Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches

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We present a review of recent advances in the statistical associating fluid theory (SAFT). In contrast to the “chemical theory”, in which nonideality is explained in terms of chemical reactions between the species, SAFT and similar approaches relate nonideality to the intermolecular forces involved. Such physical theories can be tested against molecular simulations, and improvements to the theory can be made where needed. We describe the original SAFT approach and more recent modifications to it. Emphasis is placed on pointing out that SAFT is a general method and not a unique equation of state. Applications to a wide variety of fluids and mixtures are reviewed, including aqueous mixtures and electrolytes, liquid–liquid immiscible systems, amphiphilic systems, liquid crystals, polymers, petroleum fluids, and high-pressure phase equilibria.

1. Introduction

Ten years have passed since the publication of the first papers describing statistical associating fluid theory (SAFT). From the outset, SAFT was envisioned as a method that combined Wertheim's thermodynamic perturbation theory (TPT) for associating fluids with modern ideas for formulating physically based equations of state. A review of the papers published in the past 10 years reveals more than 200 articles dealing directly with the SAFT approach and its applications. Despite this success, both hype and confusion surround SAFT, in part because the seminal articles of Wertheim are difficult to read and in part because SAFT is not a rigid equation of state, but rather a method that allows for the incorporation of the effects of association into a given theory. The purpose of this paper is to review, in hindsight, the original formulation, presenting a simplified heuristic argument for its derivation and reviewing some of the most relevant engineering applications.

Over the past four decades or so, quite accurate methods have been developed for describing the thermodynamic behavior of fluids composed of simple molecules. By simple, we mean molecules for which the most important intermolecular forces are repulsion and dispersion (van der Waals attractions), together with weak electrostatic forces due to dipoles, quadrupoles, etc. Many hydrocarbons, natural gas constituents, simple organic molecules (e.g., methyl chloride, toluene), and simple inorganics (N2, CO, O2, N2O, etc.) fall within this category. Depending on one's taste and desired application, one can use an engineering equation of state (e.g., a Peng–Robinson or Soave–Redlich–Kwong equation), a local composition model, a corresponding states theory, a group contribution method, or a more fundamental approach such as perturbation theory. If one is prepared to fit several adjustable parameters in an empirical equation or an intermolecular potential, these methods are likely to give good results for such fluids. Nevertheless, a great many fluids, and particularly mixtures, do not fall within this simple class—electrolytes, polar solvents, hydrogen-bonded fluids, polymers, liquid crystals, plasmas, and so on. Although one might, in practice, use one of these well-established methods for these systems, the limitations of these equations rapidly become evident. The correlation of data requires complex and unphysical mixing rules and temperature-dependent binary parameters, and the predictive capability of the approach is usually very poor. The reason for this is that, for such fluids, important new intermolecular forces come into play—Coulombic forces, strong polar forces, complexing forces, forces associated with chain flexibility, induction forces, etc.—that are not taken into account in an explicit way.

An important class of these complex fluids consists of those that associate to form relatively long-lived dimers or higher n-mers. This class of fluids includes those in which hydrogen bonding, charge transfer, and other types of complexing can occur. The intermolecular forces involved are stronger than those due to dispersion or weak electrostatic interactions, often by an order of magnitude or more, but still weaker than those char-
characteristic of true chemical bonds. In Figure 1, we show how the “bond” strength varies continuously over several orders of magnitude from the interactions between simple molecules and those corresponding to chemical bonds. Associating fluids fall between these two extremes, and so they require special treatment when being modeled. This review focuses on methods for describing fluid mixtures that contain these types of associating compounds.

The existing engineering folklore for dealing with associating mixtures is largely based on the “chemical theory”, in which the associating complexes are treated as distinct new chemical species, so that the apparently anomalous physical behavior is ascribed to the change in chemical composition (higher molecular mass, fewer molecules, and so on). Chemical equilibria between the initial components and these complexes are written, and the corresponding chemical equilibrium constants then appear in the equations for the thermodynamic properties. In principle, there is nothing incorrect with such an approach; in fact, the chemical approach was originally used for simple mixtures of weakly interacting molecules, before more advanced techniques were available. However, the approach is of limited predictive value as one must know in advance all of the “reactions” involved and be able to measure or predict the equilibrium constants as a function of temperature. More fundamental statistical mechanical approaches are available, one of which results from a series of papers by Wertheim. The Wertheim papers have inspired a thermodynamic perturbation theory that is the basis of SAFT. These new theoretical equations relate the thermodynamic properties to physical intermolecular forces, so that associating liquids are treated on the same footing as simple liquids of more weakly interacting molecules. However, such theories must take explicit account of the presence of long-lived complexes. This more fundamental approach has several advantages over the older chemical approach: it is not necessary to know or guess the chemical reactions in advance or to incorporate in the equations temperature-dependent equilibrium constants. Another important advantage is that, because the theory is based on a well-defined model for the molecules and their intermolecular forces (the Hamiltonian), any approximations made in the theory can be rigorously tested against computer simulation results. Such tests can be used to choose the most accurate theoretical route before embarking on comparisons of the theory with experiment. This procedure is inapplicable to more empirical theories as they do not rest on a well-defined Hamiltonian. The reader is referred to the works cited in the next section for a review of other theories for associating fluids and mixtures.

In the first parts of this paper, we provide an overview of the Wertheim theory and TPT, while in the second part, we review some of the current implementations of SAFT and comment on future applications.

2. Theories for Associating Fluids

Approaches to the modeling of associating fluid mixtures have historically been categorized as being chemical, quasi-chemical, or physical in nature. The first historically published methods to describe the nonidealities of associating systems are due to Dolezalek and are based on the premise that the association can be treated as a chemical reaction. The chemical theory represents the association phenomena by such chemical reactions, which in the simple case of a substance A that has the ability to self-associate to form dimers is

$$A + A \rightarrow AA \quad (1)$$

Examples of real substances with this behavior include gas-phase carboxylic acids, NO, and NO₂. If, as in the original theory, we consider that the pseudo-species (the monomer and the dimer) form an ideal solution, so that the activity coefficients are unity, the thermodynamic properties of the system are characterized by a single equilibrium constant, $K_{\text{ideal}}$, which is related to the concentrations of both the monomers and the dimers

$$K_{\text{ideal}} = \frac{\rho_{AA}}{\rho_A^2} \quad (2)$$

where $\rho_A$ and $\rho_{AA}$ are the number densities of the monomer and dimer, respectively. In this case, because of the simplicity of the model, the only associated species possible are dimers. For any other situation, for this approach to be followed, the type and quantity of distinct probable species encountered must be determined a priori. For example, for alkanols, the experi-
mental evidence indicates the formation of chainlike associates, so in principle, all n-mers, e.g., dimers, trimers, tetramers, and so on, would have to be taken into account. Usually, the equilibrium constants assigned to each reaction are treated as adjustable parameters, since they cannot be obtained directly from experimental measurements. Even though the selection of the number of multimers considered is arbitrary, to keep the computational effort to a reasonable size, the number of assumed species, and consequently the number of chemical reaction constants \( K_i \) to be fixed, must be minimized. In any case, as the number of association complexes in the system increases, an increasingly large number of fitted parameters is needed (at least one constant per reaction involved), making the use of these methods cumbersome. Despite this limitation, simple versions of this chemical theory have been successful in describing the solution properties of many real systems.  

