S19.1 INTRODUCTORY COMMENTS[1]

This is a supplement to Elliott and Lira Chapter 19. This material shows the development of the associating van der Waals equaition in more detail, and provides more background on the ESD equation of state.

The Helmholtz contributions to the fugacity coefficient can be expressed as

$$\ln\hat{\varphi}_k = \frac{\partial}{\partial n_k}\left(n\int_0^\rho\left(\frac{Z-1}{\rho}\right)d\rho\right)_{T,\,\underline{V},\,n_{j\neq k}} - \ln Z = \frac{\partial}{\partial n_k}\left(\left(\frac{\underline{A}-\underline{A}^{ig}}{RT}\right)_{TV}\right)_{T,\,\underline{V},\,n_{j\neq k}} - \ln Z \qquad \text{S-19.1}$$

Because we can write $Z - 1 = Z^{rep} + Z^{att} + Z^{chem} + Z^{bond}$ we assign an one-to one correspondence of the Z term with $(A - A^{ig})_{TV} = A^{rep} + A^{att} + A^{chem} + A^{bond}$, and $\ln\hat{\varphi}$ e.g.

$$A^{rep} = \int_0^\rho\left(\frac{Z^{rep}}{\rho}\right)d\rho \;\; ; \;\; A^{att} = \int_0^\rho\left(\frac{Z^{att}}{\rho}\right)d\rho \;\; ; \text{ etc.} \qquad \text{S-19.2}$$

$$\frac{\partial}{\partial n_k}\left(\frac{A^{rep}}{RT}\right)_{T,\,\underline{V},\,n_{j\neq k}} = \ln\hat{\varphi}^{rep} \;\; ; \;\; \frac{\partial}{\partial n_k}\left(\frac{A^{att}}{RT}\right)_{T,\,\underline{V},\,n_{j\neq k}} = \ln\hat{\varphi}^{att} \;\; ; \text{ etc.} \qquad \text{S-19.3}$$

S19.2 PURE SPECIES WITH LINEAR ASSOCIATION

Some species like water and alcohols form extended networks in solutions. The hydrogen bonding reactions usually occur so quickly that they can be assumed to be at equilibrium all the time.[2] It is desirable to investigate the implications of a more rigorous approach for pure species. Although the approach at first appears overwhelming, we always have just enough reaction constraints that the Gibbs phase rule works out the same for an associating component as for a single component.

We begin by describing the premise on which the model is based. We assume that association will occur by formation of linear chains of species. Dimers, trimers, tetramers, etc. will all form in a pure fluid, and the chains that form can be of infinite length. This does not require that long chains exist; the assumption simply does not forbid such behavior. Whether such behavior is found will be determined by the resulting model. Further, it should be recognized that the association that we describe is not static. The associations are truly reversible, and undergo frequent formation/decompositions; the equilibrium distributions simply tell us how many of a certain species will exist at a given instant. As one associated complex decomposes, another forms.

We need to model the chemical equilibria occurring in a given phase. The chemical formation of a dimer would be represented by

$$A + A = A_2 \qquad K_{a2}$$

where the equilibrium constant is K_{a2}. The use of subscript 2 reminds us that this equilibrium constant is for formation of dimer. We will define the true mole fraction as the mole fraction of each specie (monomer, dimer, etc.) that exists in solution. The superficial composition is the overall mole fraction in solution based on all species being monomer, which for a pure fluid is unity. The monomer and dimer appear very often in the derivations that follow so we also use subscripts M and D, respectively. However, the use of numerical subscripts is also preserved for use in generalized formulas, and occasionally both notation schemes are used within a given equation. From the reaction equilibrium constraint,

$$x_D = x_2 = x_M\left(\frac{x_M P\hat{\varphi}_M^2 K_{a2}}{\hat{\varphi}_D P^\circ}\right) = x_M x_M\left(\frac{K_{a2}P\hat{\varphi}_M\hat{\varphi}_1}{\hat{\varphi}_2 P^\circ}\right)$$

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[1] Supplement revised 5/13/17.

