 K, p=1.013 bar. Tolerance = 1e-8.

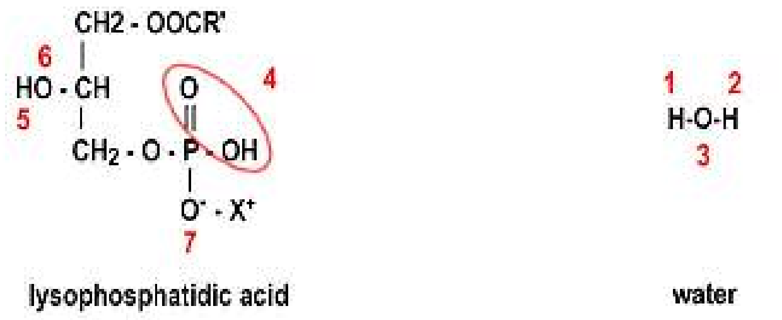
Mole fraction Ethanol	Z with equal strengths	Z with unequal strengths
0.281	1.22E-03	1.24E-03
0.477	1.55E-03	1.58E-03
0.610	1.79E-03	1.82E-03
0.881	2.32E-03	2.33E-03

The resulting compressibility roots for the case using equal association strengths and the case using unequal association strengths did not differ significantly. The reason is that for this example, it turns out that the contribution of the cross-association interaction between ethanol and water to the total residual Helmholtz energy was very little. Self-association interactions had the largest contribution toward the association Helmholtz energy, and the dispersion and hard sphere effects were actually more dominant than the association effects. Therefore, even though the simplifying assumptions did not necessarily capture the correct physics of the cross-association between alcohol and water, in the end this did not matter too much because the compressibility roots obtained did not change in either case.

For the next numerical experiment, now consider a water and surfactant mixture, where the water molecule has 3 association sites, and the surfactant (lysophosphatidic acid) has 4 association sites as shown in Figure 4. This time, the association strengths of the site-site interactions in the system are widely different, compared to the alcohol and water system earlier where only weak H-O hydrogen bonding occurred. In this system, the surfactant molecule has a charged group (site 7), which is known to form strong hydrogen bonds in water. At the same time, the surfactant also has hydroxyl groups (sites 5 and 6) that form weak hydrogen bonds. Literature values of strong hydrogen bonds are reported to be 14-40 kcal/mol, while weak hydrogen bonds are less than 4 kcal/mol[13].

To model this system, three schemes were proposed. In the first model, the cross-association strengths of all the interactions between the two molecules were set equal to each other except for the interactions with site 7. Next, in the second model, all cross-association interactions were set equal except those with sites 7 and 4. Finally, in the third model, the cross-association strengths of interactions with sites 7,4,5 and 6 were set unequal. Also, the unequal association strengths were adjusted so that the differences were about 50 to 100%, compared to the 20% difference in the alcohol and water system earlier. Parameters used for the surfactant were values chosen arbitrarily from the range of typical values found in literature (values used are given in the appendix).