Dolezalek's original theory considers that the "nonidealty" of any fluid or fluid mixture can be explained solely by the formation of distinct chemical species, i.e., the n-mers are themselves treated as ideal gases or solutions. An illuminating example of the extent to which Dolezalek's theory can be misused is a paper by Dolezalek himself in which liquid solutions of nitrogen and argon are described by assuming polymerization of the argon. Nevertheless, when used judiciously, the chemical theory of solutions provides a useful framework for correlating thermodynamic properties.

The chemical theory can be extended naturally by relaxing the restraint of considering only ideal gases and ideal solutions. The problem translates into the simultaneous solution of the chemical equilibria coupled with the solution of the thermodynamic equations using more realistic models (e.g., an equation of state for nonassociating substances). A recent review has been completed by Fischer and Zuckerman.  

Heidemann and Prausnitz (HP) presented one of the first successful methods for combining an equation of state for nonassociating substances with a chemical approach. They assumed the occurrence of consecutive "chainlike" association reactions

\[
A + A \leftrightarrow AA \\
AA + A \leftrightarrow AAA \quad \vdots 
\]

in which the equilibrium constants of all of the consecutive reactions are assumed to be equal (\( K_1 = K_2 = \ldots = K_{\text{HP}} \)). For illustration purposes, the corresponding equilibrium expression for the first of these reactions is

\[
K_1 = K_{\text{HP}} = \frac{\phi_{AA} \cdot z_A}{\phi_A^2 \cdot p} \cdot \frac{z_A}{2} = \exp(-\beta \Delta G_{\text{assoc}}) \quad (4)
\]

where \( \phi \) represents the fugacity coefficients; \( z_i = n_i/n_T \) is the mole fraction of the pseudospecies (referred to \( n_T \), the total number of moles, including the pseudospecies at equilibrium); \( \Delta G_{\text{assoc}} \) is the standard Gibbs free energy per molecule associated with the reaction; and \( \beta = 1/kT \), where \( k \) is Boltzmann's constant and \( T \) is the absolute temperature. The appearance in eq 4 of the term containing fugacity coefficients arises from the consideration of nonidealities in the constituent species. The use of an appropriate equation of state (EOS) to calculate the fugacity, along with a suitable assumption with regard to the number and type of reactions involved, allows for the analytical solution of the coupled equations. For example, in the HP approach, the expression for the fraction of monomers in the case of a dimerizing compound will be

\[
x = \frac{2}{1 + \sqrt{1 + 4\rho K^*}} \quad (5)
\]

where \( \rho K^* = 2\rho K_{\text{HP}} \), and \( g \), in this case, is equal to zero. (Other EOS described below will require different values of \( g \)).

The original HP treatment utilized a van der Waals-type EOS with some sui generis combining rules to effectively separate the "physical" from the "chemical" contributions to the compressibility factors. The HP approach is not straightforwardly extended to mixtures, and additionally, an arbitrary separation of chemical and physical interactions can be thermodynamically inconsistent. There have been several attempts to modify this approach using several types of coupled EOSs. The perturbed anisotropic chain theory (PACT) equation of state has been used as the physical part to obtain the associating PACT (APACT), and its variants. Anderko employed the Yu–Lu EOS as the physical EOS to develop the associating EOS (AEOs). Other recent examples are given by Deits and Kao. In all of these cases, the actual form and performance of the resulting equations of state are strongly dependent on (a) the equation of state used to correlate the physical effects, (b) the particular form of the combining rules for the associated species, and (c) the number and type of the reactions considered. Unfortunately, the last two factors are in principle heuristic, and thus little improvement can be obtained from theoretical considerations.

The original quasi-chemical theory proposed by Guggenheim postulated that nonidealities in fluids could be assigned to the existence of nonrandom mixing at the molecular level. In opposition to the chemical approach, in the quasi-chemical approach, the formation of distinct associating compounds is not considered. Association is not explicitly distinguished from all other van der Waals-type interactions. The strong interactions found in associating systems bias the random mixing expected in simple fluid mixtures; thus, the quasi-chemical theories account for association forces by assigning large energy parameters to actual associating interactions. Quasi-chemical theory has served as the basis for several widely used engineering correlations for liquid mixtures, such as the nonrandom two-liquid model (NRTL); the universal quasi-chemical approach (UNIQUAC); and most notably, group contribution methods such as the universal functional activity coefficient model (UNIFAC) and the analytical solution of groups (ASOG). Although quite successful for correlating and predicting the properties of liquid mixtures of normal, polar, and even associating mixtures well below their critical points, these methods are not of practical use over the whole fluid range or for very large molecules. Their application to associating mixtures is not without difficulties; for example, parameters correlated from liquid–vapor equilibrium data are not appropriate for liquid–liquid calculations within the same class of molecules, indicating some degree of inconsistency. Nevertheless, group contribution methods
are the industrial standard for low-temperature non-ideal solution (liquid) properties, because of the availability of a large database of parameters for mixtures of interest.

Most quasi-chemical approaches are expressed as correlations for activity coefficients. The very nature of the activity-coefficient approach is not convenient for the prediction of VLE over wide ranges of temperature, since it must be coupled with an EOS for the coexisting vapor phase, leading to inconsistencies in the vicinity of, or above, the critical regions. It is generally accepted that an EOS valid in the whole fluid region would be a better choice, if available. Recently, nonassociating fluid EOSs have been coupled to excess Gibbs energy models to model highly nonideal solutions, including associating fluids. This coupling extends the value of the group contribution methods, allowing for the use of cubic (or other simple) EOSs to represent complex mixtures that include associating substances. For a review of this approach, the reader is directed to ref 50 or 51.

Another related approach is the method of Panayiotou and Sanchez,52,53 which postulates the separation of the partition function into physical and chemical parts. The first part is treated with a lattice-fluid equation, and the second with an approach similar in spirit to quasi-chemical theory. Other lattice equations of state based on a quasi-chemical approach have also been extended to associating mixtures54,55 in a similar fashion.

Although the above-mentioned theories are not inherently incorrect, the fact that the equilibrium constant in chemical theories must be obtained empirically (and varies with temperature) limits the use of these theories as predictive tools. A more promising route for understanding the properties of associating fluids is provided by recent theories that are firmly based in statistical mechanics. In principle, statistical mechanics provides formal recipes for calculating the structure and thermodynamics of a fluid given its intermolecular potential function. However, for most systems of interest, this solution requires the use of one or more approximations that ultimately determine the accuracy of the theory.

