

## SAFT: Equation-of-State Solution Model for Associating Fluids

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### ABSTRACT

An equation-of-state model has been developed for predicting phase equilibria, based on the Statistical Associating Fluid Theory (SAFT). The agreement with molecular simulation data has been found to be excellent at all the stages of model development; for associating spheres, mixtures of associating spheres, and non-associating chains. The model has been shown to reproduce experimental phase equilibrium data for a few selected real pure compounds.

### INTRODUCTION

Associated fluid mixtures contain not only monomeric molecules of components but also clusters of like and unlike molecules, for example hydrogen-bonded and donor-acceptor clusters. Since effective molecular properties of the clusters (size, energy, shape) are very different from the monomeric molecules, the bulk fluid properties are also very different. One way to account for such association effects is to use statistical mechanical methods, such as the perturbation theory, to quantify the relationship between well defined site-site interactions and the bulk fluid behavior [Cummings 1984], [Cummings 1986], [Andersen], and [Wertheim]. Especially pertinent is Wertheim's contribution which provides the basis for our model of associating fluids.

Wertheim derived his theory by expanding the Helmholtz energy in a series of integrals of molecular distribution functions and the association potential. Based on physical arguments explained in the next section, Wertheim showed that many integrals in this series must be zero and, hence, a simplified expression for the Helmholtz energy can be obtained. This expression is a result of resummed terms in the expansion series (cluster expansion). Specifically, the Helmholtz energy can be calculated from Wertheim's resummed cluster expansion using perturbation theory.

The key result of Wertheim's resummed cluster expansion is an easy to use relationship between the residual Helmholtz energy due to association and the monomer density. This monomer density, in turn, is related to a function characterizing the 'association strength'. Wertheim's theory has been extended to mixtures of spheres and chain molecules, and tested against Monte Carlo simulations [Chapman 1988A, 1988B]. This paper presents an equation-of-state model of associating fluids, termed SAFT which stands for Statistical Associating Fluid Theory.

## RESIDUAL HELMHOLTZ ENERGY

The equation of state is defined in this section in terms of the residual Helmholtz energy  $a^{\text{res}}$  which is a sum of three terms representing contributions from different intermolecular forces. The first term  $a^{\text{seg}}$  accounts for that part of  $a^{\text{res}}$  which represents segment-segment interactions, such as, Lennard-Jones (LJ) interactions. The second term  $a^{\text{chain}}$  is due to the presence of covalent chain-forming bonds among the segments, for example the LJ segments. The third term  $a^{\text{assoc}}$  accounts for the increment of  $a^{\text{res}}$  due to the presence of site-site specific interactions among the segments, for example, hydrogen bonding interactions. The general expression for the Helmholtz energy is given below.

$$a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} \quad (1)$$

which is short for

$$a^{\text{res}} = a^{\text{seg}}(m^*\rho, T; \sigma, \epsilon) + a^{\text{chain}}(\rho; d, m) + a^{\text{assoc}}(\rho, T; d, \epsilon^{\text{AB}}, \kappa^{\text{AB}})$$

where  $\rho$  is the molar density of molecules, and the other symbols are defined below.

## ASSOCIATION TERM FOR PURE COMPONENTS

We start our analysis from the association term, first for pure self-associating compounds and, second for mixtures of associating components. The Helmholtz energy change due to association is calculated for pure components from

$$\frac{a^{\text{assoc}}}{RT} = \sum_A \left[ \ln X^A - \frac{X^A}{2} \right] + \frac{1}{2}M \quad (\text{general}) \quad (2)$$

where  $M$  is the number of association sites on each molecule,  $X^A$  is the mole fraction of molecules NOT bonded at site A, and  $\sum_A$  represents a sum over all associating sites on the molecule.

The mole fraction of molecules NOT bonded at site A can be determined as follows

$$X^A = \left[ 1 + N_{\text{Av}} \sum_B \rho X^B \Delta^{\text{AB}} \right]^{-1} \quad (\text{summation over ALL sites: A, B, C...}) \quad (3)$$

where  $N_{\text{Av}}$  is Avogadro's number and  $\rho$  is the molar density of molecules.  $\Delta^{\text{AB}}$  in equation (3) is the