Figure 4: Association Sites in Water (1) and Surfactant (2) System

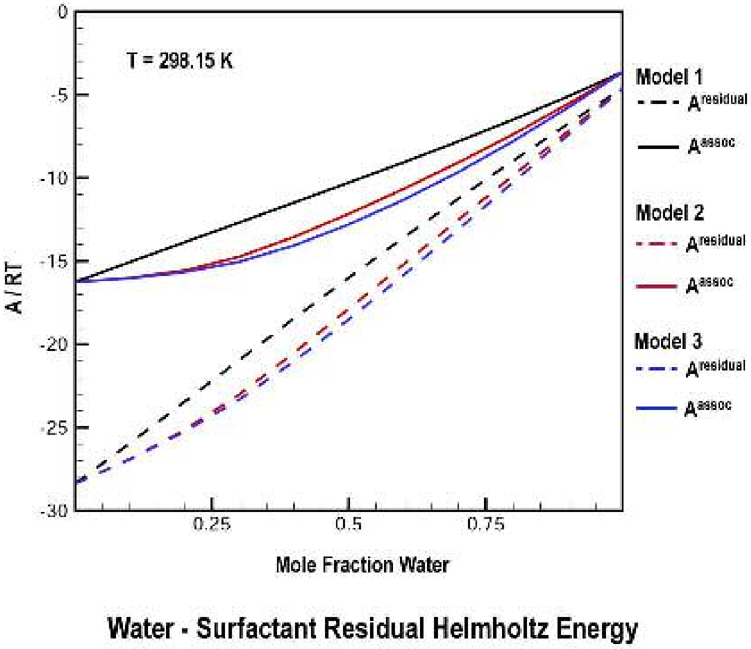


lysophosphatidic acid

water

When the effects on the Helmholtz association energy and the total residual Helmholtz energy of the cross-association interactions in this system were analyzed, we found that now the cross-association interactions contributed significantly to the Helmholtz association energy. Unlike the example earlier where the hard sphere and dispersion terms were dominant, the association term is now the dominant term. Figure 5 below shows that when modeled with most of the cross-association strengths equal to each other, the water-surfactant mixture behaves almost like an ideal mixture. But when modeled using unequal cross-association strengths, the mixture behaves more non-ideally.

Figure 5: Helmholtz Energy of Association and Total Residual Helmholtz Energy for the Water (1)-Surfactant (2) mixture at p=1.013 bar, T=298.15 K.



Finally, when compressibility calculations were done, the compressibility roots found were now significantly different, especially at mole fractions far from purity, as shown in Table 4. Thus, this example shows that simplifying assumptions made about equal association strengths might not only fail to capture the correct physics of the system, but eventually fail to give correct compressibility roots and phase equilibria behavior. The reason for this is that to perform phase equilibria calculations, the composition of phases present in equilibrium would be determined by first assuming a particular number of phases present, and then determining phase compositions that satisfied equality of chemical potentials. To calculate chemical potentials, the correct compressibility roots are required. Therefore, a significant change in the compressiblities would change the resulting phase equilibrium predictions.

Table 4: Liquid Compressibility Factor, Z, for Water (1) and Surfactant (2) at T=273.15 K, p=0.01 bar. Tolerance = 1e-8.

Mole fraction Water	Z with Model 1	Z with Model 2
0.55	5.61E-03	1.82E-02
0.6	4.67E-03	1.02E-02
0.65	3.89E-03	6.59E-03
0.8	2.16E-03	2.56E-03

Conclusion

From the investigations performed, we have found that strategies which make use of the physical quantities present in the SAFT model were successful in overcoming numerical difficulties encountered (i.e. use of Z lower bound). We have also seen that use of equal association strengths did not introduce much error in simulation of certain systems because the association effects were not dominant, but the same assumptions would introduce error in systems where the site-site interaction strengths differed widely and where association effects were dominant.

Future Work

Based on the investigation of the numerical aspects of the SAFT equation, particularly the limitations of the simplified association site strength calculations, and the successful strategies developed for monomer fraction and compressibility root calculations, the next step is to use the SAFT equation to model self-assembling systems by fitting parameters to surfactant solution data. This includes fitting association parameters where the association strengths of different sites are not constrained using simplifying assumptions (i.e., are not taken to be equal). It is hoped that by fully utilizing the unique capabilities of the SAFT equation to capture association behavior, self-assembling systems will be modeled correctly.