From this modern point of view, two methods can be envisioned for the modeling of complex homogeneous fluids, namely, integral-equation theories and perturbation theories. Both routes have been successful in solving the thermodynamic properties of some moderately complex fluids (nonspherical molecules, polar and polarizable fluids). For reviews on the subject, the reader is referred to Hansen and McDonald56 or Gray and Gubbins.57 The possibility of molecular association can be introduced into integral-equation theories by considering a strong, spherically symmetric attraction, such as would be observed in the case of ionic systems. Although initial attempts failed to reproduce the low-density limit for associating fluids, this difficulty has since been overcome.58,65 In perturbation approaches, one considers a reference fluid with well-known properties (e.g., a homomorphic, nonassociating fluid) and obtains the properties due to association through a perturbation expansion. This task, however, is not straightforward, as the association forces involved are generally incorrect, the fact that the equilibrium constant varies with temperature) limits the use of these theories as predictive tools. A more promising route for understanding the properties of associating fluids is provided by recent theories that are firmly based in statistical mechanics. In principle, statistical mechanics provides formal recipes for calculating the structure and thermodynamics of a fluid given its intermolecular potential function. However, for most systems of interest, this solution requires the use of one or more approximations that ultimately determine the accuracy of the theory.

Within the framework of SAFT, the EOS of a fluid is a perturbation expansion given in terms of the residual molar Helmholtz energy \(a^*(T,\rho)\), defined as the difference between the total molar Helmholtz energy and that of an ideal gas at the same temperature \(T\) and molar density \(\rho\)

\[
a^*(T,\rho) = a(T,\rho) - a_{\text{ideal gas}}(T,\rho)
\]
molecule. The molecule is made up of contributions from these individual contributions. As an example, the process involved in the perturbation scheme to form a chainlike molecule, and/or by including a further perturbation due to associating forces. Because the molecules are formed by m segments, the total a\textsuperscript{seg} contribution will correspond to the individual sum of all monomers composing a given molecule, summed across all components A, B, ..., α, ..., β, ..., R

\[
a\textsuperscript{seg} = \frac{a_{\text{monomer}}}{RT} \sum_{\alpha} x_{\alpha} m_{\alpha}
\]

where \(x_{\alpha}\) is the mole fraction of species \(\alpha\). \(a_{\text{monomer}}\) refers to the molar Helmholtz energy of the fluid if no chain connectivity occurred, evaluated at the monomer molar density. The description of the Helmholtz energy of the monomers is not specified within SAFT, and it can itself be given by a perturbation expression, the most common being an EOS based on a hard-sphere reference fluid, e.g., the Carnahan-Starling EOS with temperature-dependent diameters and an added dispersion term. Other simplified intermolecular potentials, such as the square-well (SW) potential and the Yukawa potential have been used as the model for the segment interactions. A generalized potential function with an attractive part of various range (VR-SAFT) has been proposed and implemented by Jackson et al.\textsuperscript{103} if one assumes that the EOS of state of the reference fluid is known, one can use it directly. Thus, closed-form EOSs for LJ fluids\textsuperscript{103} have been used. Otherwise, an EOS for a simple fluid such as argon\textsuperscript{116} can be used.

Although the original formulation considers spherically symmetrical potentials for the monomers, it has been extended to energetically and sterically anisotropic potentials. Electrostatic effects can be treated as perturbations at this stage. Point-charge models can also be used as segments.\textsuperscript{124} An accurate equation of state for a nonspherical reference fluid\textsuperscript{126,127} can also be used. Notably, HS, SW, and LJ dimers (or higher n-mers) have been used.

### 3.2. The Chain Contribution

The original Wertheim papers\textsuperscript{6–7} derived in an analytical way the energetic contribution (and thus the form of the corresponding EOS) that came about from the association of spherical particles. One of the successes of the theory came from the fact that, in the limit of infinitely strong bonding on an infinitely small association site placed at the edge of a given molecule, one can, in fact, account for polymerization of the monomers. The resulting equations are both reasonably simple and accurate.

Depending on the nature of the original unassociated-fluid mixture, different types of chains can be obtained. For the case of a hard sphere with one associating site, in the limit of infinite bond strength (glue points), the theory gives an expression\textsuperscript{134} for the thermodynamics of a hard-dumbbell fluid, which is found to rival the accuracy of exact simulation. If two diametrically opposed associating sites are placed on some molecules, linear chains are formed.

The contribution to the Helmholtz energy is, to first order (TPT1), equal to

\[
a_{\text{chain}} = \frac{a_{\text{seg}}}{RT} = \sum_{\alpha} x_{\alpha} (1 - m_{\alpha}) \ln y_{\alpha}^{\text{seg}}(l)
\]
where \( m \) is the number of segments per molecule and \( y^{seg}(l) \) is the cavity correlation function evaluated at a bond length \( l \), given by

\[
y^{seg}(l) = \exp[\phi^{seg}(l)/kT]g^{seg}(l) \tag{10}\]

For some potentials, simplifications can be made. Thus, for a LJ fluid of tangent spheres

\[
y^{LJ} = \exp[\phi^{LJ}(l)/kT]g^{LJ}(l) \tag{11}\]

Similarly, for a fluid of hard tangent spheres

\[
y^{HS}(d) = g^{HS}(d) \tag{12}\]

For cases where the bonding sites are near the borders of the molecules, the approximations within the theory compare well with exact simulation results. For fused-sphere chains in which the spheres overlap significantly (as opposed to chains of tangent spheres), direct application of the theory fails. Nevertheless, other more successful approaches can be taken to account for sphere overlap,\(^{135-139}\) namely, allowing noninteger values of the chain term, \( m \), or invoking a conformity between a chain fluid and an equivalent nonspherical molecule.

The first-order theory gives a good approximation for the configurational properties of linear chains,\(^{140}\) even up to the infinite-length limit.\(^{141}\) One should note that TPT1 does not make a distinction with regard to bond angles within a molecule. This bonding restriction of TPT1 can be eliminated by taking into account higher-order terms in the perturbation expansion.\(^{140,142,143}\) However, higher-order expressions are considerably more complicated than the corresponding ones for TPT1 and involve the three-body (or higher) correlation function of the reference fluid, a quantity that is difficult to obtain.\(^{144}\) In general, it has been shown\(^{145}\) that the estimation of \( g \) must be of high quality in order for accurate results to be obtained.

Gross and Sadowski\(^{146,147}\) have used a hard-chain reference and added a Barker–Henderson-type perturbation\(^{148,149}\) to account for the attraction of these chains (as opposed to adding the perturbation on the segment level). The model, named perturbed-chain SAFT (PC-SAFT), is fit to the pure-component properties of n-alkanes.