[2] An exception is the reaction of formaldehyde with water, c. Hasse and Maurer, *Fluid Phase Equilibria* 64:185 (1991)

where x_M represents the true mole fraction of monomer and x_D represents the true mole fraction of dimer. Other reactions that can occur include

$$A + A_2 = A_3 \qquad K_{a3} \qquad x_3 = \frac{x_M\hat{\varphi}_M x_2\hat{\varphi}_2 P K_{a3}}{\hat{\varphi}_3 P^\circ} = x_M x_2\left(\frac{K_{a3}P\hat{\varphi}_M\hat{\varphi}_2}{\hat{\varphi}_3 P^\circ}\right)$$

$$A + A_3 = A_4 \qquad K_{a4} \qquad x_4 = \frac{x_M\hat{\varphi}_M x_3\hat{\varphi}_3 P K_{a4}}{\hat{\varphi}_4 P^\circ} = x_M x_3\left(\frac{K_{a4}P\hat{\varphi}_M\hat{\varphi}_3}{\hat{\varphi}_4 P^\circ}\right)$$

$$A + A_4 = A_5 \qquad K_{a5} \qquad x_5 = \frac{x_M\hat{\varphi}_M x_4\hat{\varphi}_4 P K_{a5}}{\hat{\varphi}_5 P^\circ} = x_M x_4\left(\frac{K_{a5}P\hat{\varphi}_M\hat{\varphi}_4}{\hat{\varphi}_5 P^\circ}\right)$$

and linear association is assumed to continue to increasing chain sizes.

Let us *assume* that the ratio of $K_{ai}\dfrac{P}{P^\circ}\dfrac{\hat{\varphi}_M\hat{\varphi}_{i-1}}{\hat{\varphi}_i}$ is the same for all *i*. Note that the $\hat{\varphi}_i$ are based on the true mole fractions of oligomers in the mixture not the superficial mole fraction one would obtain by assuming presence of just monomer. Empirical calculations show that this is a reasonable assumption. It basically corresponds to the equilibrium being the same for each step in the oligomerization process. But *it does represent a significant assumption* that may not be accurate for all situations. This ratio appears often in the following derivation so it is helpful to abbreviate it as

$$K_{ai}\frac{P}{P^\circ}\frac{\hat{\varphi}_M\hat{\varphi}_{i-1}}{\hat{\varphi}_i} = (\Delta)q \qquad \text{S-19.4}$$

where Δ and *q* are variables defined below.[3] The point of this assumption is that it facilitates several substantial simplifications through our material balance relations. Including this assumption, Eqn. S- becomes $x_2 = x_M (x_M\Delta\cdot q)$. Substitution of the expression for x_2 into the formula for x_3, yields $x_3 = x_M (x_M\Delta\cdot q)^2$. Substitution continues to higher oligomers resulting in the general formula,

$$x_{i+1} = x_M (x_M\Delta\cdot q)^i \qquad \text{S-19.5}$$

Mass Balances

We can use material balances to obtain two simple relations between the true number of moles in the solution, n_T, and the superficial number of moles that we would expect if there was no association,[4] n_o. Note that n_o is the number of moles one would compute based on dividing the mass of solution by the molecular weight of a monomer as taught in introductory chemistry. For example, in 100cm^3 of water one would estimate

$$n_o = 100\text{ cm}^3 \cdot 1.0\text{ g/cm}^3 / (18\text{ g/mole}) = 5.556\text{ moles}$$

But how many moles of H_2O monomer do you think truly exist in that beaker of water? We will return to this question shortly. Note that each *i*-mer contains "*i*" monomers, such that the contribution to the superficial number of moles is $i \cdot n_i$. Note also that the true mole fractions, x_i, are given by n_i/n_T, but it may not look so simple at first.

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[3] The varibable α in the first edition of *Introductory Chemical Engineering Thermodynamics* is the same as Δ in the second edition. Note that $\Delta = \rho\Delta_{lit}$, where Δ_{lit} is the variable common in literature. The reason for defining this set of variables in terms of two will become clear later when we show that $q = x_M$.

[4] Here we choose to use subscript *o* to clearly distinguish the notation for superficial moles, even though it would be the quantity normally reported from a macroscopic experiment.

$$n_o = \sum_i i \cdot n_i = n_T \sum_i i \cdot x_i \qquad \text{S-19.6}$$

Substituting Eqn. S-19.5

$$n_o = x_m n_T \sum_i i((\Delta) q x_m)^{(i-1)} = x_M\, n_T\, [1 + 2(\Delta \cdot q x_M) + 3(\Delta \cdot q x_M)^2 + 4(\Delta \cdot q x_M)^3 + ...]$$

