Chemical, Quasi-Chemical and Perturbation Theories for Associating Fluids

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Pure fluids and mixtures of species that hydrogen bond behave differently from systems that interact only through dispersion forces. The deviations from classical behavior often are sufficiently large that conventional equations of state and activity models cannot be used without the introduction of large, condition-dependent empirical parameters. Consequently, three different classes of theories have been developed specifically to treat hydrogen-bonding systems. The first is based on the assumption that when molecules hydrogen-bond, they react to form new species and consequently is referred to as "chemical" theory. The second is based on lattice-fluid theory that is used to describe different types of specific interactions and is known as "quasi-chemical" theory. The last is based on the solution of integral equations using a potential function that mimics that of a hydrogen bond. It is shown here that these three approaches give essentially equivalent results. This allows one to relate the parameters in the perturbation theory to the equilibrium constant and hence greatly improves its utility for real systems. All three theories are compared with simulation data.

Introduction

Species that form hydrogen bonds often exhibit unusual thermodynamic behavior. In pure fluids, strong attractive interactions between like molecules result in the formation of molecular clusters that have considerable effect on the thermodynamic properties of the species. For example, water, which has four hydrogen bonding sites per molecule, has a boiling point that is much higher than the boiling point of neon, which is of approximately the same size and mass as water, but does not hydrogen bond. In mixtures, hydrogen bonding interactions can occur between molecules of the same species (self-association) or between molecules of different species (solvation). These interactions strongly affect the properties of the mixture. For example, strongly self-associating components usually exhibit liquid-liquid immiscibility with compounds that do not hydrogen-bond.

Probably the first attempt to describe associating systems was by Dolezalek (1908), who postulated that hydrogen bonds result in a series of equilibrium chemical reactions such that new species are formed in the system. In what has become known as chemical theory, equations are written for the chem-

ical equilibria in terms of temperature, density, composition, and the equilibrium constant. If the system behaves relatively ideally, except for the effect of the hydrogen bonding (that is, the system behaves as either an ideal gas or as an ideal solution), the equilibrium expressions can readily be solved to give solution properties including phase behavior. Simple chemical theory has been successful in describing solution properties for many real systems (Acree, 1984; Prausnitz et al., 1986).

When the system is at conditions where "physical" forces also must be considered, one must solve the expressions for phase equilibria and chemical equilibria simultaneously, usually by a trial-and-error numerical procedure. Renon and Prausnitz (1967) and Wiehe and Bagley (1967) used chemical theory to describe the vapor-liquid equilibria and excess functions for mixtures of alcohols with hydrocarbons. In both analyses, it was assumed that alcohols obey an infinite equilibrium model and that the hydrocarbons do not self-associate or solvate. Similar calculations for hydrogen bonding systems with more than one associating component have been performed (Gmehling et al., 1979; Wenzel et al., 1982; Nagata, 1985). If there is more than one associating component in the system, this approach becomes cumbersome.

Heidemann and Prausnitz (1976) showed that it is possible to solve analytically for the chemical equilibria within the equation of state so that the conditions of the phase equilibria can be solved directly; this has led to the development of several new equations of state for hydrogen-bonding systems. Ikonomou and Donohue (1986, 1988) applied this approach using the perturbed-anisotropic-chain theory (PACT) and obtained a closed form equation of state, the associated-PACT (APACT). Because of the assumptions made in the development of APACT, the resulting hydrogen bonding terms are very simple mathematically. Recently, APACT was extended to a more general association scheme that accounts explicitly for the acidic and basic properties of each component in the mixture (Economou et al., 1990). Elliott et al. (1990) simplified APACT to obtain a simple equation of state for associating systems that is cubic for nonassociating components and has only three real roots for associating components. Anderko (1989a,b) has proposed a closed-form equation of state for hydrogen bonding systems that uses an approach similar to APACT. Panayiotou (1989, 1990) combined chemical theory into the Sanchez-Lacombe equation of state (Sanchez and Lacombe, 1976; Lacombe and Sanchez, 1976), a lattice fluid theory, to describe thermodynamic properties and phase equilibria of pure alcohols and mixtures of alcohols with alkanes. His hydrogen bonding expressions are similar to those derived by Heidemann and Prausnitz (1976) and by Ikonomou and Donohue (1986).

Lattice fluid theories also are used to describe specific interactions in liquid mixtures. Originally proposed by Guggenheim (1945, 1952), quasi-chemical theory is used widely to model nonrandom mixtures (Wilson, 1964; Renon and Prausnitz, 1968; Abrams and Prausnitz, 1975; Vera et al., 1977). Panayiotou and Vera (1980) proposed explicit expressions for local surfaces and local compositions based on quasi-chemical theory and incorporated these expressions into an equation of state (Panayiotou and Vera, 1982). This equation was rederived for a multicomponent mixture and used for vapor-liquid equilibrium calculations and for solubility calculations for polymers in supercritical fluids (Kumar et al., 1987). Recently, this equation was recast as a group contribution lattice fluid equation of state (High and Danner, 1990). More recently, Panayiotou and Sanchez (1991) modified the Sanchez-Lacombe equation of state to account explicitly for hydrogen-bonding interactions. Unlike the chemical theories that focus on the distribution of associating species, their approach, which is similar in nature to quasi-chemical theory, counts the number of bonds between functional groups by defining a "chemical" partition function.

Physical theories for associating systems has advanced in the last decade by the use of statistical mechanical methods. Andersen (1973, 1974) formulated a theory for hydrogen bonding in dilute gases and in dense liquids using Mayer's cluster expansion theory. Cummings and Stell (1984) derived an analytical solution for the chemical association $A + B \rightleftharpoons AB$ in the Percus-Yevick approximation, and Cummings and Blum (1986) solved the Ornstein-Zernike equation for nonspherical molecules with anisotropic surface adhesion. Recently, Olaussen and Stell (1991) presented an "exact" statistical mechanical approach to solve the chemical association problem.

A similar approach is to use a perturbation theory with a potential function that would be expected to mimic hydrogen bonding. Wertheim (1984, 1986a–c, 1987) developed a model for systems with a repulsive core and multiple attractive sites capable of forming chains and closed rings. Using integral equations and the perturbation theory, Wertheim expanded the Helmholtz free energy in a series of integrals of molecular distribution functions. Many of the integrals are zero, and so a resummed cluster expansion was obtained. This result also was obtained by Andersen (1973, 1974) in his analysis for hydrogen-bonded fluids. Recently, Stell and Zhou (1989) derived a model for hydrogen bonding in ionic fluids that also is equivalent to Wertheim's perturbation theory. Gubbins and coworkers (Jackson et al., 1988; Chapman et al., 1988, 1990) simplified Wertheim's theory using only first-order thermodynamic perturbation theory (TPT-1) which allows chainlike and treelike clusters but not closed loops. The resulting theory is in good agreement with molecular simulation data (Jackson et al., 1988). Recently, an equation of state has been proposed based on TPT-1, the statistical associating fluid theory (SAFT) that is useful for phase equilibrium calculations of associating mixtures (Chapman et al., 1990; Huang and Radosz, 1990, 1991).

In this work, we examine equations of state for associating fluids from chemical theory, quasi-chemical theory, and perturbation theory. The physical assumptions and mathematical bases of these theories are quite different. Hence, one would expect them to have different behaviors. In fact, it has been said (Joslin et al., 1987) that Wertheim's perturbation theory "treatment is distinguished from earlier 'chemical' theories of association by a precise statistical-mechanical definition of what constitutes a monomer, dimer, etc. In contrast to these other theories, which are by essence largely empirical in nature, Wertheim's theory is completely deterministic." It, however, is likely that more traditional thermodynamicists would take exactly the opposite view. The chemical theories are derived in a way that relates both the molecular and macroscopic behavior to experimentally-accessible quantities. Though the perturbation theories may be deterministic, they are written in terms of parameters that are not accessible experimentally. Hence, one is faced with using a "rigorous" theory written in terms of unknown quantities or a theory that is considered (by some) to be less rigorous but which can be related to experimental measurements.

The purpose of this article is to show that if chemical theory and perturbation theory are applied with equal rigor, they give results that are essentially the same: that is, the analytic expressions derived (though written in terms of completely different physical parameters) are analytically identical in their functional form and are indistinguishable numerically. Comparisons are made with Monte Carlo simulation data. It is shown that all the three theories agree in their predictions of the distribution of associating species in the system. The Panayiotou-Sanchez quasi-chemical theory, however, does not give good values for the compressibility factor. This is due to the deficiencies in the Sanchez-Lacombe equation of state (Vimalchand and Donohue, 1989) and not in the quasi-chemical description of the hydrogen bonding.

Equations of State Using Chemical Theory

As discussed in the Introduction, most applications of chemical theory either assume that molecular interactions in the system result only from hydrogen bonding or that physical

interactions can be accounted for separately. When physical interactions are ignored, simple chemical theory is used to describe the thermodynamic properties of the system. When physical interactions are considered, the equations for chemical equilibria and physical equilibria usually are solved simultaneously by a trial-and-error procedure. Heidemann and Prausnitz (1976) showed that it is possible to solve for the chemical equilibria analytically and combine the results into the equation of state to solve for phase equilibria.

The Heidemann and Prausnitz (HP) approach has been applied to a number of different equations of state and for a number of different reaction schemes (Ikonomou and Donohue, 1986, 1988; Anderko, 1989a,b; Economou et al., 1990; Elliott et al., 1990). To familiarize the reader with the concepts and the notation, we review briefly the derivation for a component with one and two hydrogen-bonding sites per molecule.

In the case of a component M with two bonding sites per molecule, it is assumed that linear chains, (such as dimers and trimers) can be formed according to the chemical equilibria:

$$M_1 + M_1 \rightleftharpoons M_2$$
$$M_2 + M_1 \rightleftharpoons M_3$$
$$\vdots$$
$$M_i + M_1 \rightleftharpoons M_{i+1} \qquad (1)$$
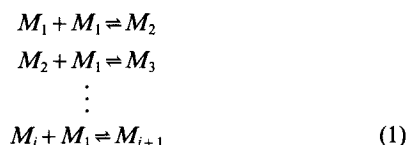
While there is spectroscopic evidence that many real compounds (such as alcohols) form cyclic species in addition to the linear species (Liddel and Becker, 1957; Becker et al., 1958), in the Heidemann and Prausnitz analysis, in APACT (Ikonomou and Donohue, 1986), and in many other models (Kretschmer and Wiebe, 1954; Acree, 1984; Painter et al., 1989), it is assumed that only linear association species are formed according to the chemical equilibria described by Eq. 1. The addition of other chemical equilibrium, and hence other equilibrium constants, complicates the problem and thus usually is avoided.

For linear chains, the true number of moles, n_T, and the number of moles that would exist in the system in the absence of any association, n_0, are:

$$n_T = n_1 + n_2 + n_3 + \cdots + n_i = \sum_i^\infty n_i \qquad (2)$$

$$n_0 = n_1 + 2n_2 + 3n_3 + \cdots + in_i = \sum_i^\infty in_i \qquad (3)$$

where n_i is the number of moles of the i-mer. The mole fractions of the associating species are defined as:

$$z_i = \frac{n_i}{n_T} \qquad (4)$$

Conservation of mass requires that the total number of moles, n_T, and the superficial number of moles, n_0 are related through the expression:

$$\frac{n_0}{n_T} = \sum_i^\infty iz_i \qquad (5)$$

The quantity n_T/n_0 is a measure of the extent of the association.