For attractive flexible chains, the Wertheim formalism does not take into account the intramolecular attraction, and therefore, the predicted low-density limit is unrealistic.\(^{109}\) No coil-up of the chains is accounted for at low temperatures, and phase diagrams of these fluids are inaccurate; at higher densities, intramolecular effects are effectively counterbalanced by intermolecular interactions, and these considerations are of lesser importance. Applications to ring structures also require particular modifications to the theory.\(^{150}\)

Typical misunderstandings surrounding SAFT derive from the chain contribution, because the same theory is used both for the description of chains and for the description of association. SAFT considers the general case of chain molecules that can form association complexes. In some cases, the association contributions are nonexistent, and the resulting equations are applied to fluid mixtures involving nonassociating chain fluids (e.g., polymer solutions, asymmetric hydrocarbon mixtures, etc.). The SAFT model can be applied either to a nonassociating chain fluid or to a general associating fluid.

3.3. The Association Contribution. Within SAFT, a given molecule can have a number, \( 1, 2, \ldots, i, \ldots, j, \ldots, M \), of associating sites. The association sites are characterized by a noncentral potential located near the perimeter of the molecule. One can include one or more different types of sites on each molecule. There is no limit to the number of sites that characterize a molecule, although in practice, it might be difficult to justify more than four different association points in a single segment. The first-order theory does not distinguish the actual positions of the sites (the angles among them).

Each of these sites has the restriction (within TPT1) of being able to bond to only one other site. Depending on the molecules of interest, different bonding scenarios can be considered. Different molecules will have sites of different types placed in different locations within each molecule. However, TPT1 places some restrictions: (1) Two molecules can only establish a single bond with each other. This can become an important limitation for some systems of interest, such as carboxylic acids, where double bonding between molecules can occur. Although a crude approximation to circumvent this limitation is the consideration of such double bonding as a single bond, this approximation will not account for the fact that, in the liquid phase, molecules such as carboxylic acids can form chains, whereas in the vapor phase, they appear only as cyclic dimers. Expressions to relax this constraint have been obtained.\(^{151}\) (2) More than two molecules can not be involved in a single bond, i.e., three molecules can not be bonded together at a unique point. However, chains and clusters can be formed, given appropriate placement to the bonds, e.g., by placing two sites per molecule on diametrically opposed positions. The bonding at a given site is not directly influenced by bonding taking place in another part of the molecule. Bond cooperativity can be explicitly built into the theory at a later stage.\(^{152}\) (3) A site on a molecule can not bond to more than one site on another molecule. (4) A molecule can not bond to another site on the same molecule. This limitation can be of importance for polymer systems, where intramolecular bonding might be relevant. Again, this restriction can be relaxed with appropriate modifications of the theory.\(^{153-156}\) (5) No ringlike structures are allowed among the sites. Again, this restriction can be relaxed through modifications of the original theory.\(^{157,158}\)

The resulting working equation of the theory is very compact

\[
\frac{\delta_{assoc}}{RT} = \sum_{\alpha} X_{ai} \left[ \sum \ln X_{ai} - \frac{X_{ai}}{2} + \frac{M_{ai}}{2} \right] \tag{13}\]

where \( X_{ai} \) is the mole fraction of molecules of component \( \alpha \) not bonded at site \( i \). Component (macroscopic) compositions are denoted by lowercase \( x_{ai} \), while the fraction of nonbonded molecules is denoted by uppercase \( \chi_{ai} \). The internal sum is over all associating sites on a molecule. The values of the \( X \)'s are obtained from the solution of the mass balances

\[
X_{ai} = \left( 1 + N_{av} \phi \sum_{j=1}^{n} \Delta_{ij} X_{aj} \right)^{-1} \tag{14}\]

where the internal sum runs over all of the sites in a molecule. When developing the working equations for
macroscopic systems, one must bear in mind that the original theory is statistical in nature and that the usual nomenclature involves quantities per molecule whereas engineering equations are usually expressed on a per mole basis. One relates the two quantities through Avogadro's number, \( N_{av} \). The quantity \( \Delta_{ij} \) is related to the strength of the \( i-j \) association bond and is given formally by

\[
\Delta_{ij} = \int g^{seg}(d) f_i(d) d(12) \tag{15}
\]

where \( g^{seg} \) is the segment fluid pair correlation function, \( f_i = \exp(-\phi_{ij}(12)/kT) - 1 \) is the Mayer f-function for the association interaction, \( \phi_{ij} \) is the potential function used to define the association, \( k \) is Boltzmann's constant, and the integration \( \int d(12) \) denotes an unweighted average over all orientations of molecules 1 and 2 and integration over all separations of molecules 1 and 2. An assumption is made that, for the purposes of the integration, the segment pair correlation function is equivalent to that of the segment as part of a chain. This is a reasonable approximation if the bonding site is thought to be diatomically opposed to the backbone of the chain. Further refinement of this approximation requires higher-order theories.\(^{140,142} \) For many applications, a simple form of \( \phi_{ij} \) such as a SW potential can be used. Under these circumstances, the association strength can be expressed as the simple term\(^{159} \)

\[
\Delta_{ij} = K_{ij} f_{ij} g^{seg}(d) \tag{16}
\]

where \( K_{ij} \) is the volume available for bonding\(^{160} \) and \( d \) is the bonding distance.

In the case of a simple dimerizing fluid, i.e., a substance with a single associating site that can bond to form dimers according to eq 1, one obtains

\[
\frac{a_{assoc}}{RT} = \ln X - \frac{X}{2} + \frac{1}{2} \tag{17}
\]

with

\[
X = (1 + N_{av} \rho X \Delta_{ij})^{-1} \tag{18}
\]

which can be solved to obtain

\[
X = \frac{-1 + \sqrt{1 + 4 \rho N_{av} \Delta_{ij}}}{2 \rho N_{av} \Delta_{ij}} = \frac{2}{1 + \sqrt{1 + 4 \rho N_{av} \Delta_{ij}}} \tag{19}
\]

Although this result coincides with that from the chemical approach (cf. eq 5), it does not imply that the Wertheim theory is chemical in nature; it merely points out that it obeys the correct limits. Similarities between the physical and chemical approaches persist as long as the number and type of chemical reactions are finite and well-defined, which, in most cases, is not true.\(^{161} \)

Figure 3 presents a cartoon of an alkanol molecule in which one could envision the i site as being a proton and the j site as being the lone electron pair of the oxygen in the –OH radical. (In principle, an alkanol molecule can form three hydrogen bonds, one on the hydrogen site and one on each of the lone electrons of the oxygen, for a total of two more bonds. In practice, steric hindrance usually precludes all three bonds from forming, and thus, a two-site model such as proposed is more feasible.) Such a molecule can exist in one of three bonding states: (a) unbonded, (b) with an i site bonded to a j site of another molecule, or (c) with both i and j sites bonded to a j and an i site of two other molecules. Note that i–i association and j–j association are precluded. In this case, the contribution from association is

\[
\frac{a_{assoc}}{RT} = \ln X_i - \frac{X_j}{2} + \ln X_j - \frac{X_i}{2} + 1 \tag{20}
\]

where \( X_i \) and \( X_j \) are obtained by simultaneous solution of eq 14 above, which, for this case, has an analytical solution

\[
X_i = X_j = \frac{2}{1 + \sqrt{1 + 4 \rho N_{av} \Delta_{ij}}} \tag{21}
\]

Not all cases have analytical solutions; therefore, the final SAFT equations for derived properties, such as fugacities or chemical potentials, might not always be explicit.