'association strength' defined as

$$\Delta^{AB} = 4\pi F^{AB} \int_0^{r_c} r^2 g(r)^{seg} dr \quad (4)$$

where  $F^{AB}$  is given by

$$F^{AB} = \exp(\epsilon^{AB}/T) - 1 \quad (5)$$

The integral in equation (4) can be approximated, as explained in [Chapman, 1988A, 1988B], as follows

$$\Delta^{AB} = d^3 g(d)^{seg} \kappa^{AB} [\exp(\epsilon^{AB}/T) - 1] \quad (6)$$

which is our key property characterizing the association bonds. The association strength  $\Delta^{AB}$  given by equation (6) depends on two segment properties, the segment diameter  $d$ , and the segment radial distribution function  $g(d)^{seg}$ . Since we approximate our segments as hard spheres, we approximate  $g(d)^{seg}$  as the hard sphere radial distribution function [Carnahan]:

$$g(d)^{seg} \approx g(d)^{hs} = \frac{1 - \frac{1}{2}\eta}{(1 - \eta)^3} \quad (7)$$

where  $\eta$  is the reduced density defined as

$$\eta = \frac{\pi N_{Av}}{6} \rho d^3 m \quad (8)$$

where  $\rho$  is the molar density of molecules.

The association strength  $\Delta^{AB}$  given by equation (6) also depends on two parameters characterizing the association energy,  $\epsilon^{AB}$ , and volume,  $\kappa^{AB}$ . The only density dependence in  $\Delta^{AB}$  is given by  $g(d)^{seg}$  and the only explicit temperature dependence is given by the  $\epsilon^{AB}/T$ , in equation (6).

## ASSOCIATION TERM FOR MIXTURES

Extension to multicomponent mixtures is straightforward. The Helmholtz energy of association is calculated as an average which is linear with respect to mole fractions  $X_i$

$$\frac{a_{assoc}}{RT} = \sum_i X_i \left[ \sum_{A_i} \left[ \ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right] \quad (9)$$

where  $X^{A_i}$ , the mole fraction of molecules  $i$  NOT bonded at site A, is given below

$$X^{A_i} = \left[ 1 + N_{Av} \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \quad (10)$$

( $\sum_{B_j}$ , over ALL sites on molecule  $j$ :  $A_j, B_j, C_j, \dots$ ,  $\sum_j$ , over all components)

As we can see,  $X^A_i$  depends on the molar density  $\rho_j$

$$\rho_j = X_j \rho_{\text{mixture}} \quad (11)$$

and on the association strength  $\Delta^{A_i B_j}$

$$\Delta^{A_i B_j} = (d_{ij})^3 g_{ij}(d_{ij})^{\text{seg}} \kappa^{A_i B_j} \left[ \exp(\epsilon^{A_i B_j}/T) - 1 \right] \quad (12)$$

### CHAIN TERM

The increment of the Helmholtz energy due to bonding, on the other hand, can be determined from equation (13)

$$\frac{a^{\text{chain}}}{RT} = \sum_i X_i (1 - m_i) \ln(g_{ii}(d_{ii})^{hs}) \quad (13)$$

where  $m_i$  is the number of spherical segments in molecules of component  $i$ , and  $g_{ii}$  is the hard sphere pair correlation function for the interaction of two spheres  $i$  in a mixture of spheres, evaluated at the hard sphere contact. Equation (13) is derived based on the associating fluid theory where the association bonds are replaced by covalent, chain-forming bonds.

### RESULTS

The equation of state model described in the previous section, an extension of Wertheim's theory, is a result of a systematic development, from simple associating spheres and nonassociating chains, to associating mixtures of chains. At the early stages of this development the prototype versions of the model were carefully verified against molecular simulation data. Since detailed comparisons have been reported elsewhere [Chapman 1986, 1987, 1988A, 1988B], [Jackson], [Joslin], only sample results are shown here.

The initial version of the theory, for the associating pure spheres, was found to be in an excellent agreement with the canonical (NVT) Monte Carlo simulations of hard-core fluids [Joslin], [Chapman 1988A], [Jackson]. This agreement is illustrated for the compressibility factor of a hard-sphere fluid with single sites in Figure 1. Similar agreement was obtained for two-site systems and for other properties, such as, the configurational energy and the fraction of monomers.

The initial simplified extension of the associating fluid theory to chain molecules has also been tested with the computer simulation results of [Dickman] for dimers, tetramers, and octamers. The agreement shown in Figure 2 is believed to be satisfactory for our equation of state model.