In the absence of any association in the system, n_T/n_0 is unity, whereas for strongly associating species n_T/n_0 is always less than unity. The chemical equilibria in Eq. 1 must obey the expression:

$$K_i = \frac{\phi_{i+1}}{\phi_i\phi_1 P} \frac{z_{i+1}}{z_i z_1} = \exp\left(-\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}\right) \qquad (6)$$

where the ϕ's are fugacity coefficients, ΔH^o is the standard enthalpy of association, and ΔS^o is the standard entropy of association. In the HP equation of state as well as in APACT, the simplifying assumption is made that the equilibrium constant K_i is independent of the degree of association ($K_2 = K_3 = \cdots = K$). The fugacity coefficients can be calculated through classical thermodynamics (Prausnitz et al., 1986), according to the equation:

$$\ln\phi_i = \int_V^\infty \left[\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{1}{V}\right]dV - \ln Z \qquad (7)$$

To evaluate the partial derivative in Eq. 7, an equation of state is needed. Heidemann and Prausnitz used a Carnahan-Starling-van der Waals-type equation of state to calculate the fugacity coefficient in Eq. 7. The ratio $P\phi_1\phi_i/\phi_{i+1}$ finally is obtained (Heidemann and Prausnitz, 1976):

$$\frac{P\phi_1\phi_i}{\phi_{i+1}} = \frac{n_T}{n_0}RT\rho e^g \qquad (8)$$

where ρ is the density, $\rho = 1/v_0$. In Eq. 8, g is a function of density and depends on the equation of state used to evaluate the fugacity coefficients and on the expressions used to calculate the equation-of-state parameters for the association species from the parameters for the monomer species. Heidemann and Prausnitz (1976) used the simple one fluid van der Waals mixing rules for both the size parameter, b, and the energy parameter, a. These mixing rules result in the following expression for g (Heidemann and Prausnitz, 1976):

$$g = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \qquad (9)$$

where η is the reduced density. The expression from Eq. 8 is substituted back to Eq. 6. From Eq. 6, an expression for z_i in terms of z_1 can be obtained by applying this equation to the formation of dimer, trimer, etc. The result is:

$$z_i = \left(K\frac{n_T}{n_0}RT\rho e^g\right)^{i-1} z_1^i \qquad (10)$$

The expression for z_i is substituted back to the material balance expression (Eq. 5) to give:

$$\frac{n_0}{n_T} = \sum_i^\infty i\left(K\frac{n_T}{n_0}RT\rho e^g\right)^{i-1} z_1^i \qquad (11)$$

Another equation can be written based on the constraint $\sum_i^\infty z_i = 1$:

$$\sum_i^\infty \left(K\frac{n_T}{n_0}RT\rho e^g \right)^{i-1} z_1^i = 1 \qquad (12)$$

Equations 11 and 12 are solved simultaneously for z_1 and n_T/n_0, and the result is:

$$z_1 = \frac{n_T}{n_0} = \frac{2}{1+\sqrt{1+4KRT\rho e^g}} \qquad (13)$$

The mole fraction of monomers (based on the superficial number of moles) is:

$$\frac{n_1}{n_0} = z_1 \frac{n_T}{n_0} = \frac{2}{1+2KRT\rho e^g + \sqrt{1+4KRT\rho e^g}} \qquad (14)$$

Finally, the equation of state is given in terms of the compressibility factor, Z, from the expression (Heidemann and Prausnitz, 1976):

$$Z = \frac{PV}{n_0RT} = 1 + Z^{\text{assoc}} + Z^{\text{rep}} + Z^{\text{attr}} \qquad (15)$$

where

$$Z^{\text{assoc}} = \frac{n_T}{n_0} - 1 \qquad (16)$$

$$Z^{\text{rep}} = \frac{n_T}{n_0}\frac{\eta(4-2\eta)}{(1-\eta)^3} \qquad (17)$$

$$Z^{\text{attr}} = -\frac{a}{bRT}\eta(1-4\eta) \qquad (18)$$

For compounds with two hydrogen-bonding sites per molecule $n_T/n_0 = (n_1/n_0)^{1/2}$, and so Z^{assoc} is obtained from Eqs. 14 and 16:

$$Z^{\text{assoc}} = \left(\frac{n_1}{n_0}\right)^{1/2} - 1 = -\frac{n_1}{n_0}\rho KRTe^g \qquad (19)$$

In APACT, the derivation is similar to the derivation described for the HP equation of state. The number of moles are defined according to Eqs. 2 and 3 and the equilibrium constant is defined as in Eq. 6. The perturbed anisotropic chain theory (PACT) of Vimalchand and Donohue (1985) was used to calculate the fugacity coefficient in Eq. 7. The molecular parameters for the associating species are calculated based on the parameters for the monomers using simple linear relations. One-fluid van der Waals-type mixing rules are used for mixtures. The particular expressions used in APACT result in a zero value for g in Eq. 8 over the whole range of density. If one relaxes, however, some of the assumptions made in the original derivation of the APACT, a nonzero function for g is obtained (Elliott et al., 1990). Finally, the expression for z_1 and n_T/n_0 is given from Eq. 13, and the expression for n_1/n_0 is given from Eq. 14, where $g=0$. The equation of state in terms of the compressibility factor, Z, is given from Eq. 15, where Z^{assoc} is calculated from Eqs. 16 and 19 and:

$$Z^{\text{rep}} = \frac{n_T}{n_0}\langle c \rangle \frac{\eta(4-2\eta)}{(1-\eta)^3} \qquad (20)$$

$$Z^{\text{attr}} = Z^{LJ} + Z^{\text{ani}} \qquad (21)$$

Lennard-Jones and anisotropic interactions are calculated using a perturbation expansion (Vimalchand, 1985). In this article, we present results for hard spheres with one or two hydrogen-bonding sites. Therefore, the attractive term of the equation of state is neglected. In Eq. 20, $\langle c \rangle$ is $1/3$ the number of external degrees of freedom of the molecules. A linear mixing rule is used to calculate $\langle c \rangle$:

$$\langle c \rangle = \sum_i^\infty z_i c_i \qquad (22)$$

To keep the equation simple, Ikonomou and Donohue (1986) made the assumption that the c parameter of an i-mer is simply $c_i = ic_1$, so the repulsive compressibility factor becomes association-independent:

$$Z^{\text{rep}} = c_1 \frac{\eta(4-2\eta)}{(1-\eta)^3} \qquad (23)$$

Panayiotou (1989) derived Eq. 13 for n_T/n_0 and Eq. 14 for n_1/n_0 independently using a completely different thermodynamic formalism. The resulting expressions were incorporated into the Sanchez-Lacombe equation of state.

For compounds with one hydrogen-bonding site per molecule, chemical equilibria between the acting sites result in the formation only of dimer species. The equilibrium between monomers and dimers is described by the expression:

$$K = \frac{\phi_2}{\phi_1^2 P}\frac{z_2}{z_1^2} \qquad (24)$$

The ratio of fugacity coefficients again is evaluated using Eq. 7, and z_2 can be expressed in terms of z_1. The material balance is of the form:

$$\frac{n_0}{n_T} = z_1 + 2z_2 \qquad (25)$$

and is solved simultaneously with the equation:

$$z_1 + z_2 = 1 \qquad (26)$$

to obtain the result:

$$\frac{n_T}{n_0} = \frac{2(KRT\rho e^g - 1)}{4KRT\rho e^g - 1 - \sqrt{1+8KRT\rho e^g}} \qquad (27)$$

$$z_1 = 2 - \frac{n_0}{n_T} \qquad (28)$$

From Eqs. 27 and 28, an expression for n_1/n_0 is obtained:

$$\frac{n_1}{n_0} = 2\frac{n_T}{n_0} - 1 = \frac{2}{1+\sqrt{1+8KRT\rho e^g}} \qquad (29)$$

The association compressibility factor, Z^{assoc}, for one hydrogen-bonding site per molecule is obtained through Eqs. 16, 27 and 29:

$$Z^{\text{assoc}} = \frac{n_1/n_0}{2} - \frac{1}{2} = -\left(\frac{n_1}{n_0}\right)^2 \rho K R T e^g \qquad (30)$$

For the case of a component with two bonding sites per molecule, the two sites are distinguishable, namely site A and site B, and only bonding of the type $A - B$ is allowed. For these systems, when two molecules hydrogen-bond to form a new species, two different equilibrium constants should be defined depending on which sites of the two molecules interact. Hence, for a pure component with two bonding sites, molecules may be indistinguishable, and the equilibrium constant defined in Eq. 6 is twice the equilibrium constant for the component with one bonding site. An extensive discussion on this issue is given by Economou et al. (1990).

Equations 24 through 30 were derived based on the APACT (Ikonomou and Donohue, 1986). However, if one applies the monomer-dimer equilibria to the HP equation of state, the same expressions for n_T/n_0 (Eq. 27), for z_1 (Eq. 28), for n_1/n_0 (Eq. 29) and for Z^{assoc} (Eq. 30) are obtained. The only difference between the two equations of state is that in APACT g is zero, whereas for HP g has a nonzero value given by Eq. 9. In APACT, the repulsive compressibility factor is given from Eq. 20, and it can be shown (Ikonomou and Donohue, 1986) that it is association-independent, whereas in the HP equation of state Z^{rep} is given from Eq. 17 and is association-dependent.

Elliott et al. (1990) showed that the extent of hydrogen bonding calculated from the chemical theory is numerically equivalent to that calculated from the perturbation theory, if the assumption made by Ikonomou and Donohue (1986) about the variation of the parameter c with the extent of association is relaxed. In this equation of state, referred to as ESD hereafter, they did not make any a priori assumption about the variation of c_i with i. Instead, c_i was calculated from the expressions used for the other molecular parameters for the associating chains. Finally, the ESD equation of state is given from Eq. 15 where Z^{assoc} is calculated from Eq. 16 and:

$$Z^{\text{rep}} = \frac{4c\eta}{1 - 1.9\eta} \qquad (31)$$

$$Z^{\text{attr}} = -\frac{9.49 q\eta Y}{1 + 1.7745 Y\eta} \qquad (32)$$

where q is a shape parameter and Y is given by Elliott et al. (1990). Both the repulsive and the attractive terms in the ESD equation of state are association-independent. The ESD equation of state derivation for associating systems was based on the approach used in APACT, and as a result the expressions for n_T/n_0, n_1/n_0 and z_1 are identical to the expressions derived for APACT and are not repeated. The only difference is the functional form of g which depends on the physical terms of the equation of state and on the mixing rules. In ESD, g is a nonzero function given by:

$$g = -\ln(1.0 - 1.9\eta) \qquad (33)$$

In this work, we also relax the assumption about the c_i parameter being equal to ic_1 and rederive APACT. We have determined values for the parameter c for chains of various lengths from the generalized Flory-dimer (GF-D) equation of state of Honnel and Hall (1989). The expression for c_i derived from this procedure is:

$$c_i = c_1 + 0.8(i - 1)c_1 \qquad (34)$$

The resulting equation is referred as APACT-2 and is given from Eq. 15. The association and the repulsive term in Eq. 15 are modified as follows. For compounds with two hydrogen-bonding sites per molecule, the association term is given from Eq. 19 and the mole fraction of the monomers is given from Eq. 14. However, g is a nonzero function for APACT-2. It is evaluated from Eq. 7 and given by the expression:

$$g = 0.2c_1 \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \qquad (35)$$

In addition, the repulsive term is calculated through Eqs. 20, 22, and 34:

$$Z^{\text{rep}} = c_1 \frac{n_T}{n_0} \frac{z_1}{1 - K z_1 \frac{n_T}{n_0} R T \rho e^g} \left(\frac{0.8}{1 - K z_1 \frac{n_T}{n_0} R T \rho e^g} + 0.2 \right)$$
$$\times \frac{\eta(4 - 2\eta)}{(1 - \eta)^3} \qquad (36)$$

For compounds with one hydrogen-bonding site per molecule, Z^{assoc} is calculated from Eq. 30, and n_1/n_0 is calculated from Eq. 29, where the g function is given from Eq. 35. The repulsive term in the compressibility equation is given from the expression:

$$Z^{\text{rep}} = c_1 z_1 \frac{n_T}{n_0} \left(1 + 1.8 K z_1 \frac{n_T}{n_0} R T \rho e^g \right) \frac{\eta(4 - 2\eta)}{(1 - \eta)^3} \qquad (37)$$

In APACT-2, the repulsive term in the compressibility expression becomes association-dependent (Eqs. 36 and 37) in contrast with the original APACT where only Z^{assoc} is association-dependent. The attractive term in APACT-2 is modified according to the assumption made in Eq. 34 and becomes association-dependent as well. The Z^{attr} term for APACT-2 is not given here, since this work is concerned only with hard spheres with hydrogen-bonding sites.

By setting the fugacity coefficients equal to unity in Eq. 6, the ideal gas equilibrium constant is obtained. In addition, in the ideal solution theory the equilibrium constant is written in terms of molar concentrations. For both cases, the derivation for n_T/n_0 and n_1/n_0 for components with one and two bonding sites per molecule results in the same expressions as the other chemical theories. However, g has a zero value over the whole range of density. As a result, the expressions obtained from APACT, ideal gas law, and ideal solution theory are identical for these quantities. However, there is a fundamental difference between these approaches. The result $g = 0$ in APACT is not an a priori assumption, but it is a result of the mixing rules and of the particular assumptions made in the derivation

of the equation. By relaxing some of these assumptions, a nonzero value for g is obtained. On the other hand, in the ideal gas calculations the fugacity coefficients are set equal to unity because of the ideal gas assumption, and this results in a zero value for g. Finally, in the ideal gas law the repulsive and the attractive contribution to the compressibility factor, Z^{rep} and Z^{attr}, are zero, and only Z^{assoc} has a nonzero value given by Eq. 16.

Quasi-Chemical Theory of Hydrogen Bonding

Quasi-chemical theory was introduced by Guggenheim (1945, 1952) to describe nonrandomness in mixtures. In this context, hydrogen bonding, which introduces strong specific interactions to the system, should be described quite well by the quasi-chemical approach. However, hydrogen bonding is not distinguished from the other types of specific interactions such as polar interactions, and hence it is not treated explicitly in the resulting equation of state.