In summary, SAFT requires a minimum of two parameters, the characteristic energy and the characteristic size of a monomeric segment, to describe simple conformal fluids. A third parameter, \( m \), is required to describe the nonsphericity for nonassociating fluids. For associating fluids, one must also assign two parameters to characterize both the association energy, \( \phi_{ij} \), and the volume available for bonding, \( K_{ij} \). For each species, one must additionally define the associating sites and their bonding correspondence (which site bonds to which). All of these parameters are usually regressed from experimental properties. Nevertheless, because of the well-defined physical meaning of each parameter, they can be estimated from ab initio calculations\(^{162–164} \) or from direct measurements, such as Fourier transform infrared spectra.\(^{165–169} \)

4. Applications of the SAFT Model

4.1. The Huang–Radosz Parametrization. By far the most widely used version of SAFT is the implementation of Huang and Radosz\(^{170,171} \), who fitted the potential parameters (\( m \), \( \sigma \), and \( \epsilon \) for nonassociating fluids, plus two H-bonding parameters, \( \epsilon_{AA} \) and \( \sigma_{AA} \), for associating fluids) to the experimental vapor pressure and saturated liquid density data of over 100 real fluids. For the segment term, they use the sum of a hard-sphere part, given by the Carnahan–Starling equation, and a dispersion part, given by the BACK equation of Chen and Kreglewski.\(^{81}\) The fluids considered include simple inorganics, alkanes, polyacrylates, cyclic molecules, aromatics, ethers, ketones, esters, alkenes, chlorinated hydrocarbons, water, ammonia, hydrogen sulfide, alkanols, acids, and primary and secondary amines. The fitted parameters were found to be well-behaved and physically reasonable, following simple relationships with molar mass within a given homologous series, so that extrapolations could be made to fluids not included in the fit. The average deviations were on the order one or a few percent for both vapor pressure and liquid density. For mixtures,\(^{171} \) only the dispersion part of the segment Helmholtz energy requires the use of mixing rules; the composition dependence is built into the chain and association terms by the statistical thermodynamics. Generally, good agreement with experiment was found for binary VLE calculations with the use of a single unlike-pair potential parameter to represent dispersion. Figure 4 shows the phase diagram for the
C38/ethylene/1-butene mixture. Experimental results are 

Figure 4. Pressure-temperature diagram for the mixture of C38/ 
ethylene/1-butene. Curves are obtained with SAFT with a binary 
interaction parameter, \( k_{ij} \), interpolated from other data. Inverted 
open triangle (\( \circ \)) is the calculated mixture critical point; solid 
upright triangle (\( \bullet \)) is the solvent critical point. Open and closed 
circles (\( \odot, \bullet \)) are experimental data. From ref 189.

Figure 5. Solubility of water in the ethane-rich phase for water/ 
ethane mixtures from experiment (points) and SAFT. From ref 189.

C38/ethylene/1-butene mixture. Experimental results are 
well modeled even up to the solid–fluid transition.

4.2. Water and Electrolytes. Primitive models of 
water have been proposed that incorporate a hard-
sphere\(^{172,173}\) or LJ\(^{174}\) core with four square-well sites 
mimicking the two hydrogen atoms and the lone-pair 
electrons. These models can be solved within TPT1, 
since the geometry of the sites is tetrahedral, i.e., the 
sites are separated by angles of 109.5° and thus are 
sufficiently far apart that higher-order corrections are 
unnecessary.\(^{140}\) These models are successful in predicting 
some of the abnormal structural and thermodynamic 
properties of water that are due to H bonding, such as 
the relatively high vaporization energy and critical 
temperatures. Many applications of SAFT deal with 
aqueous mixtures, since it is here that the method 
should have advantages over conventional engineering 
EOSs. Figure 5 presents an example of the prediction 
of ethane solubility in water. These models also predict 
the high-pressure immiscibility found in water/alkane 
mixtures.\(^{175}\)

Using TPT1, one can account only for the short-range 
directional properties of associating fluids. Association 
is inevitably accompanied by long-range electrostatic 
effects, which in the case of small molecules, such as 
water, can be significant. Electrostatic effects can be 
treated as an additional perturbation, and examples of 
such treatments are presented by Walsh et al.\(^{117}\) and 
Müller and Gubbins.\(^{121}\) The latter formulation has been 
successfully applied to water/hydrocarbon systems.\(^{122,123}\)

In a general context, ion pairing is just one example 
of a strong association, and the theory can be extended 
to take electrolytes into account. The principal difficulty 
is that, for electrolytes, the long range of the Coulombic 
interactions requires a clever separation between the 
reference and the associating potential. Additionally, 
the charge is now in a central (as opposed to an off-center) 
location, so multiple bonding must be considered 
explicitly. The Wertheim formulation has allowed for 
the development of multidensity theories for the case of 
electrolytes\(^{176,177}\) that can be incorporated in a SAFT 
formalism. Aqueous ionic solutions have been studied 
where SAFT is used to model water\(^{178}\) or the actual 
ions.\(^{179}\)

4.3. Closed-Loop Liquid–Liquid Immiscibility.

Many liquid mixtures present regions in which two 
liquid phases are in equilibrium. These are mainly 
mixtures in which the unlike-pair interactions are much 
weaker than the self-interactions, thus leading to phase 
separation. In most cases, as the temperature is raised, 
the region of the phase diagram that corresponds to 
liquid–liquid equilibrium (LLE) decreases; the molec-
ular kinetic energy overcomes the unfavorable interac-
tions; and eventually, the LLE disappears at the mix-
ture's upper critical solution temperature (UCST). In 
most immiscible systems, a decrease in temperature has 
the opposite effect, augmenting the regions of phase 
separation. However, in some mixtures, labeled type VI 
by Gubbins and Twu\(^{180}\) (in extension of the classification 
of Scott and van Konynenburg\(^{181,182}\)), a closed-loop 
immiscibility region is observed. In these mixtures, there 
is an UCST, but when the temperature is lowered, the 
region of LLE eventually disappears at a lower critical 
solution temperature (LCST). It is interesting to note 
that this abnormal behavior is not observed for fluids 
with simple isotropic potentials, e.g., inert gases. It is 
the unlike-pair association that drives the type VI 
behavior. At low temperatures, the unlike pairs are 
oriented so as to permit association and complete 
mixing. As the temperature is increased, many of these 
association bonds are broken, leading to immiscibility. 
As the temperature is increased further, this unmixing 
at first increases, but eventually the increased kinetic 
motion leads to increased miscibility, and complete 
mixing at an UCST. A clear presentation of these 
phenomena is given by Walker and Vause,\(^{183}\) and 
a more complete review is given by Narayanan and 
Kumar.\(^{184}\) Jackson et al. have applied SAFT to a 
mixture of hard spheres\(^{185}\) and chains\(^{186}\) with a van der 
Waals-type mean-field attraction plus unlike-pair as-
sociation through off-center bonding sites, showing that 
it can predict a closed-loop solubility region. Square-
well molecules with single associating sites will also 
produce this type of closed-loop diagram.\(^{187}\) Polymer 
systems can present this behavior and can be ade-
quately modeled by SAFT\(^{188,189}\), Kraska et al.\(^{190,191}\) and
Nezbeda et al.\textsuperscript{192–195} have produced global phase diagrams for binary mixtures with an associating component with similar models. Comparisons of UCST/LCST predictions of SAFT with other models have been made by Tork et al.\textsuperscript{196}