Representative vapor pressure and saturated liquid density results for a chain alkane (n-octane) are shown in Figure 3. Representative vapor pressure and saturated liquid density results for self-associating compounds (acidic acid and methanol) are shown in Figures 4 and 5. These results were obtained using an argon equation of state, developed by Twu [1980], for  $a^{\text{seg}}$  in equation (1).

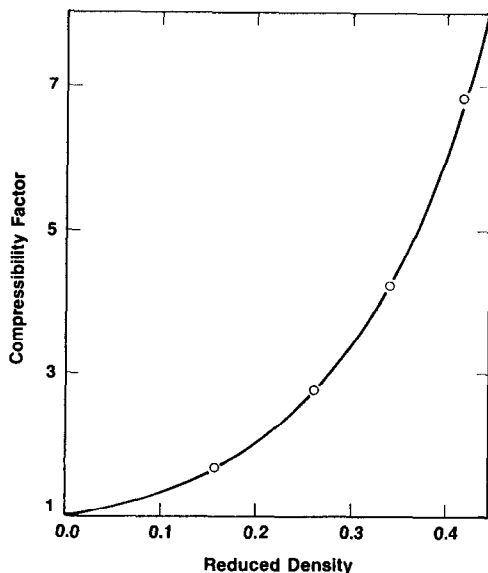


Figure 1. The compressibility factor  $Z = P/(\rho RT)$  for a hard sphere system with one attractive site as a function of reduced density ( $\eta$ ). The results of Monte Carlo simulations are represented by the circles, the solid curve represents theoretical predictions obtained from numerical integration which are essentially the same as those obtained from the approximated model, for  $\epsilon^{AA} = 7T$ ,  $\kappa^{AA} = 1.485E-4$  [Jackson].

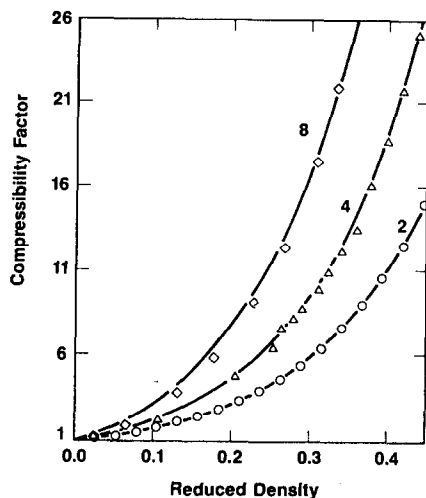


Figure 2. The compressibility factor, from Monte Carlo simulations of [Dickman] (points) and from theory (solid curves), for varying chain lengths of 2, 4, 8, as a function of reduced density  $\eta$  (equation 8).