APPENDIX

Nomenclature

v^{00} – molar segment volume at T=0 K
μ – potential well depth
m – number of segments in the molecule
ε^{AB} – energy of interaction site
κ^{AB} – volume of interaction site
ρ – molar density
Nav – Avogadro's number
C – constant; 0.333
τ – constant; 0.74048
k – Boltzmann constant; 1.38e-33 J/K
T – temperature
R – universal gas constant
x – mole fraction
d_{ii} – effective segment diameter
$g_{ii}(d_{ii})$ – radial distribution function
X^{Ai} – mole fraction of molecules *not* bonded at site A
M – total number of association sites
Δ^{AB}– energy of association

Justification for Lower Bound Z not occurring at Asymptote

The denominator in the hard sphere term is $(1-\zeta_3)$, where $\zeta_3 = (\pi\ Nav\ \rho\ m\ d^3)/6$ for a pure component. In the expression for ζ_3, the term d is the effective segment diameter, given by $d= [(v^{00}\ 6\tau)/(\pi\ Nav)]^{1/3}$. At the lower bound for Z, the molar density is $\rho = 1/(mv^{00})$.

$$\zeta_3 = (\pi\ Nav\ \rho\ m\ d^3)/6$$
$$\zeta_3 = (\pi\ Nav\ (1/(mv^{00}))\ m\ [(v^{00}\ 6\tau)/(\pi\ Nav)]\ )/6$$
$$\zeta_3 = (\cancel{\pi\ Nav}\ (1/(\cancel{mv}^{00}))\ \cancel{m}\ [(\cancel{v}^{00}\ \cancel{6}\tau)/(\cancel{\pi\ Nav})]\ )/\cancel{6}$$

$\zeta_3 = \tau$, where $\tau = 0.74048$.

Therefore at the lower bound for Z, the denominator in the hard sphere term, $(1-\zeta_3)$, is always a positive number and not zero, which would cause the asymptote.

Partial Derivatives of X^{Ai} using Implicit Function Theorem

For a single association site, X^A is given by $X^A = 1/(1 + \mathrm{Nav}\,\rho X^A \Delta)$.

Let $G(X^A, \rho) = 1/(1 + \mathrm{Nav}\,\rho X^A \Delta)$, and define $F(X^A, \rho) = X^A - G(X^A, \rho)$.
By the implicit function theorem:

$$F(\mathit{X}^A, \mathit{\rho}) = F(X^A, \rho) + F'_{XA}\,\Delta X^A + F'_{\rho}\,\Delta\rho$$

Where X^A and $\mathit{\rho}$ are $X^A + \Delta X^A$ and $\rho + \Delta\rho$ respectively. At infinitesimally small $\Delta\rho$ and ΔX^A, $F(\mathit{X}^A, \mathit{\rho}) = F(X^A, \rho)$ so that the above equation can be rewritten as

$\Delta X^A/\Delta\rho = -F'_{\rho}/F'_{XA}$ or
$\delta X^A/\delta\rho = -F'_{\rho}/F'_{XA}$

For systems with more than one association site, analogous equations can be written:

$$DXU = -J_X^{-1} J_p$$

$$D2XU = -\{J_X^{-1} J_p' + \mathbf{[J_X^{-1}]'_p}\, J_p\}$$

$$D3XU = -\{2\,[J_X^{-1}]'_p\, J_p' + J_X^{-1} J_p'' + \mathbf{[J_X^{-1}]''_p}\, J_p\}$$

$$J_X J_X\, \mathbf{[J_X^{-1}]'_p} = -[J_X]'_p$$

$$J_X J_X J_X\, \mathbf{[J_X^{-1}]''_p} = 2\,[J_X]'_p [J_X]'_p - [J_X]''_p\, J_X$$

Where J_X, J_X' and J_X'' = matrix of first, second and third partial derivatives of $G(X^A, \rho)$ with respect to X^A respectively,

J_p, J_p' and J_p'' = vector of first, second and third partial derivatives of $G(X^A, \rho)$ with respect to ρ respectively

DXU, D2XU and D3XU = matrix of first, second and third partial derivatives of X^A with respect to molar density ρ

Note that to obtain the matrix of the partial derivatives of the elements in an inverse matrix (the quantities in bold above), the last two equations were solved using Gaussian elimination.

Parameters Used for the Surfactant

$\mu/k = 100$ K
$v^{00} = 15$ mL
$m = 9$
Values of Δ^{AB} were chosen to be between 1.E-16 and 1.E-20.

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