The behavior of fluids close to the critical point can be modeled using appropriate scaling laws. Such approaches can also be used within SAFT.\textsuperscript{197,198}

4.4. Amphiphilic Systems. Amphiphilic systems are characterized by the presence of a component (usually called surfactant or amphiphile) that, on a macroscopic level, appears to homogenize two otherwise immiscible phases. In most cases, one of the fluid phases will be characterized by strong self-association, and the amphiphile itself will have compatible association sites. Sear and Jackson, for example, have considered ternary water/oil/amphiphile mixtures.\textsuperscript{199} A temperature–composition plot for this case is shown in Figure 6. Each of the vertexes of the prism represents a pure compound, and the opposing face of the prism represents the binary mixture devoid of that component. The water/amphiphile mixture faces the reader; the water/oil is behind and to the left. The water/amphiphile binary mixture exhibits a closed-loop behavior, and it is clear that the addition of the amphiphile to the oil/water mixture reduces the immiscibility. Garcia-Lisbona et al.\textsuperscript{200} modeled aqueous solutions of alkyl polyoxyethylene surfactants, and Clements et al.\textsuperscript{201} modeled hexane/hexamethyldisiloxane/perfluorohexane, systems that exhibit both UCSTs and LCSTs. Kuexpert et al.\textsuperscript{202,203} and Talanquer and Oxtoby\textsuperscript{204} obtained both microscale and macroscopic predictions from simple model amphiphilic mixtures within the SAFT formalism. Surface and interfacial tensions\textsuperscript{205,206} and critical micellar concentrations\textsuperscript{207,208} of several surfactant systems have been correlated using a SAFT-based model.

4.5. Associating Liquid Crystals. Prolate molecules of sufficient length are known to form liquid crystalline phases. Their description requires a theory that takes into account the effects of their rigid elongated shapes.\textsuperscript{209}

Such theories can be used to provide a reference for considering associating liquid crystals. Sear and Jackson\textsuperscript{210} considered the case of associating hard spherocylinders that can dimerize through a bond placed at the end of the molecules. The bonding enhances the stability of the nematic phase.\textsuperscript{210,211} An interesting feature of the phase diagram is the nonmonotonic variation of the density of the nematic phase at coexistence. This produces a nematic–isotropic–nematic reentrant behavior, analogous to that found experimentally.\textsuperscript{212}

4.6. Inhomogeneous Fluids. TPT1 is but one of several “closures” of the originally proposed formulation. Integral-equation versions of the theory have also been studied\textsuperscript{134,213–216} and are useful for obtaining structural properties in addition to macroscopic properties. Wertheim's theory is derived in terms of density functionals, and in principle, its application to inhomogeneous fluids (where density is a function of position) is possible.\textsuperscript{78,217–225} The uncertainty encompassing the calculation of correlation functions for inhomogeneous fluids is the principal reason that this aspect of the theory has not been investigated as much as its homogeneous counterparts. Some studies have appeared that apply density functional theory to inhomogeneous polyatomic systems;\textsuperscript{226–228} Suresh and Naik\textsuperscript{229} applied TPT1 to a model for predicting interfacial properties (surface tensions) and contact angles on associating solid surfaces of aqueous liquid mixtures. Nucleation phenomena of associated fluids were considered by Talanquer and Oxtoby.\textsuperscript{230}

4.7. Polymers. The chain term in SAFT is successful in reproducing the equilibrium properties of even very long chains. Thus, the representation of polymers is a natural application of SAFT. In dealing with polymer systems, special care must be taken. As the size of a chain increases, so does the critical temperature of the substance. In terms of the calculated phase equilibria, as the segment parameter, $m$, is increased, the calculated critical temperature increases (all other parameters being the same), so that a fixed experimental temperature effectively corresponds to a lower reduced temperature. The attractive terms used in many versions of SAFT are obtained from correlations of simulation data of small molecules, and their use should be restricted to the range, in reduced temperature, in which the correlations were carried out.\textsuperscript{109,231} Phase equilibria of polymer\textsuperscript{168,232–239} and copolymer solutions,\textsuperscript{240–245} cloud points of polymer solutions,\textsuperscript{246–260} and even infinite-dilution activity coefficients of organics in polycarbonate systems\textsuperscript{261} have all been successfully modeled using SAFT. Figure 7 shows an example of the calculation of solubilities of gases in polyethylene using SAFT.

4.8. Petroleum Fluids. SAFT is trivially applicable to the VLE of n-alkane and simple hydrocarbon mixtures.\textsuperscript{34,99,106,262–265} Its main advantage, however, is that the SAFT parameters are well-behaved and suggest predictable trends with macroscopic properties. Based on this fact, Huang and Radosz\textsuperscript{270} proposed correlations of SAFT parameters in terms of the average molecular weight for poorly characterized oil fractions. The correlations are given in terms of the different families, e.g., n-alkanes, polynuclear aromatics, etc. This model has been successfully applied to correlate the extraction of petroleum pitch with supercritical toluene.\textsuperscript{266–268} which, despite the limited characterization data, rea-
sonably represents the liquid–liquid equilibria. Solubility in CO$_2$/bitumen systems\textsuperscript{269,270} (Figure 8) and asphaltene deposition\textsuperscript{271,272} are other examples of the application of SAFT in the oil industry.

### 4.9. High-Pressure Equilibria and Supercritical Fluid Extraction

As is the case for most EOS models, SAFT is well-suited to describe high-pressure phase equilibria as long as no quantitative description of critical points is involved. It is particularly well suited for the description of systems involving strong size asymmetries, such as those in which polymers and solvents are present. A recent review by Kirby and McHugh\textsuperscript{273} describes some of the applications involving supercritical fluid extraction in polymer systems. In particular, it offers some guidelines in the application of the Huang–Radosz parametrization to polymer systems.