Recently, Panayiotou and Sanchez (1991) incorporated hydrogen bonding into a lattice model, specifically the Sanchez-Lacombe equation of state (Sanchez and Lacombe, 1975; Lacombe and Sanchez, 1976) using an approach that is similar in nature to the quasi-chemical theory. Their basic assumption is that intermolecular interactions can be divided into physical and chemical (hydrogen bonding) interactions. As a result, one can write the partition function as a product of a physical term and a chemical (association) term:

$$Q = Q^{phys} Q^{assoc} \tag{38}$$

The physical term is the usual Sanchez-Lacombe expression, whereas the chemical term is evaluated by calculating the total number of ways of distributing the hydrogen bonds among the different functional groups of the system by preserving the total hydrogen-bonding energy. In the Sanchez-Lacombe-Panayiotou (SLP) equation of state, a distinction is made between the proton donor groups and the proton acceptor groups. The chemical partition function at temperature T is written as (Panayiotou and Sanchez, 1991):

$$Q^{assoc} = \left(\frac{\eta}{rN}\right)^{N_H} \prod_i^m \frac{N_d^i!}{N_{i0}!} \prod_j^n \frac{N_a^j!}{N_{0j}!}$$

$$\times \prod_i^m \prod_j^n \frac{\exp(-\Delta G_0^{assoc}/RT)}{N_{ij}!} \tag{39}$$

where
rN = total number of molecular segments in the system
N_H = total number of hydrogen bonds
N_d^i = total number of donor groups of type i
N_a^j = total number of acceptor groups of type j that is not hydrogen-bonded
N_{i0} = number of donor groups of type i
N_{0j} = number of acceptor groups of type j that are not hydrogen-bonded
ΔG_0^{assoc} = total Gibbs free energy change of hydrogen bonding
N_{ij} = total number of hydrogen bonds between donor group of type i and acceptor group of type j

There are m types of proton donor groups and n types of proton acceptor groups in the system, and:

$$N_{i0} = \sum_k^t d_i^k N_k - \sum_j^n N_{ij} \tag{40}$$

$$N_{0j} = \sum_k^t a_j^k N_k - \sum_i^m N_{ij} \tag{41}$$

where t is the total number of components in the system.

The Gibbs free energy is evaluated based on the maximum term approximation and then is minimized with respect to reduced volume and each of the N_{ij}. Minimization of G with respect to reduced volume leads to the equation of state. The resulting equation of state (SLP equation of state) can be expressed in terms of the compressibility factor and is given by Eq. 15. Unlike the chemical theories, in the SLP equation of state the number of hydrogen bonds is calculated rather than the number of the associating species. However, it is straightforward to calculate the ratio n_T/n_0 for chain molecules (noncyclic species). It is: $N_H = n_0 - n_T$ and so:

$$\frac{N_H}{n_0} = 1 - \frac{n_T}{n_0} \tag{42}$$

and finally Z^{assoc} is given from Eq. 16, and Z^{rep} and Z^{attr} are given from the expressions:

$$Z^{rep} = r\left[-\frac{1}{\eta}\ln(1-\eta) - 1\right] \tag{43}$$

$$Z^{attr} = -\frac{r\eta}{\tilde{T}} \tag{44}$$

Minimization of G with respect to N_{ij} leads to the following expression (Panayiotou and Sanchez, 1991):

$$\left(N_d^i - \sum_k^n N_{ik}\right)\left(N_a^j - \sum_k^m N_{kj}\right) = N_{ij}\frac{rN}{\eta}\exp(\Delta G_{ij}^{assoc}/RT) \tag{45}$$

Equation 45 can be applied for any number of components with different numbers of proton donor and proton acceptor groups per molecule. In the case of a pure component with one donor group and one acceptor group per molecule, there is only one type of hydrogen bonds in the system, and Eq. 45 simplifies to:

$$(N - N_{11})^2 = N_{11}\frac{rN}{\eta}\exp(\Delta G_{11}^{assoc}/RT) \tag{46}$$

Equations 42 and 46 result in the following expression for n_T/n_0:

$$\frac{n_T}{n_0} = \frac{2}{1 + \sqrt{1 + 4K\rho\frac{v^*}{r}}} \tag{47}$$

where $K = \exp(-\Delta G_{11}^{assoc}/RT)$ is defined as the equilibrium constant for the hydrogen-bond formation. Based on quasi-chemical theory, Guggenheim (1952) derived an expression for the nonrandomness in a mixture that is of the same functional form as Eq. 47.

For this system, the probability of finding a nonbonded site is equal to $1 - N_H/n_0$, and so the mole fraction of monomers, which is equal to the probability of finding a molecule with both of its sites nonbonded, is given by the expression:

$$\frac{n_1}{n_0} = \left(1 - \frac{N_H}{n_0}\right)^2 \qquad (48)$$

From Eqs. 42 and 48, one obtains:

$$\frac{n_1}{n_0} = \left(\frac{n_T}{n_0}\right)^2 = \frac{2}{1 + 2K\rho\frac{v^*}{r} + \sqrt{1 + 4K\rho\frac{v^*}{r}}} \qquad (49)$$

Therefore, Eqs. 16, 47 and 49 result in the following expression for Z^{assoc}:

$$Z^{\text{assoc}} = -\frac{n_1}{n_0}\rho K\frac{v^*}{r} \qquad (50)$$

The formalism of the SLP equation of state cannot be applied to components with one hydrogen-bonding site per molecule, because a distinction has to be made for the type of the bonding site and so self-association is not allowed. For components with more than two associating groups per molecule, Eq. 45 results in expressions that do not have an analytic solution, in general. In that case, the expressions for n_T/n_0 and n_1/n_0 can be evaluated numerically.

Physical Theories of Hydrogen Bonding

Cummings and Stell (1984) presented a statistical mechanical analysis of the chemical reaction of the type $A + B \rightleftharpoons AB$. To model the dimer formation, they used a hard sphere potential for the $A - A$ and $B - B$ interactions and a square well potential for the $A - B$ interactions that allowed only dimer formation and precluded formation of higher chains. Their model has an analytic solution in the Percus-Yevick approximation, and the equilibrium constant for the reaction could be expressed using statistical mechanical arguments.

Wertheim (1984) used a similar approach but developed equations that are much more general. He treats hydrogen bonding by perturbing a hard-core with off-center attractive sites. This pair potential model between molecules 1 and 2 is:

$$\phi(r, \omega_1, \omega_2) = \phi_R(r, \omega_1, \omega_2) + \sum_{A\in\Gamma}\sum_{B\in\Gamma}\phi_{AB}(r, \omega_1, \omega_2) \qquad (51)$$

where r denotes the magnitude of the vector r connecting the centers of molecules 1 and 2, and ω_1, ω_2 denote the orientations of molecules 1 and 2 relative to vector r. The repulsive part of the potential, $\phi_R(r, \omega_1, \omega_2)$, represents the interactions between two hard cores. The hydrogen-bonding potential, $\phi_{AB}(r, \omega_1, \omega_2)$, is purely attractive, $\phi_{AB}(r, \omega_1, \omega_2) < 0$, and is modeled as a square well potential with an energy depth of $-\epsilon_{AB}$. A is an attractive site on molecule 1, and B is an attractive site on molecule 2. Γ denotes the set of all independent attraction sites per molecule. This potential imposes various types of steric incompatibilities described in detail by Wertheim (1984) and Jackson et al. (1988).

Using this model potential, Wertheim developed a thermodynamic perturbation theory for compounds with one or multiple association sites per molecule. The reference system was the hard-sphere system. For a pure component with M attractive sites per molecule, the Helmholtz free energy due to association is given by the expression (Jackson et al., 1988):

$$\frac{A^{\text{assoc}}}{NkT} = \sum_{A\in\Gamma}\left(\ln X_A - \frac{X_A}{2}\right) + \frac{1}{2}M \qquad (52)$$

where X_A is the fraction of molecules not bonded at site A, N is the total number of molecules, k is the Boltzmann constant, and T is the temperature. The quantity X_A is calculated from the mass-action equation according to the expression:

$$X_A = \left(1 + \sum_{B\in\Gamma}\rho X_B\Delta_{AB}\right)^{-1} \qquad (53)$$

where $\rho = N/V$ is the total density, and Δ_{AB} is defined as:

$$\Delta_{AB} = \int g_r(r, \omega_1, \omega_2)f_{AB}(r, \omega_1, \omega_2)d(r, \omega_1, \omega_2) \qquad (54)$$

where $g_r(r, \omega_1, \omega_2)$ is the reference fluid pair correlation function, $f_{AB}(r, \omega_1, \omega_2)$ is the Mayer f-function defined as $f_{AB}(r, \omega_1, \omega_2) = \exp[-\phi_{AB}(r, \omega_1, \omega_2)/kT] - 1$, and the integration is performed over all orientations and separations of molecules 1 and 2. Δ_{AB} is a key function in Wertheim and subsequent analyses characterizing the association strength. Jackson et al. (1988) simplified the expression for Δ_{AB} and derived the following approximation that is applicable over the whole range of density:

$$\Delta_{AB} = 4\pi g_{HS}(\sigma^+)V_{AB}[\exp(\epsilon_{AB}/kT) - 1] \qquad (55)$$

where V_{AB} is the association volume of the component, and $g_{HS}(\sigma^+)$ is the contact value of the distribution function for the hard-sphere reference fluid given by:

$$g_{HS}(\sigma^+) = \frac{2 - \eta}{2(1 - \eta)^3} \qquad (56)$$

where $\eta = (N_{av}\pi/6)\rho m\sigma^3$ is the reduced density, N_{av} is the Avogadro number, m is the number of segments per molecule, and σ is the temperature-independent diameter of the spherical segment. In SAFT (Chapman et al., 1990; Huang and Radosz, 1990), a temperature-dependent hard-sphere diameter, d, is defined based on σ, and the temperature dependency of Δ_{AB} becomes slightly more complicated. In general, the solution for X_A in Eq. 53 is found using an iterative procedure. However, for some special cases, an analytic expression for X_A can be derived (Jackson et al., 1988; Huang and Radosz, 1990). The analytic expressions for one and two bonding sites per molecule are discussed later in this article.

The equation of state in terms of the compressibility factor, Z, is obtained from the expression for the Helmholtz free energy, and it can be written, as before, as a sum of the contributions from the ideal gas term, association interactions, repulsive interactions, and attractive (dispersion or mean field) interactions as given by Eq. 15, where

$$Z^{assoc} = \eta \sum_{A \in \Gamma} \left(\frac{\partial X_A}{\partial \eta}\right)_{T,N} \left(\frac{1}{X_A} - \frac{1}{2}\right) \qquad (57)$$

$$Z^{rep} = Z^{HS} + Z^{chain} = \frac{\eta(4-2\eta)}{(1-\eta)^3} - \frac{m-1}{m}\frac{1+\eta-\eta^2/2}{(1-\eta)(1-\eta/2)} \qquad (58)$$

where Eq. 58 is a general expression for a chain molecule with m the number of spherical segments in the chain. For spherical molecules, $m = 1$, and the second term in the right side of Eq. 58 vanishes. Dispersion interactions are taken into account in the equation of state through a simple van der Waals term:

$$Z^{attr} = -\frac{\epsilon_{MF}\eta}{kT} \qquad (59)$$

where ϵ_{MF} is a measure of the strength of the mean-field forces and a characteristic parameter for each component. For practical engineering calculations, a more complicated expression is used to take into account the dispersion interactions (Chapman et al., 1990; Huang and Radosz, 1990, 1991). However, it is not the purpose of this article to show the applicability of the perturbation theory to real systems, and so this expression is not presented here.

For a system with one bonding site per molecule, X_A represents the mole fraction of the monomers in the system, $X_A \equiv n_1/n_0$, and Eq. 53 reduces to:

$$\frac{n_1}{n_0} = \left(1 + \rho\frac{n_1}{n_0}\Delta_{AB}\right)^{-1} \qquad (60)$$

Solving this equation, one obtains:

$$\frac{n_1}{n_0} = \frac{2}{1 + \sqrt{1 + 4\rho\Delta_{AB}}} \qquad (61)$$

To calculate Z^{assoc}, the derivative $[(\partial n_1/n_0)/\partial\eta]_{T,N}$ must be evaluated. After tedious, but straightforward, algebra, one obtains:

$$\left(\frac{\partial n_1/n_0}{\partial \eta}\right)_{T,N} = -\frac{4\rho\Delta_{AB}}{(1+\sqrt{1+4\rho\Delta_{AB}})^2\sqrt{1+4\rho\Delta_{AB}}}\frac{2+2\eta-\eta^2}{\eta(2-3\eta+\eta^2)} \qquad (62)$$

and so:

$$Z^{assoc} = -\left(\frac{n_1}{n_0}\right)^2\rho\Delta_{AB}\frac{2+2\eta-\eta^2}{2(2-3\eta+\eta^2)} \qquad (63)$$

For a system with two hydrogen-bonding sites per molecule A and B, where only bonds of the form $A - B$ are allowed, Eq. 53 reduces to:

$$X_A = (1 + \rho X_B\Delta_{AB})^{-1} \qquad (64)$$

and for $X_A = X_B$, Eq. 64 is the same as Eq. 60, and the analytic expression for X_A is given by:

$$X_A = \frac{2}{1 + \sqrt{1 + 4\rho\Delta_{AB}}} \qquad (65)$$

However, in this case, X_A is not equal to the mole fraction of monomers, n_1/n_0. The first-order perturbation theory (Jackson et al., 1988) assumes that the activity of one bonding site is independent of the remaining sites on the same molecule. As a result, the fraction of the monomers, which essentially is the fraction of molecules that are not bonded to either of their sites A or B, is:

$$\frac{n_1}{n_0} = X_A X_B = \frac{2}{1 + 2\rho\Delta_{AB} + \sqrt{1 + 4\rho\Delta_{AB}}} \qquad (66)$$

The association term in the compressibility factor expression, Z^{assoc}, is evaluated as before, and an analytic expression is obtained:

$$Z^{assoc} = -\frac{n_1}{n_0}\rho\Delta_{AB}\frac{2+2\eta-\eta^2}{2-3\eta+\eta^2} \qquad (67)$$

Unlike the analytic expressions for X_A for one and two bonding sites per molecule that have been previously discussed (Jackson et al., 1988), this is the first time that analytic expressions for Z^{assoc} are presented. Based on these expressions, one can appreciate the similarity of the perturbation theory to the chemical theory and quasi-chemical theory.