This series may not appear familiar but it is a common converging series. Referring to series formulas in a math handbook, we find that

$$n_T\, x_M\, [1 + 2(\Delta \cdot q x_M) + 3(\Delta \cdot q x_M)^2 + 4(\Delta \cdot q x_M)^3 + ...] = n_T\, x_M\, [1/(1 - \Delta \cdot q x_M)^2]$$

$$\boxed{\frac{n_o}{n_T} = \frac{x_M}{(1 - (x_M \Delta \cdot q))^2} = \sum_i i \cdot x_i} \qquad \text{S-19.7}$$

Since the mole fractions must sum to unity, we can write a second balance, and using Eqn. S-19.5 for x_i,

$$1 = \sum_i x_i = x_m[1 + (\Delta \cdot q x_m) + (\Delta \cdot q x_m)^2 + (\Delta \cdot q x_m)^3 + \ldots] \qquad \text{S-19.8}$$

and again recognizing the series,

$$1 = x_M\, [1 + (\Delta \cdot q x_M) + (\Delta \cdot q x_M)^2 + (\Delta \cdot q x_M)^3 + \ldots] = x_M\, [1/(1 - \Delta \cdot q x_M)]$$

$$\boxed{x_M = (1 - (x_M \Delta \cdot q))} \qquad \text{S-19.9}$$

Substituting x_M for $(1 - x_M \Delta \cdot q)$ in Eqn. S-19.7 results in,

$$n_o / n_T = x_M / x_M^2 = 1/x_M$$

$$\boxed{\frac{n_T}{n_o} = x_M} \quad \text{(pure chain-forming fluid)} \qquad \text{S-19.10}$$

This equation turns out to be extremely important. It makes clear that the properties of the mixture are closely related to the properties of the monomer. The next step in our derivation is to reconsider Eqn. S-19.4, this time focusing on the left-hand side. The pressure term and its relation to the equation of state are particularly interesting. Before we take this step, let's work through some of the implications of what we have derived thus far. There are a number of insights that can be gained based simply on the material balances.

Interpretations of Molar Densities

At this stage we get to some of the really confusing aspects of associating fluids. For instance, what is density? Mass density is the number of grams divided by the volume. But what about the molar density? We should take the true number of moles and divide by the volume. The true number of moles in our system depends on the degree of association, $n_T = x_M n_o$. We do not know the number of moles until we know x_M. What we do know is that what we call the superficial molar density, i.e., the molar density that we would get if we divided the mass density by the molecular weight of the monomer. *The superficial molar density is the molar density that would be reported from an experiment* where all species are assumed to be monomer, which is the commonly applied measurement technique. To relate the true molar density and the superficial molar density we seek a relationship between x_M, T, and ρ, where ρ is the superficial density. We develop this relation by means of the equation of state. In order to develop the equation of state, we must make additional assumptions about the combining rules.

$$\boxed{\frac{n_o}{\underline{V}} = \rho\text{, superficial molar density, experimentally reported}}$$

$$\frac{n_T}{\underline{V}} = \rho_T\text{, true molar density}$$

$$\boxed{\rho_T = \rho\frac{n_T}{n_o} = \rho x_M} \qquad \text{S-19.11}$$

Combining/Mixing Rules

Before we get into the specifics of developing an equation of state, we can anticipate the need for determining equation of state parameters for the mixture. These relations can be developed before the actual equation of state, and are independent of the actual equation of state. Heidemann and Prausnitz[5] show that some very simple relations result when simplifying assumptions are made on the attractive and size parameters for conventional equation of state mixing rules. These assumptions and simplifications are presented here.

Size parameter, b. To develop an equation of state, we must make approximations about the properties of the associating species. For instance, we can *assume* that the volume of a dimer is twice that of the monomer. The volume of the trimer would be three times the volume of a monomer. In terms of the molecular size parameter

$$b_i = i \cdot b_M \qquad \text{S-19.12}$$

Inserting this into the normal mixing rule for a mixture of monomers, dimers, trimers, etc., and incorporating Eqn. S-19.7,

$$b = \sum_i x_i b_i = b_M \sum_i i \cdot x_i$$

$$\boxed{b = b_M\frac{n_o}{n_T} = \frac{b_M}{x_M}} \qquad \text{S-19.13}$$

Packing fraction, $b_M\rho$. The representation of density in an equation of state can always be rearranged into the dimensionless packing fraction. Can you anticipate the special property exhibited by the packing fraction? Let's see what happens when we combine Eqn. S-19.13 with Eqn. S-19.11.

$$\boxed{b\rho_T = \left(\frac{b_M}{x_M}\right)\rho x_M = b_M\rho} \qquad \text{S-19.14}$$

Note that $b_M\rho$ is the packing fraction we would have computed if we neglected association entirely. Thus we are free to apply either form interchangeably. The packing fraction is entirely independent of the extent of association. This result might seem obvious if you remember the definition of packing fraction. It is the volume occupied by molecules divided by the total volume. By setting the volume of an *i*-mer to be *i* times the volume of the monomer, we are assuming that there is no overlap caused by association. So the volumes of

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[5] Heidemann, R. A. and Prausnitz, J. M., *Proc. Nat. Acad. Sci.,* 73:1773(1976).

the molecules are the same before or after association. When you look at it this way, it should be no surprise that the packing fraction is constant.