Examples of some applications to supercritical fluid extraction are the modeling of high-pressure gas extraction systems\textsuperscript{274} including polymers and their precursor monomers (polyethylene/ethylene and polybutane/1-butene\textsuperscript{275}), the solubilities of polymers in supercritical carbon dioxide\textsuperscript{276,277} and other solvents,\textsuperscript{277} the fractionation of polymers in supercritical gases,\textsuperscript{278–280} separation of monodisperse and polydisperse polymer systems using compressed gases,\textsuperscript{281} and supercritical fluid extraction of polynuclear aromatics (PNAs)\textsuperscript{282,283} and other organic substances.\textsuperscript{284}

Care should be taken when modeling CO$_2$ mixtures using SAFT (or any other model) to account for the strong quadrupole interactions in the pure solvent. Otherwise, large binary interaction parameters or unphysical values of the pure-component parameters will be needed to correlate the data.

### 4.10. Other Highly Nonideal Systems

SAFT has been applied to model a wide variety of phase equilibria of industrially important fluids. Vapor–liquid equilibria results have been reported for systems containing long n-alkane mixtures,\textsuperscript{93} hydrogen fluoride,\textsuperscript{285,286} hydrogen chloride,\textsuperscript{287} alcohols,\textsuperscript{288–290} aqueous ethanolamine solutions,\textsuperscript{291} and acetonitrile and acrylic acid.\textsuperscript{292} Additionally, refrigerant mixtures\textsuperscript{97} and fluoroalkanes\textsuperscript{98} have also been modeled.

Liquid–liquid equilibria of organic substances\textsuperscript{293,294} including the water/alkane/n-alkyl polyoxyethylene ether\textsuperscript{295} system and solid–liquid equilibria of naphthenic/polyethylene\textsuperscript{296} mixtures have been successfully described. Figure 9 shows an example of a ternary LLE prediction in comparison with the UNIFAC prediction.

### 4.11. Other Implementations of SAFT

SAFT-like association terms have been incorporated into group-contribution,\textsuperscript{297–299} lattice,\textsuperscript{300} and cubic\textsuperscript{301–307} EOSs and into the UNIQUAC\textsuperscript{308} and UNIFAC\textsuperscript{309} models. Additionally, attempts have been made to simplify the mathematical form of the equations\textsuperscript{310–312} and to provide algorithms for calculating phase equilibria\textsuperscript{313,314} using SAFT and for more efficiently solving the root-finding problem.\textsuperscript{231,315}

Gross and Sadowski\textsuperscript{147} presented a new parametrization of SAFT with constants for a wide range of substances. This new parametrization does not suffer from the numerical inconsistencies\textsuperscript{231} of the original Huang–Radosz model.

Some recent papers\textsuperscript{147,234,236,316–323} compare the SAFT EOS and extensions of it against other existing methods. In general, SAFT, with its more rigorous foundation, is found to be more reliable both for fitting data and for...
prediction; this is particularly the case for associating fluids and chain molecules.

5. Conclusions

There have been major advances in the theoretical treatment of the thermodynamics of associating liquids in the past 10 years, particularly as a result of Wertheim’s theory. The theory is now finding application to a range of complex fluid problems, including polymers and their mixtures, surfactants and micellar systems, liquid crystals, liquid immiscible mixtures, water and electrolytes, and fluids in which intramolecular bonding is important. Much remains to be done for these more complex fluids, and for the application of this kind of theoretical approach to interfacial phenomena and adsorption.

The SAFT methodology has proven to be a significant improvement over more empirical equations of state and to have a firmer basis in its inclusion of chain and association effects in the reference term. As a result, it gives better results for associating and chain-molecule fluids. Such calculations are typically 8 or 9 orders of magnitude cheaper, and about 6 orders of magnitude faster, than an experimental phase-equilibrium measurement for a binary mixture.324

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Appendix: Heuristic Derivation of the SAFT Equations

Wertheim’s theory4 makes use of graphical expansions for the logarithm of the grand partition function and the number density of the given species. The full graphical treatment is lengthy and relies on a detailed knowledge of graph manipulation;56 we provide only a brief outline of the theory here. The reader is referred to the original papers4 for full details; the extension to mixtures is given by J. oslin et al.325 and by Chapman.78 Here, we provide a simpler and more heuristic derivation due to J. oslin et al.325

We consider a fluid of associating molecules interacting only through pair potentials. These potentials are assumed to have a core potential that includes a strongly repulsive component (nonspherical, in general) and a sum of interactions between association sites. We consider a mixture of components A, B, ..., α, ..., β, ..., R. Association sites in each molecule are labeled 1, 2, ..., i, ..., j, ..., M. Thus, the pair potential can be written as

$$\phi_{\alpha\beta}(12) = \phi^{\alpha}_0(12) + \phi^{1}_0(12) = \phi^{\alpha}_0(12) + \sum_{i j} \phi^{\alpha i j}(r_{i j})$$  

(A-1)

where $$\phi^{\alpha}_0(12)$$ is the reference (core) potential and $$\phi^{\alpha i j}(r_{i j})$$ is the short-range attractive potential between site i in a molecule of species α and site j in a molecule of species β. It is the short-range attractive potentials that give rise to the association. Here, (12) represents $$(r_{12}, \alpha_1, \alpha_2)$$. Wertheim takes the core potential to be purely repulsive, but this restriction is not necessary, and some later authors take the core potential to include dispersion and other isotropic attractive interactions.

To keep the notation simple, we treat the case where the molecules have only one association site. The extension to the multiple-site case is straightforward. The total Helmholtz energy, A (the total Helmholtz energy is equal to the molar Helmholtz energy, a, multiplied by the number of moles, n. Similarly, A/(NK) is written as the sum of ideal-gas and a residual contributions

$$A = A^{\text{ideal gas}} + A'$$  

(A-2)

where $$A^{\text{ideal gas}} = -kT \ln Q^\text{ideal gas}$$ and $$Q^\text{ideal gas}$$ is the partition function for the ideal gas at the temperature, density, and composition of interest. $$A'^{\text{ideal gas}}$$ is given by

$$\frac{A^{\text{ideal gas}}}{kT} = \sum_{\alpha} [\rho_{\alpha} \ln(\rho_{\alpha}/\rho_{\alpha}) - \rho_{\alpha}]$$  

(A-3)

where $$\rho_{\alpha}$$ is the number density, $$\Lambda_{\alpha} = (\Lambda_{\alpha i}^{\text{trans}}, \Lambda_{\alpha i}^{\text{rot}})$$, and $$\Lambda_{\alpha i}^{\text{trans}}, \Lambda_{\alpha i}^{\text{rot}}$$ are the translational, rotational, and quantal parts, respectively, of the molecular partition function.57 The residual contribution to the Helmholtz energy, A', derives solely from the interactions between molecules. In conventional perturbation theory, the first-order term for the Helmholtz energy is given by

$$A_1 = \frac{1}{2} \sum_{\alpha \beta} \rho_{\alpha} \rho_{\beta} \int dr_1 dr_2 \left[ g^\alpha_0(12) \frac{\partial \phi^{\alpha i j}(12)}{\partial \lambda} \right]_{\lambda=0, \alpha_1=\beta_1}$$  