Huang and Radosz (1990) derived analytic expressions for X_A for various number of bonding sites per molecule and bonding types. With these expressions, Z^{assoc} can be derived analytically using the procedure described.

Results and Discussion

While it requires a great deal of manipulation to compare these theories because they are written in terms of different parameters and are derived in different ways, it is possible to make direct comparisons, as shown in Table 1. Shown are expressions for n_1/n_0, and for the association contribution to the compressibility factor, Z^{assoc}, for APACT, SAFT, and SLP. Equations 29 and 14 give n_1/n_0 for one and two bonding sites per molecule, respectively, from APACT. Equations 61 and 66 give n_1/n_0 for one and two bonding sites per molecule from SAFT, and Eq. 49 gives n_1/n_0 for two bonding sites per molecule from SLP. In addition, Eqs. 30 and 19 give Z^{assoc} for one and two bonding sites derived from APACT, Eqs. 63 and 67 give Z^{assoc} for one and two bonding sites from SAFT, and Eq. 50 gives Z^{assoc} for two bonding sites from SLP. After a great deal of algebraic manipulation, it is shown that the functional form of the expressions derived from APACT and SAFT are identical. Elliott et al. (1990) were the first to show that the chemical and perturbation theory give numerically equivalent results. However, this is the first time that the two theories are proven to be analytically equivalent also. In addition, the expressions derived from SLP for compounds with two bonding sites per molecule are the same as the expressions from APACT and SAFT. However, the formalism of SLP does not treat the case of a component with one bonding site that self-associates. Although there are no real components that have one site per molecule and are capable of self-association to

Table 1. Comparison of the Expressions for n_1/n_0 and Z^{assoc} in APACT, SAFT, and SLP for Compounds with One and Two Hydrogen-Bonding Sites per Molecule*

| | n_1/n_0 | | Z^{assoc} | |
	1 Bonding Site	2 Bonding Sites	1 Bonding Site	2 Bonding Sites
APACT	$\dfrac{2}{1+\sqrt{1+4\rho K''}}$	$\dfrac{2}{1+2\rho K'+\sqrt{1+4\rho K'}}$	$-\left(\dfrac{n_1}{n_0}\right)^2 \rho\dfrac{K''}{2}$	$-\left(\dfrac{n_1}{n_0}\right)\rho K'$
SAFT	$\dfrac{2}{1+\sqrt{1+4\rho\Delta}}$	$\dfrac{2}{1+2\rho\Delta'+\sqrt{1+4\rho\Delta}}$	$-\left(\dfrac{n_1}{n_0}\right)^2 \rho\dfrac{\Delta'}{2}$	$-\left(\dfrac{n_1}{n_0}\right)\rho\Delta'$
SLP	—	$\dfrac{2}{1+2\rho K^*+\sqrt{1+4\rho K^*}}$	—	$-\left(\dfrac{n_1}{n_0}\right)\rho K^*$

*In APACT, it is $K'=KRTe^g$ and $K''=2KRTe^g$. In SAFT, the subscripts in Δ were omitted for simplicity and $\Delta'=\Delta f(\eta)$ where $f(\eta)=(2+2\eta-\eta^2)/(2-3\eta+\eta^2)$. In SLP, it is $K^*=K\dfrac{v^*}{r}$.

dimers, carboxylic acids are often modeled as such.

In the expressions given in Table 1, density appears explicitly in the denominator for n_1/n_0 and in the numerator for Z^{assoc}. In addition, K', K'', and Δ are density-dependent. The density dependence of K' and K'' comes from the e^g term (and so K' and K'' for the original APACT are density-independent), and the density dependence of Δ comes from the $g_{HS}(\sigma^+)$ expression. The density variation of these expressions is numerically similar. The density dependency of K', K'', and Δ are due to the fact that chemical and physical terms are coupled in the equation of state. For the original APACT where chemical and physical terms are decoupled because of the mixing rules and for the SLP where the assumption is made that chemical and physical forces are independent, K', K'', and K^*, respectively, are density-independent. The temperature dependence of all the expressions shown in Table 1 is similar. K and Δ are given by a Van't Hoff-type expression in terms of temperature (see Eqs. 6, 55 and 47). In addition, temperature appears explicitly in the expressions for K' and K'' in Table 1. More important, hydrogen bonding is expressed in APACT and SLP in terms of experimentally measurable quantities, namely the standard enthalpy and standard entropy of association (Eq. 6). In SAFT, the association is written in terms of quantities that cannot be measured experimentally such as the association volume V_{AB} and the association energy ϵ_{AB}. As a result, most users would prefer APACT and SLP over SAFT.

Jackson et al. (1988) performed isothermal-isobaric (NPT) Monte Carlo (MC) simulations for 864 hard spheres with one or two hydrogen bonding sites. From the simulations, the compressibility factor, Z, the configurational energy, U_c, and the mole fraction of the monomers, n_1/n_0, were calculated. Here, we compare the values obtained from the simulations with the predictions from SAFT, ideal gas law, APACT, APACT-2, HP, ESD, and SLP for the compressibility factor and for the mole fraction of the monomers.

In the simulations performed for the system of hard spheres with one bonding site, the square well energy depth had a value of $\epsilon_{AB}=7kT$, and the association volume had a value of $V_{AB}=1.485\times 10^{-4}\sigma^3$. For the system with two bonding sites per molecule, the square well energy depth was $\epsilon_{AB}=5kT$, whereas the association volume was $V_{AB}=2.970\times 10^{-4}\sigma^3$. Since these calculations were performed using parameters that cannot be measured experimentally, the equilibrium constants needed for the chemical and quasi-chemical theories were calculated by fitting the simulation data for n_1/n_0. In Tables 2 and 3 and in Figures 1 through 4, the results from the simulations are given together with the values obtained from the various theories described.

In Table 2, results for the mole fraction of the monomers, n_1/n_0, are presented for one and two bonding sites per molecule. In Figure 1 the results for n_1/n_0 for one bonding site are shown, and in Figure 2 the results for n_1/n_0 for two bonding sites are shown as a function of the reduced density, η. At zero density, no association occurs, and as a result $n_1/n_0=1$. As the density increases, the association increases, and so n_1/n_0 decreases. SAFT predictions are in a good agreement with the simulation data. APACT and ideal gas predictions are only in qualitative agreement with the simulation data for

Table 2. Mole Fraction of Monomers, n_1/n_0, from Monte Carlo (MC) Simulations (Jackson et al., 1988), SAFT, Ideal Gas (IG), APACT-2, HP, ESD, and SLP for Hard Spheres with One or Two Hydrogen-Bonding Sites*

| No. of Sites | η | X | | | | | | |
		MC	SAFT	IG	APACT-2	HP	ESD	SLP
1	0.1560 ± 0.001	0.632 ± 0.023	0.630	0.576	0.603	0.706	0.634	—
1	0.2608 ± 0.001	0.490 ± 0.014	0.485	0.490	0.490	0.491	0.490	—
1	0.3409 ± 0.001	0.394 ± 0.012	0.396	0.446	0.421	0.330	0.392	—
1	0.4163 ± 0.001	0.350 ± 0.015	0.323	0.415	0.361	0.196	0.294	—
2	0.1576 ± 0.001	0.666 ± 0.014	0.682	0.598	0.632	0.753	0.671	0.598
2	0.2618 ± 0.001	0.485 ± 0.012	0.497	0.484	0.484	0.485	0.485	0.484
2	0.3398 ± 0.001	0.391 ± 0.016	0.376	0.426	0.392	0.271	0.353	0.426
2	0.4168 ± 0.001	0.292 ± 0.020	0.273	0.382	0.309	0.109	0.221	0.382

*Calculations based on the ideal gas assumption are the same as APACT calculations.

Table 3. Compressibility Factor, $Z = 1 + Z^{assoc} + Z^{rep}$, from Monte Carlo (MC) Simulations (Jackson et al., 1988), SAFT, Ideal Gas (IG), APACT, APACT-2, HP, ESD and SLP for Hard Spheres with One or Two Hydrogen-Bonding Sites

No. of Sites	η	$Z = 1 + Z^{assoc} + Z^{rep}$							
		MC	SAFT	IG	APACT	APACT-2	HP	ESD	SLP
1	0.1560 ± 0.001	1.700	1.685	0.788	1.745	1.720	1.670	1.704	—
1	0.2608 ± 0.001	2.778	2.754	0.745	2.991	2.876	2.420	2.813	—
1	0.3409 ± 0.001	4.225	4.242	0.723	4.674	4.433	3.293	4.566	—
1	0.4163 ± 0.001	6.817	6.657	0.708	7.338	6.888	4.564	8.613	—
2	0.1576 ± 0.001	1.692	1.715	0.773	1.745	1.727	1.710	1.719	0.862
2	0.2618 ± 0.001	2.689	2.698	0.696	2.958	2.821	2.272	2.780	0.855
2	0.3398 ± 0.001	4.039	4.016	0.653	4.573	4.254	2.561	4.429	0.875
2	0.4168 ± 0.001	6.426	6.278	0.618	7.271	6.618	2.521	8.482	0.912

n_1/n_0. For low reduced densities APACT underpredicts the values for n_1/n_0, whereas for reduced densities higher than 0.25 APACT overpredicts the simulation data. However, APACT-2 does a good job in predicting the values for n_1/n_0 and is in good agreement with the simulation data and with the SAFT for the entire range of reduced density examined, for both the systems with one and two bonding sites per molecule. HP calculations are very bad over the entire range of density both for systems with one and two bonding sites per molecule. For low reduced densities, HP overpredicts the mole fraction of the monomer, n_1/n_0, whereas for high reduced densities HP calculations are lower than the simulation data. This is a consequence of the fact the HP's Carnahan-Starling repulsive term is adequate only for spherical molecules, and it does not describe accurately the behavior of the mixtures of chains that are formed by hydrogen bonding. The ESD predictions for n_1/n_0 are in good agreement with the simulation data and with the SAFT and APACT-2 calculations for re-

duced density up to 0.4. For higher reduced density, ESD calculations deviate considerably from the simulation data. The simulation data have a concave shape, whereas ESD predicts a convex behavior. Elliott et al. (1990) point out that their equation is applicable only up to $\eta = 0.4$ and that it was derived for engineering calculations where the reduced density rarely exceeds this value; hence, the inaccuracy of ESD at high reduced densities is not a practical limitation. Finally, the SLP results for n_1/n_0 for two bonding sites per molecule are essentially the same with the results from APACT and ideal gas calculations.

In Table 3, the results for the compressibility factor, Z, are given from the MC simulations and from SAFT, the ideal gas law, the two versions of APACT, the HP, the ESD, and the SLP equations of state. Since the systems examined were hard spheres with one or two hydrogen-bonding sites, the compressibility factor is given from the expression:

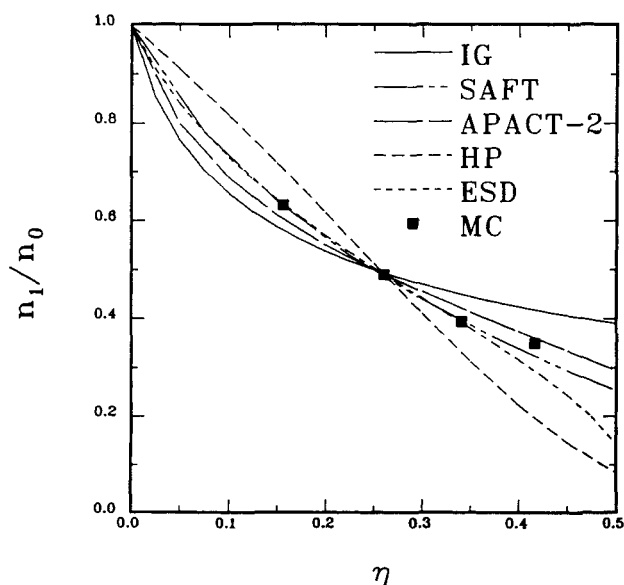$$Z = 1 + Z^{assoc} + Z^{rep} \tag{68}$$

Figure 1. Mole fraction of monomers, n_1/n_0, as a function of reduced density, η, from Monte Carlo (MC) simulations (Jackson et al., 1988), ideal gas (IG), SAFT, APACT-2, HP and ESD for hard spheres with one bonding site.