Attractive parameter, *a*. If the molecular interactions are pairwise additive, then it is reasonable to assume that the interaction energy for a pair of dimers should be four times that of a monomer-monomer interaction, and the trimer should be nine times, as shown in Fig. S-19.6. Therefore, $a_D = 4a_M$, $a_3 = 9a_M$, $a_4 = 16a_M$ etc. This means $a_i = i^2 a_M$, or

$$\sqrt{a_i} = i \cdot \sqrt{a_M} \qquad \text{S-19.15}$$

The normal combining rule is $a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$,where it is reasonable to set $k_{ij} = 0$ for all ij. This means,

$$a_{ij} = \sqrt{a_i a_j} = \sqrt{i^2 a_M j^2 a_M} = i \cdot j \cdot a_M \qquad \text{S-19.16}$$

In addition, when $k_{ij} = 0$ for all ij, the normal mixing rule, $a = \sum_i \sum_j x_i x_j a_{ij}$, becomes $a = \left(\sum_i x_i \sqrt{a_i}\right)^2$, which by substituting Eqn. S-19.15 becomes $a = a_M\left(\sum_i i \cdot x_i\right)^2$, which by substituting Eqn. S-19.7 becomes,

$$\boxed{a = a_M\left(\frac{n_o}{n_T}\right)^2 = \frac{a_M}{x_M^2}} \qquad \text{S-19.17}$$

S19.3 A VAN DER WAALS H-BONDING MODEL

For purposes of illustration, we return to the van der Waals equation, as usual when considering a new application. The principal modification is to write out explicitly what is meant by terms like density and n_T. The pressure will be determined by the true number of moles and the true density. We introduce the true compressibility factor, $Z_T = P\,V_T / RT$.

$$Z_T = \frac{P\underline{V}}{n_T RT} = 1 + \frac{b\rho_T}{(1 - b\rho_T)} - \frac{a\rho_T}{RT} \qquad \text{S-19.18}$$

where a and b are the mixture parameters given by the mixing rules above. We can obtain the superficial compressibility factor if we multiply both sides of Eqn. S-19.18 by n_T / n_o. However, since $n_T / n_o = x_M$, we have

$$Z = \frac{P\underline{V}}{n_o RT} = x_M + \frac{x_M b\rho_T}{(1 - b\rho_T)} - \frac{a\rho_T x_M}{RT} = \frac{x_M}{(1 - b\rho_T)} - \frac{a\rho_T x_M}{RT} \qquad \text{S-19.19}$$

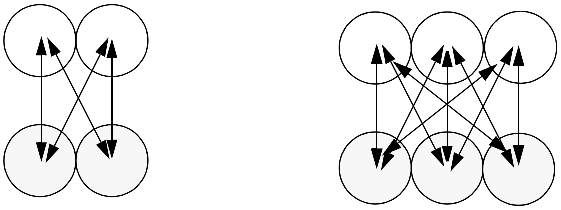

Figure S-19.6 *Illustration that $a_{DD} = 4\,a_{MM}$ and $a_{33} = 9\,a_{MM}$ are reasonable by adding the number of pair interactions.*

Thus the equation of state differs from the original van der Waals only in the incorporation of the factor x_M. However, let us investigate how the right-hand side can be written in terms of a_M, b_M, and ρ_T. Recalling the simplification that occurred for the packing fraction in the repulsive term, a similar simplification occurs for the attractive term using Eqn. S-19.11 and Eqn. S-19.17 becomes $a\rho_T x_M = \left(\frac{a_M}{x_M^2}\right)(\rho x_M)x_M = a_M\rho$. The equation of state then becomes

$$\boxed{Z = \frac{P\underline{V}}{n_o RT} = \frac{x_M}{(1-b_M\rho)} - \frac{a_M\rho}{RT} = 1 + \frac{b_M\rho}{(1-b_M\rho)} - \frac{a_M\rho}{RT} - \frac{(1-x_M)}{(1-b_M\rho)}} \qquad \text{S-19.20}$$