(A-4)

where $$\phi^{\alpha i j}(12)$$ is a pair potential defined so that it becomes the full potential, $$\phi^{\alpha}_{ij}$$, when $$\lambda = 1$$ and the reference fluid potential, $$\phi^{\alpha}_0(12)$$, when $$\lambda = 0$$. In the f expansion, $$\phi^{\alpha i j}(12) = \phi^{\alpha}_0(12) - kT \ln[1 + \lambda f^{\alpha i j}(12)]$$, so that $$[\lambda f^{\alpha i j}(12)/\partial \lambda]_{\lambda=0} = -kT f^{\alpha i j}(12)$$. Here, $$f^{\alpha i j}(12) = \exp(-\phi^{\alpha i j}_0(12)/kT) - 1$$ is the Mayer function for the attractive (perturbation) part of the pair potential, $$\phi^{\alpha i j}_0 = \phi^{\alpha}_0 - \phi^{\alpha}_{ij}$$; Using the results in eq A-4 gives the first-order contribution to the Helmholtz energy as

$$\frac{(A' - A'^{\beta \alpha})}{kT} = \frac{1}{2} \sum_{\alpha \beta} \rho_{\alpha} \rho_{\beta} \int dr_1 dr_2 \left[ g^\beta_0(12) f^{\alpha i j}(12) \right]_{\alpha_1=\beta_1, \alpha_2=\beta_2}$$  

(A-5)

In the usual treatment of the f expansion, the reference potential is taken to be $$\exp(-\phi^{\alpha i j}_0(12)/kT) = \exp(-\phi^{\alpha i j}_0(12)/kT)$$, so that the first-order term of eq A-3 vanishes. Here, we do not wish to make this specific choice of reference system. Equation A-5 neglects higher terms in the series, of relative order $$\rho \int dr_1 dr_2 \left[ g^\beta_0(12) f^{\alpha i j}(12) \right]_{\alpha_1=\beta_1, \alpha_2=\beta_2}$$.

For strongly associating fluids, the attractive potential $$\phi^{\alpha i j}_0(12)$$ will be large and negative for orientations corresponding to the molecular association, so that $$f^{\alpha i j}_0(12)$$ will be large and positive. Consequently, the conventional perturbation theory approach fails for strongly associated liquids.

As a way around this difficulty, Wertheim4 proposed treating monomers, dimers, etc., as distinct entities, so that the total number density of species α can be written as

$$\rho_{\alpha} = \rho_{\alpha \alpha} + \rho_{\alpha \beta}$$  

(A-6)
where \( \rho_{\text{mon}} \) is the density of \( \alpha \) monomers and \( \rho_{\alpha} \) is the density of \( \alpha \) molecules that are present as dimers. For weak association, \( \rho_{\alpha} \approx \rho_{\text{mon}} \) but when the association is strong, \( \rho_{\alpha} \gg \rho_{\text{mon}} \). For strong association, this suggests a renormalization of the splitting of \( \Lambda_{\alpha} \) and of the series for \( A' \), into two parts

\[
A = \langle A^{\text{ideal gas}} \rangle' + \langle A' \rangle
\]  

where \( \langle A^{\text{ideal gas}} \rangle' \) and \( \langle A' \rangle \) are renormalized quantities given by

\[
\frac{\langle A^{\text{ideal gas}} \rangle'}{VkT} = \Sigma \alpha [\rho_{\alpha} \ln(\rho_{\text{mon}} \Lambda_{\alpha}) - \rho_{\text{mon}}]
\]

\[
\frac{\langle A' \rangle - \langle A^{\text{ideal gas}} \rangle'}{VkT} = -\frac{1}{2} \sum_{\alpha} \Sigma_{\rho_{\text{mon}} \rho_{\text{mij}}} \int dr_1 <g_{\alpha i}(12) r_{i j}^2>_{r_1 r_2} (A-9)
\]

A comparison of eqs A-5 and A-9 shows that, in A-9, we are including only the configurational interactions between monomers at density \( \rho_{\text{mon}} \). Thus, eq A-9 neglects higher terms of relative order \( \rho_{\text{mon}} \int dr_1 <r^2>_{r_1 r_2} \), i.e., substantially smaller than the neglected terms in eq A-5 since \( \rho_{\alpha} \gg \rho_{\text{mon}} \) for strong association. We note, however, that the contributions to the free energy from the densities of bonded molecules are not neglected; rather, they are implicitly summed in the expression for \( \langle A^{\text{ideal gas}} \rangle' \) in eq A-8.

To determine \( \rho_{\text{mon}} \), the number density of monomers of species \( \alpha \), we note that, at equilibrium in the canonical ensemble, the Helmholtz energy must be a minimum, i.e., \( \partial \langle A^{\text{ideal gas}} \rangle' / \partial \rho_{\text{mon}} \) at \( \rho_{\text{mon}} = 0 \). Applying this condition to eqs A-7–A-9 gives

\[
\rho_{\alpha} = \rho_{\text{mon}} + \rho_{\text{mon}} \sum_{\rho_{\text{mij}}} \int dr_1 <g_{\alpha i}(12) r_{i j}^2>_{r_1 r_2} (A-10)
\]

Equations A-7–A-10 can be combined to give a simpler form for the free energy. We first note that, for the reference system in which bonding interactions are absent, \( \rho_{\alpha} = \rho_{\text{mon}} \), and

\[
\frac{\langle A^{\text{ideal gas}} \rangle'}{VkT} = \Sigma \alpha [\rho_{\alpha} \ln(\rho_{\text{mon}} \Lambda_{\alpha}) - \rho_{\text{mon}}] (A-11)
\]

and from this and eq A-8 we have

\[
\frac{\langle A^{\text{ideal gas}} \rangle'}{VkT} - \frac{\langle A^{\text{ideal gas}} \rangle'}{VkT} = \Sigma \alpha [\rho_{\alpha} \ln(\rho_{\alpha} \Lambda_{\alpha}) - \rho_{\alpha}]
\]

\[
\frac{A - A^0}{VkT} = \Sigma \rho_{\alpha} [\ln(\rho_{\alpha} - \frac{1}{2} X_{\alpha} - \frac{1}{2})] (A-15)
\]

which is eq 17. Moreover, by dividing eq A-10 by \( \rho_{\alpha} \), we obtain the fraction of \( \alpha \) molecules not bonded as

\[
X_{\alpha} = \frac{1}{1 + \Sigma \rho_{\alpha} \Lambda_{\alpha}} (A-16)
\]

which is eq 18 for the case of a single dimerizing component.

For an ideal gas in which association occurs, it is possible to derive equations analogous to those derived above without making any approximations. These equations are the same as those given above, but with the reference pair correlation function replaced by its low-density limit

\[
g_{\alpha i}(12) = \exp(-\phi_{\alpha i}(12)) (A-17)
\]

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(19) The equilibrium constant defined in this way is different from the ideal-gas equilibrium constant used in the rest of this work. For a detailed explanation, see: Hill, T. L. An Introduction


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