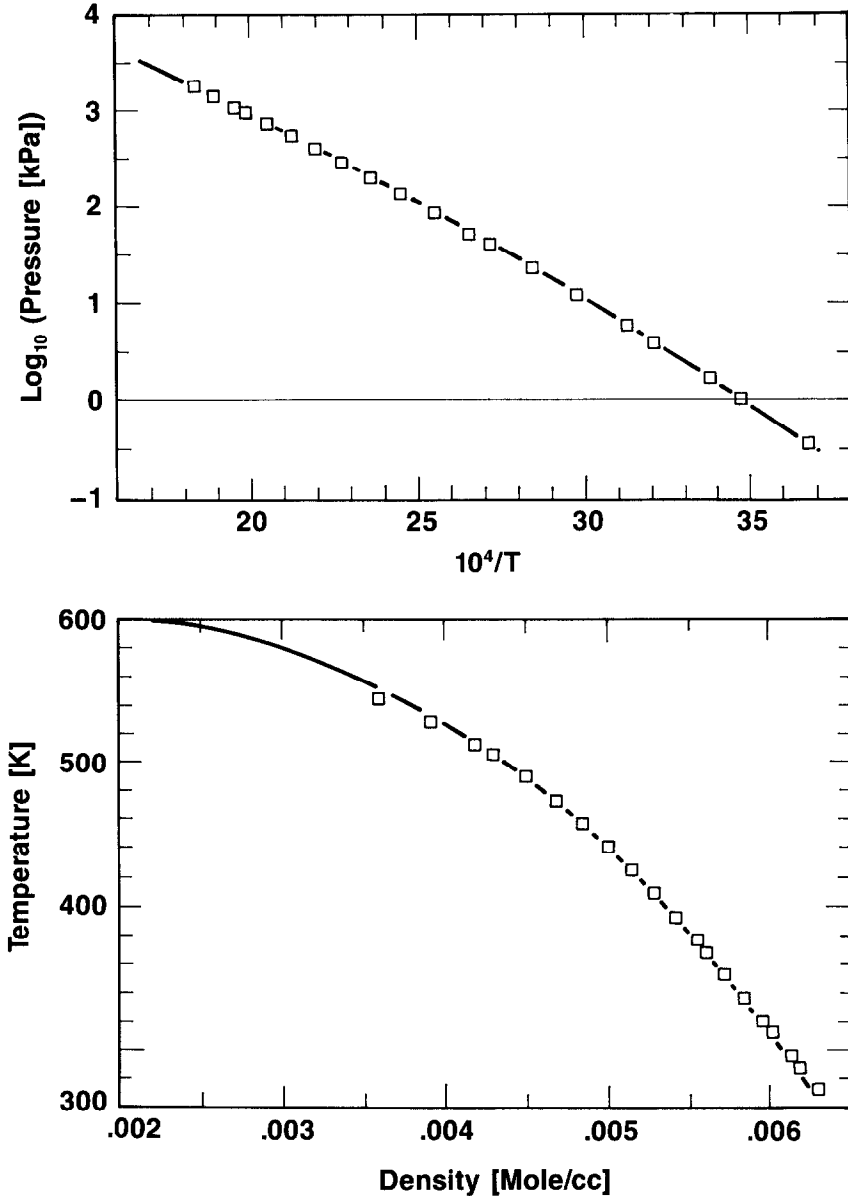


Figure 3. n-Octane vapor pressure and liquid density, experimental (squares [Anonymous]) and m predicted (solid curves).

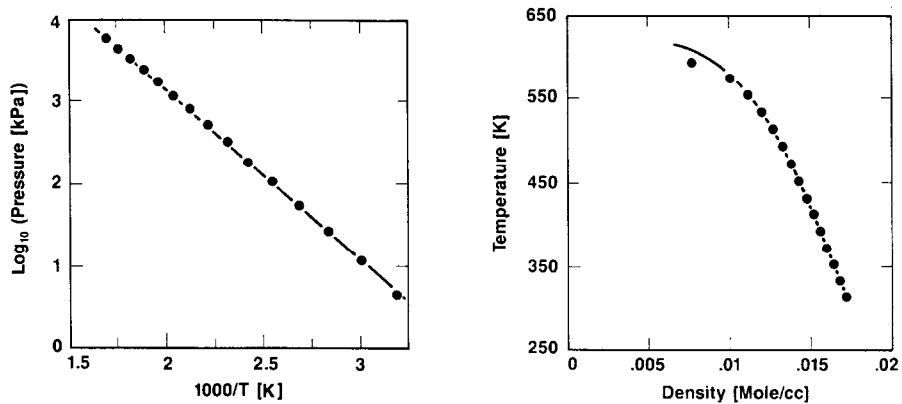


Figure 4. Acetic acid vapor pressure and liquid density, experimental (points [Anonymous]) and model predicted (solid curves).

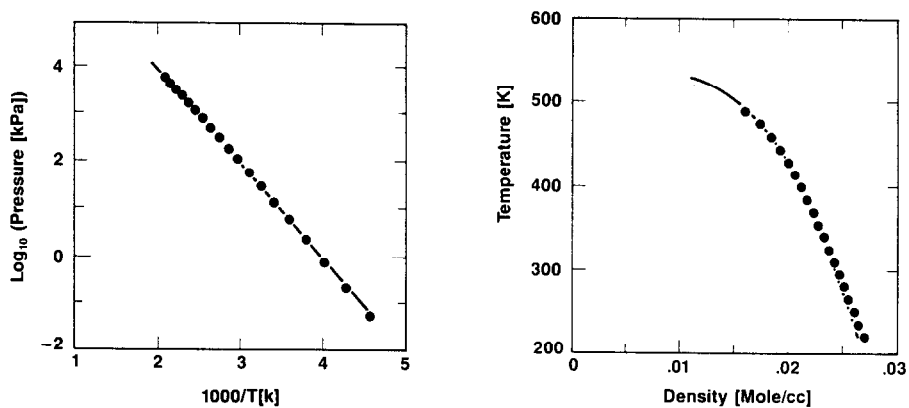


Figure 5. Methanol vapor pressure and liquid density, experimental (points [Anonymous]) and model predicted (solid curves).

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