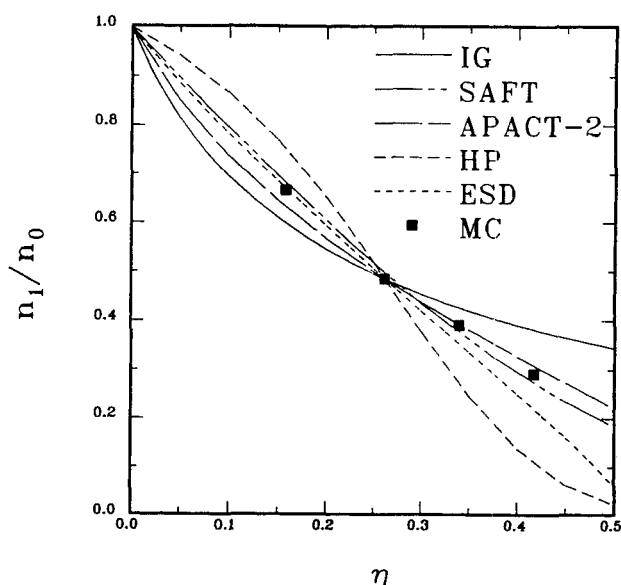Calculations based on the ideal gas law are the same as APACT calculations.

Figure 2. Mole fraction of monomers, n_1/n_0, as a function of reduced density, η, from Monte Carlo (MC) simulations (Jackson et al., 1988), ideal gas (IG), SAFT, APACT-2, HP and ESD for hard spheres with two bonding sites.

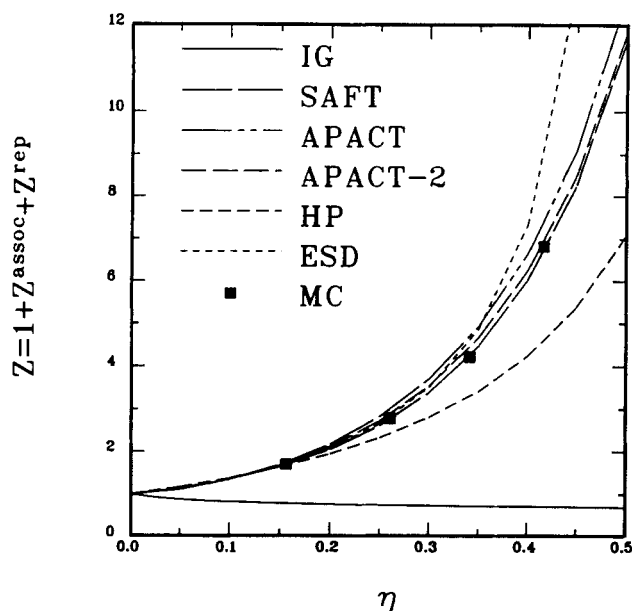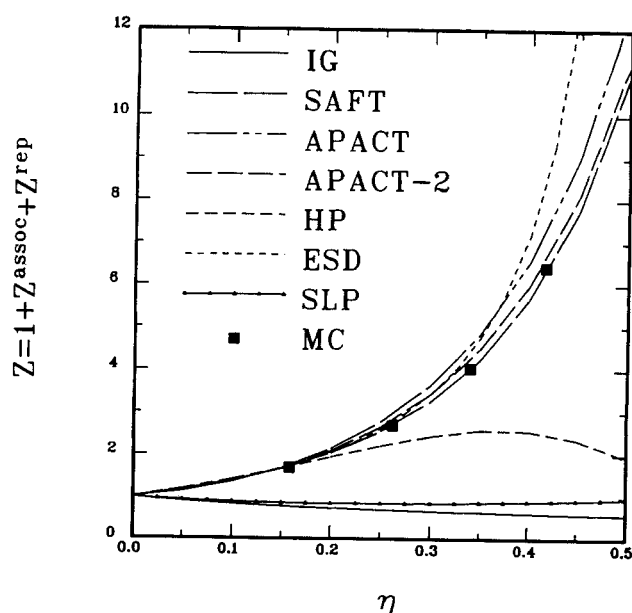Calculations based on the ideal gas law are the same as APACT calculations and as SLP calculations.

Figure 3. Compressibility factor, $Z = 1 + Z^{assoc} + Z^{rep}$, as a function of reduced density, η, from Monte Carlo (MC) simulations (Jackson et al., 1988), ideal gas (IG), SAFT, APACT, APACT-2, HP and ESD for hard spheres with one bonding site.

Figure 4. Compressibility factor, $Z = 1 + Z^{assoc} + Z^{rep}$, as a function of reduced density, η, from Monte Carlo (MC) simulations (Jackson et al., 1988), ideal gas (IG), SAFT, APACT, APACT-2, HP and ESD for hard spheres with two bonding sites.

In Figures 3 and 4, results are plotted for Z as a function of the reduced density, η, for one and two bonding sites per molecule, respectively. Ideal gas law calculations are very bad over the entire range of density. This is a consequence of the fact that ideal gas theory ignores the repulsive interactions and takes into account only the association interactions. As the density increases, the association increases and the ratio n_T/n_0 becomes less than unity and decreases.

SAFT predictions show good agreement with the simulation data. APACT agrees quantitatively with the simulation data and the SAFT predictions only at low reduced densities, whereas at reduced densities higher than 0.15 APACT overpredicts the values for Z. By relaxing the assumption made in the original APACT concerning the i dependence of c_i, improvement is obtained (Elliott et al., 1990). APACT-2 predictions for the compressibility factor, Z, are in good agreement with the simulation data and the SAFT predictions over the entire range of density. HP predictions for the compressibility factor are bad at moderate and high densities. HP calculated values for Z are much lower than the corresponding simulation data and the predictions from the other theories. Moreover, for the system with two bonding sites per molecule, HP values for Z decrease for reduced density higher than 0.35. This is a consequence of the very low values for n_1/n_0 predicted by HP (see Figure 2) for η greater than 0.35.

ESD values for Z agree quantitatively with the simulation data for reduced densities up to 0.32, but for higher values of η, ESD predictions are higher than the simulation values. This deviation is a consequence of the repulsive term used in the ESD equation of state given by Eq. 31. This expression for Z^{rep} is not accurate at high densities, but was used by Elliott et al. (1990) to get a simple cubic equation of state for non-associating components. SLP calculations for Z fail to describe

even qualitatively the behavior of a system of hard spheres with two bonding sites. The values obtained for Z are less than unity for all densities and are similar to the values obtained from the ideal gas assumption. This failure of the SLP equation of state is due to the inability of the Sanchez-Lacombe equation of state to describe the compressibility factor of a hard sphere or a hard chain (Vimalchand and Donohue, 1989).

SAFT (TPT-1) takes into account only chainlike and treelike species and ignores the formation of closed rings. In additon, the activity of each bonding site in a molecule is independent of the other bonding sites of the same molecule. Thus, steric self-hindrances are neglected. This is a good approximation for molecules where the angle between two bonding sites is close to π. However, it is bad for molecules where two bonding sites are close to one another, and bonding on one site prevents bonding on the other one. Wertheim (1987) developed a second-order thermodynamic perturbation theory (TPT-2) to take into account ring formation and angular dependence of the bonding of a particular site. TPT-2 results in expressions for the thermodynamic properties that are more complicated than those presented here. However, the differences between TPT-1 and TPT-2 are small, and so the simpler TPT-1 is preferred (Jackson et al., 1988). A comparison between TPT-1 and TPT-2 for chain molecules is given by Honnell and Hall (1989).

APACT formalism also takes into account chain formation but ignores the formation of closed rings. This is done so that the simplicity of equation of state is retained. However, an equilibrium scheme for the formation of cyclic species can be assumed in addition to the infinite equilibrium model (Ikonomou, 1987). This increases the complexity of the equations and the number of parameters in the equation of state (an additional temperature-dependent equilibrium constant for the ring formation is needed). For closed rings the expressions,

derived based on the SLP equation of state are not valid, since Eq. 42 is valid only for chain molecules.

In general, chemical theory, quasi-chemical theory, and perturbation theory differ in the physical approach to the problem as well as in the mathematical analysis of it. In addition, the chemical theory has been characterized as "largely empirical in nature" (Joslin et al., 1987), and hence agreement between the chemical theory and perturbation theory would not be expected. However, it is shown in this work that the chemical theory, quasi-chemical theory and perturbation theory result in equivalent expressions for hydrogen-bonding systems. The small differences between APACT-2 and SAFT are due to the differences in the reference equations of state used. For APACT-2, the reference equation essentially is the generalized Flory (GF) equation of state (Dickman and Hall, 1986). Perturbed-hard-chain theory (PHCT) (Donohue and Prausnitz, 1978) was derived in a phenomenological way, whereas GF, which essentially is the same as PHCT, was derived in a more theoretical way. On the other hand, for SAFT the reference equation is Wertheim's repulsive term (Wertheim, 1986b). A comparison between the GF equation of state and the thermodynamic perturbation theory is given by Honnell and Hall (1989). Finally, the deviation of the results of the SLP equation of state with the simulation data is due to the inaccuracy of the Sanchez-Lacombe equation of state for hard spheres and hard chains. A comparison of the various theories for chain molecules is given by Vimalchand and Donohue (1989).

Mixtures

For mixtures of associating components, APACT, SAFT, and SLP give expressions for n_1/n_0, and for Z^{assoc} that are complicated and in general have no analytic solution (Ikonomou and Donohue, 1988; Chapman et al., 1990; Economou et al., 1990; Panayiotou and Sanchez, 1991). However, for several specific cases, analytic expressions have been obtained.

For a binary mixture of components M and N, the mole fraction of monomers M_1 is defined as: $W_M = n_{M_1}/n_0$ where n_{M_1} is the number of moles of monomers M_1. For the case where component M has one bonding site per molecule and component N has no bonding sites, dimer species of component M can be formed. In that case, APACT results in the following expression for W_M (see the Appendix for derivation):

$$W_M = \frac{2x_M}{1+\sqrt{1+8KRT\rho e^g x_M}} \quad (69)$$

where x_M is the mole fraction of component M in the absence of association. From Eq. 69, the mole fraction of monomers M_1 with respect to the total number of moles of component M in the absence of any association can be calculated:

$$\frac{n_{M_1}}{n_M} = \frac{n_{M_1}}{n_0}\frac{n_0}{n_M} = \frac{W_M}{x_M} = \frac{2}{1+\sqrt{1+8KRT\rho e^g x_M}} \quad (70)$$

where n_M is the total number of moles of component M in the absence of any association. In addition, an analytic expression is obtained for Z^{assoc}:

$$Z^{assoc} = -\frac{2KRT\rho e^g x_M^2}{1+4KRT\rho e^g x_M+\sqrt{1+8KRT\rho e^g x_M}}$$

$$= -\left(\frac{n_{M_1}}{n_M}\right)^2 KRT\rho e^g x_M^2 \quad (71)$$

Using SAFT for a multicomponent mixture of associating components, the mole fraction of species i not bonded at site A is given by the expression (Chapman et al., 1988):

$$X_A^i = \left(1+\sum_j\sum_{B\in\Gamma^{(j)}}\rho_j X_B^j \Delta_{A_i B_j}\right)^{-1} \quad (72)$$

where the first sum is over all components j in the mixture and the second sum is over all sites B in component j. The density ρ_j of component j is defined as $\rho_j = x_j\rho$ where x_j is the mole fraction of species j. The association contribution to the compressibility factor, Z^{assoc}, is given from the expression (Chapman et al., 1988):

$$Z^{assoc} = \sum_i x_i\sum_j\rho_j\sum_{A\in\Gamma^{(j)}}\left[\left(\frac{\partial X_A^j}{\partial \rho_i}\right)_{T,\rho_{k\neq i}}\left(\frac{1}{X_A^j}-\frac{1}{2}\right)\right] \quad (73)$$

For the binary system examined, Eq. 72 simplifies to:

$$\frac{n_{M_1}}{n_M} = \left(1+\rho_M\frac{n_{M_1}}{n_M}\Delta_{MM}\right)^{-1} \quad (74)$$

Solving the latter, one obtains:

$$\frac{n_{M_1}}{n_M} = \frac{2}{1+\sqrt{1+4\rho\Delta_{MM}x_M}} \quad (75)$$

Equation 73 also reduces to the following expression:

$$Z^{assoc} = \rho x_M\left(\frac{1}{n_{M_1}/n_M}-\frac{1}{2}\right)\left[x_M\left(\frac{\partial n_{M_1}/n_M}{\partial\rho_M}\right)_{T,\rho_N}\right.$$
$$\left.+x_N\left(\frac{\partial n_{M_1}/n_M}{\partial\rho_N}\right)_{T,\rho_M}\right] \quad (76)$$

After evaluating the derivative, the following expression is obtained:

$$Z^{assoc} = -\left(\frac{n_{M_1}}{n_M}\right)^2\rho\frac{x_M^2}{2}\left[\Delta_{MM}+\rho x_M\left(\frac{\partial\Delta_{MM}}{\partial\rho_M}\right)_{T,\rho_N}\right.$$
$$\left.+\rho x_N\left(\frac{\partial\Delta_{MM}}{\partial\rho_N}\right)_{T,\rho_M}\right] \quad (77)$$

where

$$\left(\frac{\partial\Delta_{MM}}{\partial\rho_M}\right)_{T,\rho_N} \quad \text{and} \quad \left(\frac{\partial\Delta_{MM}}{\partial\rho_N}\right)_{T,\rho_M}$$

are given by Chapman et al. (1990).

Table 4. Binary Mixtures of Components M and N. A comparison of the expressions for n_{M_1}/n_M, n_{N_1}/n_N and Z^{assoc} in APACT, SAFT, and SLP*

	$(1-0)$		
	n_{M_1}/n_M	n_{N_1}/n_N	Z^{assoc}
APACT	$\dfrac{2}{1+\sqrt{1+4\rho K''x_M}}$	1	$-\left(\dfrac{n_{M_1}}{n_M}\right)^2 \rho\dfrac{x_M^2}{2}K''$
SAFT	$\dfrac{1}{1+\sqrt{1+4\rho\Delta x_M}}$	1	$-\left(\dfrac{n_{M_1}}{n_M}\right)^2 \rho\dfrac{x_M^2}{2}g(\Delta)$
SLP	—	—	—

	$(1-1)$		
	n_{M_1}/n_M	n_{N_1}/n_N	Z^{assoc}
APACT	$\dfrac{2}{1+\rho K'(x_N-x_M)+\sqrt{(1+\rho K')^2-4(\rho K')^2 x_M x_N}}$	$\left(1+\rho K'x_M\dfrac{n_{M_1}}{n_M}\right)^{-1}$	$\dfrac{2\rho K' x_M x_N}{1+\rho K'+\sqrt{1(1+\rho K')^2-4(\rho K')^2 x_M x_N}}$
SAFT	$\dfrac{2}{1+\rho\Delta(x_N-x_M)+\sqrt{(1+\rho\Delta)^2-4(\rho\Delta)^2 x_M x_N}}$	$\left(1+\rho\Delta x_M\dfrac{n_{M_1}}{n_M}\right)^{-1}$	Eq. 86
SLP	$\dfrac{2}{1+\rho K^*(x_N-x_M)+\sqrt{(1+\rho K^*)^2-4(\rho K^*)^2 x_M x_N}}$	$\left(1+\rho K^*x_M\dfrac{n_{M_1}}{n_M}\right)^{-1}$	$\dfrac{2\rho K^* x_M x_N}{1+\rho K^*+\sqrt{1(1+\rho K^*)^2-4(\rho K^*)^2 x_M x_N}}$

	$(2-0)$		
	n_{M_1}/n_M	n_{N_1}/n_N	Z^{assoc}
APACT	$\dfrac{2}{1+2\rho K'x_M+\sqrt{1+4\rho K'x_M}}$	1	$-\dfrac{n_{M_1}}{n_M}\rho x_M^2 K'$
SAFT	$\dfrac{2}{1+2\rho\Delta x_M+\sqrt{1+4\rho\Delta x_M}}$	1	$-\dfrac{n_{M_1}}{n_M}\rho x_M^2 g(\Delta)$
SLP	$\dfrac{2}{1+2\rho K^*x_M+\sqrt{1+4\rho K^*x_M}}$	1	$-\dfrac{n_{M_1}}{n_M}\rho x_M^2 K^*$

*(a) Component M has one hydrogen-bonding site per molecule, whereas component N has no bonding sites $(1-0)$; (b) both components M and N has one hydrogen bonding site per molecule $(1-1)$; (c) component M has two hydrogen-bonding sites per molecule, and component N has no bonding sites $(2-0)$. In APACT, it is $K'=KRTe^g$ and $K''=2KRTe^g$. In SAFT, the subscripts in Δ were omitted for simplicity and $g(\Delta)=\Delta+\rho x_M(\partial\Delta/\partial\rho_M)_{T,\rho_N}+\rho x_N(\partial\Delta/\partial\rho_N)_{T,\rho_M}$. In SLP, it is $K^*=Kv^*/r$.

The formalism used by Panayiotou and Sanchez (1991) to describe hydrogen bonding using a quasi-chemical approach cannot be applied to a binary mixture of a component with one bonding site per molecule and a component without bonding sites. In that case, the lefthand side of Eq. 45 becomes zero.

It is obvious that the functional forms of the expressions for n_{M_1}/n_M and Z^{assoc} obtained from APACT (Eqs. 70 and 71) are similar to the functional forms of the expressions for n_{M_1}/n_M and Z^{assoc} from SAFT (Eqs. 75 and 77). In Table 4, these equations are presented so that a clear comparison can be made. Calculations based on these theories gave similar results. In Figure 5, calculations are shown for a binary mixture of two spherical molecules where one of the components has one bonding site and the other has no bonding sites. n_T/n_0 from SAFT, ideal gas law (IG), and APACT-2 is plotted as a function of the mole fraction of the associating component x_M. APACT calculations are the same as ideal gas law calculations. The reduced density was set constant at $\eta=0.35$. The molecular parameters for the associating component had the same value as the parameters used for the pure component with one bonding site. Good agreement is obtained among the three models. No simulation data are available for comparisons. The deviations among the three equations are smaller at lower reduced densities.

We examine next the case of a binary mixture of components M and N, where each of the components has one bonding site per molecule and only cross-association of the type $M-N$ is permitted. In that case, Acid-Base-PACT (ABPACT), an extension of APACT that takes explicitly into account the acidic and basic properties of associating components, results in the following expression for W_M (Economou et al., 1990):

$$W_M=\frac{K_{MN}RT\rho e^g(x_M-x_N)-1+\sqrt{(1+K_{MN}RT\rho e^g)^2-4(K_{MN}RT\rho e^g)^2 x_M x_N}}{2K_{MN}RT\rho e^g} \tag{78}$$
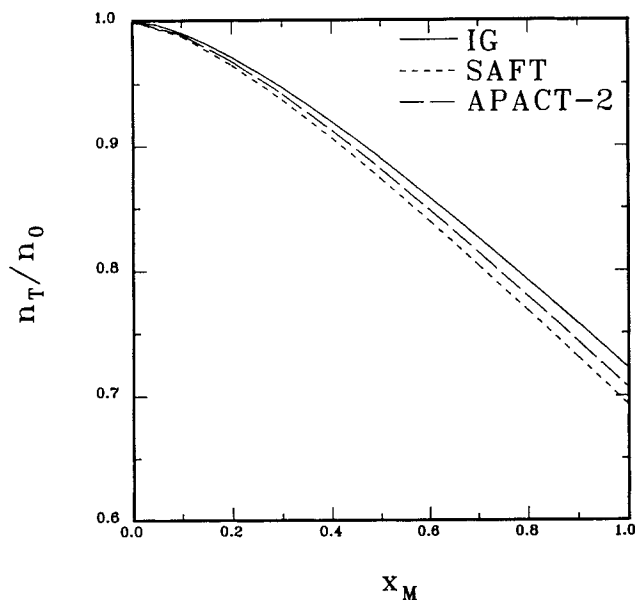
Figure 5. n_T/n_0 **as a function of the mole fraction of the associating component,** x_M**, for a binary mixture of a spherical component with one bonding site per molecule and a spherical component with no bonding sites from ideal gas (IG), SAFT and APACT-2.**

Calculations based on the ideal gas law are the same as APACT calculations. The reduced density was constant at $\eta = 0.35$ for all compositions.

where K_{MN} is the equilibrium constant for the cross-association. A rearrangement of Eq. 78 results in the following expression for n_{M_1}/n_M, the mole fraction of monomers M_1 with respect to the total number of moles of component M:

$$\frac{n_{M_1}}{n_M} = \frac{2}{1 + K_{MN}RT\rho e^g (x_N - x_M) + \sqrt{(1 + K_{MN}RT\rho e^g)^2 - 4(K_{MN}RT\rho e^g)^2 x_M x_N}} \quad (79)$$

For the second component N, the mole fraction of monomers N_1 with respect to the total number of moles of component N is given from the expression (Economou et al., 1990):

$$\frac{n_{N_1}}{n_N} = \frac{W_N}{x_N} = \left(1 + K_{MN}RT\rho e^g x_M \frac{n_{M_1}}{n_M}\right)^{-1} \quad (80)$$

An analytic expression also is obtained for the Z^{assoc} term:

$$Z^{\text{assoc}} =$$
$$-\frac{2K_{MN}RT\rho e^g x_M x_N}{1 + K_{MN}RT\rho e^g + \sqrt{(1 + K_{MN}RT\rho e^g)^2 - 4(K_{MN}RT\rho e^g)^2 x_M x_N}}$$
$$(81)$$

For a binary mixture of components M and N with one bonding site per molecule for both components and where only bonding of the type $M-N$ is permitted, Eq. 72 for SAFT simplifies to:

$$\frac{n_{M_1}}{n_M} = \left(1 + \rho_N \frac{n_{N_1}}{n_N} \Delta_{MN}\right)^{-1} \quad (82)$$

and

$$\frac{n_{N_1}}{n_N} = \left(1 + \rho_M \frac{n_{M_1}}{n_M} \Delta_{MN}\right)^{-1} \quad (83)$$

Substituting Eq. 83 to Eq. 82, one obtains:

$$\frac{n_{M_1}}{n_M} =$$
$$\frac{2}{1 + \Delta_{MN}\rho (x_N - x_M) + \sqrt{(1 + \Delta_{MN}\rho)^2 - 4(\Delta_{MN}\rho)^2 x_M x_N}} \quad (84)$$

and

$$\frac{n_{N_1}}{n_N} = \left(1 + \Delta_{MN}\rho x_M \frac{n_{M_1}}{n_M}\right)^{-1} \quad (85)$$

For this binary mixture, Eq. 73 reduces to the expression:

$$Z^{\text{assoc}} = \left[x_M \left(\frac{\partial n_{M_1}/n_M}{\partial \rho_M}\right)_{T,\rho_N} + x_N \left(\frac{\partial n_{M_1}/n_M}{\partial \rho_N}\right)_{T,\rho_M} \right]$$
$$\times \rho x_M \left[\frac{\Delta_{MN}\rho (x_N - x_M) + \sqrt{Q}}{2}\right]$$
$$+ \left[x_M \left(\frac{\partial n_{N_1}/n_N}{\partial \rho_M}\right)_{T,\rho_N} + x_N \left(\frac{\partial n_{N_1}/n_N}{\partial \rho_N}\right)_{T,\rho_M} \right]$$
$$\times \rho x_N \left[\frac{\Delta_{MN}\rho (x_M - x_N) + \sqrt{Q}}{2}\right] \quad (86)$$

where

$$Q = (1 + \Delta_{MN}\rho)^2 - 4(\Delta_{MN}\rho)^2 x_M x_N \quad (87)$$

$$\left(\frac{\partial n_{M_1}/n_M}{\partial \rho_M}\right)_{T,\rho_N} = -\frac{(n_{M_1}/n_M)^2}{2}\left\{-\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}\rho\,(x_N-x_M)\right.$$

$$\left.+\frac{[1+\Delta_{MN}\rho\,(x_N-x_M)]\left[-\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}\rho\,(x_N-x_M)\right]+2\Delta_{MN}+2\rho x_M\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}}{\sqrt{Q}}\right\} \quad (88)$$

$$\left(\frac{\partial n_{M_1}/n_M}{\partial \rho_N}\right)_{T,\rho_M} = -\frac{(n_{M_1}/n_M)^2}{2}\left\{\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}\rho\,(x_N-x_M)\right.$$

$$\left.+\frac{[1+\Delta_{MN}\rho\,(x_N-x_M)]\left[\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}\rho\,(x_N-x_M)\right]+2\rho x_M\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}}{\sqrt{Q}}\right\} \quad (89)$$

$$\left(\frac{\partial n_{N_1}/n_N}{\partial \rho_M}\right)_{T,\rho_N} = -\frac{(n_{N_1}/n_N)^2}{2}\left\{\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}\rho\,(x_M-x_N)\right.$$

$$\left.+\frac{[1+\Delta_{MN}\rho\,(x_N-x_M)]\left[-\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}\rho\,(x_N-x_M)\right]+2\Delta_{MN}+2\rho x_M\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}}{\sqrt{Q}}\right\} \quad (90)$$

$$\left(\frac{\partial n_{N_1}/n_N}{\partial \rho_N}\right)_{T,\rho_M} = -\frac{(n_{N_1}/n_N)^2}{2}\left\{-\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}\rho\,(x_M-x_N)\right.$$

$$\left.+\frac{[1+\Delta_{MN}\rho\,(x_N-x_M)]\left[\Delta_{MN}+\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}\rho\,(x_N-x_M)\right]+2\rho x_M\left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}}{\sqrt{Q}}\right\} \quad (91)$$

and

$$\left(\frac{\partial \Delta_{MN}}{\partial \rho_M}\right)_{T,\rho_N}, \quad \left(\frac{\partial \Delta_{MN}}{\partial \rho_N}\right)_{T,\rho_M}$$

are given by Chapman et al. (1990).

For a binary mixture of components M and N where one of the components has a proton donor group and the other component has a proton acceptor group, Eq. 45 for SLP model results in the following expression for N_H/n_0:

$$\frac{N_H}{n_0} = \frac{2K\rho\frac{v^*}{r}x_M x_N}{1+K\rho\frac{v^*}{r}+\sqrt{\left(1+K\rho\frac{v^*}{r}\right)^2-4\left(K\rho\frac{v^*}{r}\right)^2 x_M x_N}} \quad (92)$$

In that case, the fraction of the monomers of component M is given from the expression:

$$\frac{n_{M_1}}{n_0} = x_M\left(1-\frac{N_H}{n_M}\right) = x_M\left(1-\frac{N_H}{n_0 x_M}\right) \quad (93)$$

and so:

$$\frac{n_{M_1}}{n_M} = \frac{2}{1+K\rho\frac{v^*}{r}(x_N-x_M)+\sqrt{\left(1+K\rho\frac{v^*}{r}\right)^2-4\left(K\rho\frac{v^*}{r}\right)^2 x_M x_N}} \quad (94)$$

The corresponding expression for component N is obtained from Eq. 94 by interchanging the indices M and N. In addition, the following expression for Z^{assoc} is obtained:

$$Z^{assoc} = -\frac{2K\rho\frac{v^*}{r}x_M x_N}{1+K\rho\frac{v^*}{r}+\sqrt{\left(1+K\rho\frac{v^*}{r}\right)^2-4\left(K\rho\frac{v^*}{r}\right)^2 x_M x_N}} \quad (95)$$

Here again, the expressions for n_{M_1}/n_M and n_{N_1}/n_N obtained from ABPACT (Eqs. 79 and 80), from SAFT (Eqs. 84 and 85) and from SLP (Eq. 94) are similar. In addition, the expression for Z^{assoc} from ABPACT, given by Eq. 81, is similar to the expression for Z^{assoc} obtained from SLP (Eq. 95). However, in this case, the expression for Z^{assoc} obtained by SAFT (Eq. 86) does not have the same functional form as the expressions obtained by APACT and SLP. In Table 4, these equations also are included. Since no simulation data are available for this type of binary mixture, no quantitative comparisons were made for the four models, SAFT, ideal gas law, APACT-2, and SLP. However, based on the results for the other binary mixtures examined, it is expected that all four models would be in quantitative agreement.

We examine finally the case of a binary mixture of components M and N where component M has two bonding sites per molecule, defined as sites A and B, and component N has no available sites capable of hydrogen bonding. As for the pure component with two sites per molecule, only bonding of type $A - B$ is permitted. For APACT, it is shown that the mole fraction of monomers M_1 with respect to the total number of moles of component M is given from the expression (see the Appendix for derivation):

$$\frac{n_{M_1}}{n_M} = \frac{2}{1 + 2KRT\rho e^g x_M + \sqrt{1 + 4KRT\rho e^g x_M}} \quad (96)$$

After algebraic manipulation Z^{assoc} can be expressed as:

$$Z^{assoc} = -\frac{2KRT\rho e^g x_M^2}{1 + 2KRT\rho e^g x_M + \sqrt{1 + 4KRT\rho e^g x_M}}$$

$$= -\frac{n_{M_1}}{n_M}KRT\rho e^g x_M^2 \quad (97)$$

For this binary mixture, Eq. 72 for SAFT reduces to the expression:

$$X_A^M = (1 + \rho_M X_B^M \Delta_{AB})^{-1} \quad (98)$$

For $X_A^M = X_B^M$ the following expression is obtained for n_{M_1}/n_M:

$$\frac{n_{M_1}}{n_M} = X_A^M X_B^M = \frac{2}{1 + 2\rho\Delta_{AB}x_M + \sqrt{1 + 4\rho\Delta_{AB}x_M}} \quad (99)$$

In addition, Eq. 73 reduces to the expression:

$$Z^{assoc} = -\frac{n_{M_1}}{n_M}\rho x_M^2 \left[\Delta_{AB} + \rho x_M \left(\frac{\partial \Delta_{AB}}{\partial \rho_M}\right)_{T,\rho_N} + \rho x_N \left(\frac{\partial \Delta_{AB}}{\partial \rho_N}\right)_{T,\rho_M} \right] \quad (100)$$

where

$$\left(\frac{\partial \Delta_{AB}}{\partial \rho_M}\right)_{T,\rho_N} \quad \text{and} \quad \left(\frac{\partial \Delta_{AB}}{\partial \rho_N}\right)_{T,\rho_M}$$
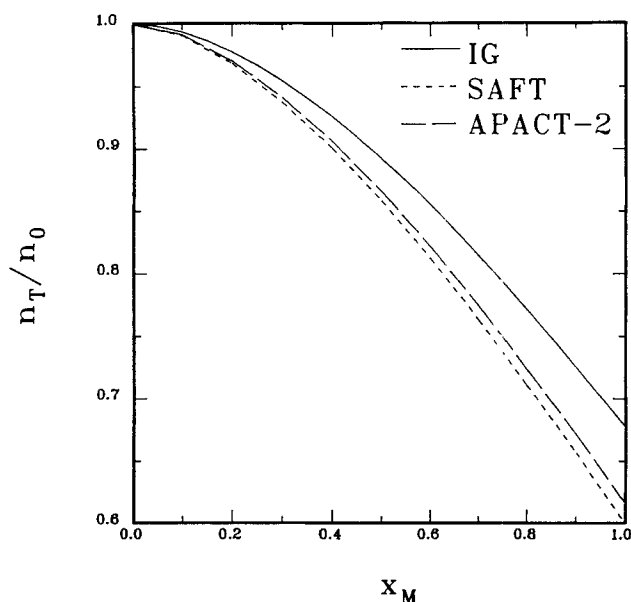
are given by Chapman et al. (1990).

Figure 6. n_T/n_0 as a function of the mole fraction of the associating component, x_M, for a binary mixture of a spherical component with two bonding sites per molecule and a spherical component with no bonding sites from ideal gas (IG), SAFT, and APACT-2.

Calculations based on the ideal gas law are the same as APACT calculations and as SLP calculations. The reduced density was constant at $\eta = 0.35$ for all compositions.

For this binary mixture, SLP equation of state results in the following expression for n_{M_1}/n_M:

$$\frac{n_{M_1}}{n_M} = \frac{2}{1 + 2K\rho\frac{v^*}{r}x_M + \sqrt{1 + 4K\rho\frac{v^*}{r}x_M}} \quad (101)$$

and for Z^{assoc}:

$$Z^{assoc} = -\frac{2K\rho\frac{v^*}{r}x_M^2}{1 + 2K\rho\frac{v^*}{r}x_M + \sqrt{1 + 4K\rho\frac{v^*}{r}x_M}}$$

$$= -\frac{n_{M_1}}{n_M}K\rho\frac{v^*}{r}x_M^2 \quad (102)$$

The expressions for n_{M_1}/n_M and Z^{assoc} calculated from APACT, SAFT, and SLP are given in Table 4 for comparison. It is obvious that the functional form of these expressions are the same. In Figure 6, calculations are shown for a binary mixture of spherical components of the same size where one of the components has two bonding sites per molecule, whereas the other component has no bonding sites. The reduced density had a constant value of $\eta = 0.35$. The molecular parameters for the associating component were the same as the parameters for the pure associating component with two bonding sites per molecule presented in Figures 2 and 4. n_T/n_0 is plotted as a

function of mole fraction of the associating component, x_M. APACT and SLP calculations are the same as ideal gas law calculations. It is clear that SAFT and APACT-2 are in quantitative agreement for all compositions. Ideal-gas-law-based calculations agree only qualitatively with APACT-2 and SAFT. For smaller reduced densities, a better agreement is obtained among these equations.

In the case of a binary mixture of components M and N, where one of the components has two bonding sites per molecule and the other component has one bonding site per molecule, ABPACT gives analytic expressions for the mole fraction of the monomers, n_{M_1}/n_M and n_{N_1}/n_N, and for Z^{assoc} (Economou et al., 1990). SAFT expressions for n_{M_1}/n_M and n_{N_1}/n_N do not have an analytic solution, and as a result a numerical solution is needed (Chapman et al., 1990). SLP formalism results in two coupled quadratic equations that are solved numerically. For more complicated systems, none of the three models have an analytic solution for n_{M_1}/n_M and n_{N_1}/n_N, and an approximate expression or a numerical solution is needed (Anderko, 1989b; Chapman et al., 1990; Economou et al., 1990; Panayiotou and Sanchez, 1991).

Conclusions

In this article, we have examined chemical, quasi-chemical and physical equations of state that take into account explicitly hydrogen-bonding interactions. The approaches used in deriving these equations are quite different. The chemical equations of state incorporate hydrogen bonding through a chemical equilibrium scheme. The quasi-chemical equations of state calculate the total number of ways of distributing the hydrogen bonds among the different proton donor and proton acceptor groups of the system, and the perturbation equations of state account for hydrogen bonding through a potential function. It was shown that all three approaches lead to expressions that are of the same functional form for pure components and for mixtures. In addition, by correcting the simplifying assumption concerning the c parameter in APACT, calculations based on APACT and on SAFT give results that are in agreement with simulation data for the compressibility factor of a hard sphere with one or two bonding sites. Calculations for the compressibility factor from the SLP were not in agreement with the simulation data and with the other theories because of the inability of the Sanchez-Lacombe equation of state to describe qualitatively systems of hard spheres or hard chains.

The equivalence of these theories shows that the chemical theory is as rigorous as the perturbation theory. In addition, this equivalence allows parameters in the perturbation theory, which are written in terms of experimentally unmeasurable quantities, to be related to the experimentally measurable equilibrium constant.

For multicomponent systems, the chemical theory can be written to take into account all the various chemical equilibria among the components. While this might seem intractable, for all systems studied to date, the equations derived using the chemical theory are less complicated than the corresponding equations from the perturbation theory. Further, in the chemical theory, hydrogen bonding is expressed in terms of measurable quantities that, in principle, can be determined from spectroscopic studies of the constituent binary mixtures.

Notation

a = energy parameter
A = Helmholtz free energy
b = size parameter
c = 1/3 number of external degrees of freedom
ΔG_0^{assoc} = Gibbs free energy change of association
ΔH^o = standard enthalpy of association
ΔS^o = standard entropy of association
f_{AB} = Mayer f-function
g = function defined in Eq. 8
g_r = reference fluid pair correlation function
$g_{HS}(\sigma^+)$ = contact value of the distribution function
k = Boltzmann constant
K = equilibrium constant
m = number of segments per molecule
M = self-associating component
M = number of association sites per molecule
n = number of moles
N = component N
N = number of molecules
N_H = total number of hydrogen bonds
P = pressure
q = shape parameter
Q = partition function
r = number of segments per molecule
$\mathbf{r}$ = magnitude of vector $\mathbf{r}$
R = gas constant
T = temperature
v_0 = molar volume
v^* = characteristic volume
V = volume
V_{AB} = association volume
W_M = fraction of the monomers of component M in a mixture
x = mole fraction
X_A = fraction of molecules not bonded at site A
z = mole fraction
Z = compressibility factor
$\langle\,\rangle$ = mixture properties

Greek letters

Δ_{AB} = association strength between sites A and B
ϵ = molecular energy
η = reduced density
ρ = molar density
σ = segmental diameter
ϕ = fugacity coefficient
ϕ = pair potential
ω = angle

Superscripts

ani = anisotropic
assoc = association
attr = attractive
i = species i
LJ = Lennard-Jones
phys = physical
rep = repulsive
~ = reduced quantity

Subscripts

0 = quantity calculated ignoring association
$1, 2, ..., i$ = monomer, dimer, ..., i-mer
a = acceptor
d = donor
MF = mean field
T = true association species

Literature Cited

Abrams, D., and J. M. Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: a New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Acree, W. E., *Thermodynamic Properties of Nonelectrolyte Solutions*, Academic Press, New York (1984).

Anderko, A., "A Simple Equation of State Incorporating Association," *Fluid Phase Equil.*, **45**, 39 (1989).

Anderko, A., "Extension of the AEOS Equation of State to Systems Containing Any Number of Associating and Inert Components," *Fluid Phase Equil.*, **50**, 21 (1989).

Andersen, H. C., "Cluster Expansion for Hydrogen Bonded Fluids: I. Molecular Association in Dilute Gases," *J. Chem. Phys.*, **59**, 4714 (1973).

Andersen, H. C., "Cluster Expansion for Hydrogen Bonded Fluids: II. Dense Liquids," *J. Chem. Phys.*, **61**, 4985 (1974).

Becker, E. D., U. Liddel, and J. N. Shoolery, "Nuclear Magnetic Resonance Studies of Hydrogen Bonding in Ethanol," *J. Mol. Spectry.*, **2**, 1 (1958).

Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, "New Reference Equation of State for Associating Liquids," *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).

Chapman, W. G., G. Jackson, and K. E. Gubbins, "Phase Equilibria of Associating Fluids: Chain Molecules with Multiple Sites," *Molec. Phys.*, **65**, 1057 (1988).

Cummings, P. T., and L. Blum, "Analytic Solution of the Molecular Ornstein-Zernike Equation of Nonspherical Molecules: Spheres with Anisotropic Surface Adhesion," *J. Chem. Phys.*, **84**, 1833 (1986).

Cummings, P. T., and G. Stell, "Statistical Mechanical Models of Chemical Reactions: Analytic Solution of Models of $A + B \rightleftharpoons AB$ in the Percus-Yevick Approximation," *Molec. Phys.*, **51**, 253 (1984).

Dickman, R., and C. K. Hall, "Equation of State for Chain Molecules: Continuous-Space Analog of Flory Theory," *J. Chem. Phys.*, **85**, 4108 (1986).

Dolezalek, F., "Zur Theorie der Binären Gemische und Konzentrierten Löungen," *Z. Phys. Chem.*, **64**, 727 (1908).

Donohue, M. D., and J. M. Prausnitz, "Perturbed-Hard-Chain-Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**, 849 (1978).

Economou, I. G., G. D. Ikonomou, P. Vimalchand, and M. D. Donohue, "Thermodynamics of Lewis Acid-Base Mixtures," *AIChE J.*, **36**, 1851 (1990).

Elliott, J. R., S. J. Suresh, and M. D. Donohue, "A Simple Equation for Nonspherical and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 1476 (1990).

Gmehling, J. D., D. D. Liu, and J. M. Prausnitz, "High Pressure Vapor-Liquid Equilibria for Mixtures Containing One or More Polar Components," *Chem. Eng. Sci.*, **34**, 951 (1979).

Guggenheim, E. A., "Statistical Thermodynamics of Mixtures with Non-zero Energies of Mixing," *Proc. R. Soc. London Ser. A*, **183**, 213 (1945).

Guggenheim, E. A., *Mixtures*, Clarendon (1952).

Heidemann, R. A., and J. M. Prausnitz, "A Van der Waals-type Equation of State for Fluids With Associating Molecules," *Proc. Nat. Acad. Sci.*, **73**, 1773 (1976).

High, M. S., and R. P. Danner, "Application of the Group Contribution Lattice-Fluid EOS to Polymer Solutions," *AIChE J.*, **36**, 1625 (1990).

Honnel, K. G., and C. K. Hall, "A New Equation of State for Athermal Chains," *J. Chem. Phys.*, **90**, 1841 (1989).

Huang, S. H., and M. Radosz, "Equation of State for Small, Large, Polydisperse, and Associating Molecules," *Ind. Eng. Chem. Res.*, **29**, 2284 (1990).

Huang, S. H., and M. Radosz, "Equation of State for Small, Large, Polydisperse, and Associating Molecules: Extension to Fluid Mixtures," *Ind. Eng. Chem. Res.*, **30**, 1994 (1991).

Ikonomou, G. D., "Equation of State Description of Thermodynamic Properties for Hydrogen Bonding Systems," PhD Diss., Johns Hopkins Univ. (1987).

Ikonomou, G. D., and M. D. Donohue, "Thermodynamics of Hydrogen-Bonded Molecules: The Associated Perturbed Anisotropic Chain Theory," *AIChE J.*, **32**, 1716 (1986).

Ikonomou, G. D., and M. D. Donohue, "Extension of the Associated Perturbed Anisotropic Chain Theory to Mixtures with More Than One Associating Component," *Fluid Phase Equil.*, **39**, 129 (1988).

Jackson, G., W. G. Chapman, and K. E. Gubbins, "Phase Equilibria of Associating Fluids: Spherical Molecules with Multiple Bonding Sites," *Molec. Phys.*, **65**, 1 (1988).

Joslin, C. G., C. G. Gray, W. G. Chapman, and K. E. Gubbins, "Theory and Simulation of Associating Liquid Mixtures: II," *Molec. Phys.*, **62**, 843 (1987).

Kretschmer, C. B., and R. Wiebe, "Thermodynamics of Alcohol-Hydrocarbon Mixtures," *J. Chem. Phys.*, **22**, 1697 (1954).

Kumar, S. K., U. W. Suter, and R. C. Reid, "A Statistical Mechanics Based Lattice Model Equation of State," *Ind. Eng. Chem. Res.*, **26**, 2532 (1987).

Lacombe, R. H., and I. C. Sanchez, "Statistical Thermodynamics of Fluid Mixtures," *J. Phys. Chem.*, **80**, 2568 (1976).

Liddel, U., and E. D. Becker, "Infra-Red Spectroscopic Studies of Hydrogen Bonding in Methanol, Ethanol, and t-Butanol," *Spectrochim. Acta*, **10**, 70 (1957).

Nagata, I., "On the Thermodynamics of Alcohol Solutions: Phase Equilibria of Binary and Ternary Mixtures Containing Any Number of Alcohols," *Fluid Phase Equil.*, **19**, 153 (1985).

Olaussen, K., and G. Stell, "New Microscopic Approach to the Statistical Mechanics of Chemical Association," *J. Stat. Phys.*, **62**, 221 (1991).

Painter, P. C., Y. Park, and M. M. Coleman, "Thermodynamics of Hydrogen Bonding in Polymer Blends: 1. Application of Association Models," *Macromol.*, **22**, 570 (1989).

Panayiotou, C., "Thermodynamics of Alkanol-Alkane Mixtures," *J. Phys. Chem.*, **92**, 2960 (1989).

Panayiotou, C., "Thermodynamics of Associated Solutions: Mixtures of 1-Alkanols," *Fluid Phase Equil.*, **56**, 171 (1990).

Panayiotou, C., and I. C. Sanchez, "Hydrogen Bonding in Fluids: An Equation of State Approach," submitted to *J. Phys. Chem.* (1991).

Panayiotou, C., and J. H. Vera, "The Quasi-Chemical Approach for Nonrandomness in Liquid Mixtures: Expressions for Local Surfaces and Local Compositions with an Application to Polymer Solutions," *Fluid Phase Equil.*, **5**, 55 (1980).

Panayiotou, C., and J. H. Vera, "Statistical Thermodynamics of r-Mer Fluids and Their Mixtures," *Polymer J.*, **14**, 681 (1982).

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ (1986).

Renon, H., and J. M. Prausnitz, "On the Thermodynamics of Alcohol-Hydrocarbon Solutions," *Chem. Eng. Sci.*, **22**, 299 (1967).

Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).

Sanchez, I. C., and R. H. Lacombe, "An Elementary Molecular Theory of Classical Fluids," *J. Phys. Chem.*, **80**, 2352 (1976).

Stell, G., and Y. Zhou, "Chemical Association in Simple Models of Molecular and Ionic Fluids," *J. Chem. Phys.*, **91**, 3618 (1989).

Vera, J. H., S. G. Sayegh, and G. A. Radcliff, "A Quasi Lattice-Local Composition Model for the Excess Gibbs Free Energy of Liquid Mixtures," *Fluid Phase Equil.*, **1**, 113 (1977).

Vimalchand, P., "Thermodynamics of Multipolar Molecules: The Perturbed-Anisotropic-Chain-Theory," PhD Diss., Johns Hopkins Univ. (1985).

Vimalchand, P., and M. D. Donohue, "Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic-Chain Theory," *Ind. Eng. Chem. Fundam.*, **24**, 246 (1985).

Vimalchand, P., and M. D. Donohue, "Comparison of Equations of State for Chain Molecules," *J. Phys. Chem.*, **93**, 4355 (1989).

Wenzel, H., R. A. S. Moorwood, and M. Baumgärtner, "Calculation of Vapour-Liquid Equilibria of Associated Systems by an Equation of State," *Fluid Phase Equil.*, **9**, 225 (1982).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces: II. Thermodynamic Perturbation Theory and Integral Equations," *J. Stat. Phys.*, **35**, 35 (1984).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces: III. Multiple Attraction Sites," *J. Stat. Phys.*, **42**, 459 (1986a).

Wertheim, M. S., "Fluids with Highly Directional Attractive Forces: IV. Equilibrium Polymerization," *J. Stat. Phys.*, **42**, 477 (1986b).

Wertheim, M. S., "Fluids of Dimerizing Hard Spheres, and Fluid Mixtures of Hard Spheres and Dispheres," *J. Chem. Phys.*, **85**, 2929 (1986c).

Wertheim, M. S., "Thermodynamic Perturbation Theory of Polymerization," *J. Chem. Phys.*, **87**, 7323 (1987).

Wiehe, I. A., and E. B. Bagley, "Thermodynamic Properties of Solutions of Alcohols in Inert Solvents," *Ind. Eng. Chem. Fundam.*, **6**, 209 (1967).

Wilson, G. M., "Vapor-Liquid Equilibrium: XI. A New Expression for the Excess Free Energy of Mixing," *J. Amer. Chem. Soc.*, **86**, 127 (1964).

Appendix

We derive here hydrogen-bonding expressions for APACT for a binary mixture of components M and N, where component M has two bonding sites per molecule and component N has no bonding sites. There is an error in the derivation given by Ikonomou and Donohue (1986) for this type of binary mixture. However, the expressions derived here for W_M and for n_T/n_0 are the same as those given by Ikonomou and Donohue (1986).

In this binary mixture, component M can form dimers, trimers and higher linear species according to the chemical equilibria given by Eq. 1. Component N has no bonding sites, and as a result it behaves as a diluent species in the mixture. The true number of moles, n_T, that exist in the mixture and the number of moles that would exist in the absence of any association, n_0, are given from the expressions:

$$n_T = n_N + n_{M_1} + n_{M_2} + n_{M_3} + \cdots + n_{M_i} = n_N + \sum_i^\infty n_{M_i} \quad (A1)$$

$$n_0 = n_N + n_M = n_N + n_{M_1} + 2n_{M_2} + 3n_{M_3} + \cdots + in_{M_i}$$

$$= n_N + \sum_i^\infty in_{M_i} \quad (A2)$$

where n_N is the number of moles of species N, n_M is the number of moles of component M in the absence of any association, and n_{M_i} is the number of moles of the i-mer of component M. The mole fractions of the association species are defined as:

$$z_{M_i} = \frac{n_{M_i}}{n_T} \quad (A3)$$

The equilibrium constant for the chemical equilibria of associating species M is defined as:

$$K_i = \frac{\phi_{M_{i+1}}}{\phi_{M_i}\phi_{M_1}P} \frac{z_{M_{i+1}}}{z_{M_i}z_{M_1}} \quad (A4)$$

The ratio of fugacity coefficients is evaluated from Eq. 7 and it is given from Eq. 8. Finally, z_{M_i} is expressed in terms of z_{M_1} according to the expression:

$$z_{M_i} = \left(K\frac{n_T}{n_0}RT\rho e^g\right)^{i-1} z_{M_1}^i \quad (A5)$$

The material balance for component M, $n_M = \sum_i^\infty in_{M_i}$ can be written as:

$$\frac{n_M}{n_0} = x_M = \sum_i^\infty i\frac{n_{M_i}}{n_0} = \sum_i^\infty iz_{M_i}\frac{n_T}{n_0} \quad (A6)$$

By substituting Eq. A5 into Eq. A6, the following expression results:

$$x_M = \frac{W_M}{(1 - KRT\rho e^g W_M)^2} \quad (A7)$$

Solving the quadratic Eq. A7 for W_M, one obtains:

$$W_M = \frac{2x_M}{1 + 2KRT\rho e^g x_M + \sqrt{1 + 4KRT\rho e^g x_M}} \quad (A8)$$

The material balance for the true species given by Eq. A1 can be written as:

$$\frac{n_T}{n_0} = x_N + \sum_i^\infty iz_{M_i}\frac{n_T}{n_0} \quad (A9)$$

and by substituting Eq. A5, one obtains:

$$\frac{n_T}{n_0} = x_N + \frac{W_M}{1 - KRT\rho e^g W_M} \quad (A10)$$

Substitution of the expression for W_M into the latter results in the expression:

$$\frac{n_T}{n_0} = x_N + \frac{2x_M}{1 + \sqrt{1 + 4KRT\rho e^g x_M}} \quad (A11)$$

Further algebraic manipulation based on Eq. A11 results in Eq. 97 for Z^{assoc}. Panayiotou (1989) derived Eqs. A8 and A11 independently for mixtures of alcohols with alkanes. In his analysis, he used the Sanchez-Lacombe equation of state for the physical interactions.

For the case where component M has only one bonding site per molecule and component N has no bonding sites, the derivation is similar. In that case, though, component M can only form dimer species, and as a result the material balances should be modified accordingly. The quadratic equation for W_M is of the form:

$$x_M = W_M + 2KRT\rho e^g W_M^2 \quad (A12)$$

and so W_M is given from the expression:

$$W_M = \frac{2x_M}{1 + \sqrt{1 + 8KRT\rho e^g x_M}} \qquad \text{(A13)}$$

In addition, the expression for n_T/n_0 becomes:

$$\frac{n_T}{n_0} = x_N + W_M + KRT\rho e^g W_M^2 \qquad \text{(A14)}$$

and finally:

$$\frac{n_T}{n_0} = x_N + \frac{2x_M(KRT\rho e^g x_M - 1)}{4KRT\rho e^g x_M - 1 - \sqrt{1 + 8KRT\rho e^g x_M}} \qquad \text{(A15)}$$

From Eq. A15, an expression for Z^{assoc} is obtained (Eq. 71).