In this form we may define contributions to the compressibility factor such that $Z \equiv 1 + Z^{rep} + Z^{att} + Z^{chem}$ where there is a one-to-one correspondence with terms of the right-most expression in Eqn. S-19.20. Z^{rep} and Z^{att} are exactly as we have used them before. We may clearly identify Z^{chem}.

$$\boxed{Z^{chem} = \frac{-(1-x_M)}{(1-b_M\rho)}} \qquad \text{S-19.21}$$

Note that in a fluid that does not associate, $x_M = 1$, so the standard van der Waals equation is recovered.

Solving the Equation of State for Superficial Density

If we know the size and attractive parameters for the model, and the degree of association, we can solve the equation of state. To put the equation of state in a nondimensional form, we define $B = \frac{b_M P}{RT}$, and $A = \frac{a_M P}{(RT)^2}$. Multiplying Eqn. 15.48 by $b_M\rho$,

$$B = \frac{x_M(b_M\rho)}{(1-b_M\rho)} - \frac{A}{B}(b_M\rho)^2 \qquad \text{S-19.22}$$

❗ Our objective is to solve this equation, but first we need to determine x_M.

Rearrangement yields[6]

$$\boxed{\frac{A}{B}(b_M\rho)^3 - \frac{A}{B}(b_M\rho)^2 + (x_M + B)(b_M\rho) - B = 0} \qquad \text{S-19.23}$$

If we knew x_M (or $\Delta\cdot q$ in Eqn. S-19.9) in terms of temperature and density, then solving this problem would simplify to solving for the pressure of a mixture of known composition with known mixing rules. In other words, solving for Z is entirely analogous to our previous applications of equations of state. We would simply have the intermediate step of computing x_M before computing Z. It sounds more complicated obviously, but with a computer, one would hardly notice the difference in computational speed. Let's derive an approximate relationship for x_M. We now explore and develop the procedure to determine x_M by looking at the functionality of $\Delta\cdot q$.

Fugacity Coefficient for an Associating Species

For any practical applications, we need the superficial fugacity, which can be found quite directly using Eqn. S-19.14; if we calculate the fugacity of the monomer, this will also be the superficial fugacity. We have used this procedure already in Example 15.4 on page 591, but now we no longer need to assume the true species form an ideal solution. For a pure, associating species we start by adapting of Eqn. 15.33 by writing the equation in terms of the true mole fractions, and true densities,

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[6] An alternate form of the same equation appears later as Eqn. 15.65.

$$\ln\hat{\varphi}_i = -\ln(1-b_M\rho) + \frac{b_i\rho_T}{1-b_M\rho} - \frac{2\rho_T}{RT}\sum_j x_j a_{ij} - \ln Z_T \qquad \text{S-19.24}$$

Fugacity formula for a true specie in a pure associating van der Waals fluid.

where we have already substituted $b\rho_T = b_M\rho$. Now, for the monomer,

$$\ln\hat{\varphi}_M = -\ln(1-b_M\rho) + \frac{b_M\rho_T}{1-b_M\rho} - \frac{2\rho_T a_M}{RT}\sum_j jx_j - \ln Z_T \qquad \text{S-19.25}$$

Now, recognize $Z_T = P\underline{V}/n_TRT = P\underline{V}/n_oRT\cdot(n_o/n_T) = Z/x_M$. Also, using Eqn. S-19.11

$$\ln\hat{\varphi}_M = -\ln(1-b_M\rho) + \frac{b_M\rho x_M}{1-b_M\rho} - \frac{2\rho a_M}{RT} - \ln Z + \ln x_M \qquad \text{S-19.26}$$

Now, applying Eqn. S-19.14, and rearranging the repulsive term involving x_M,

$$\ln\varphi = \ln x_M\hat{\varphi}_M = -\ln(1-b_M\rho) + \frac{b_M\rho x_M}{1-b_M\rho} - \frac{2\rho a_M}{RT} - \ln Z + 2\ln x_M \qquad \text{S-19.27}$$

Superficial fugacity coefficient for pure associating van der Waals fluid.

Determination of x_M for van der Waals' Equation

Returning to the left-hand side of Eqn. S-19.4, we see that the function $\Delta\cdot q$ involves the ratio $\frac{\hat{\varphi}_M\hat{\varphi}_{i-1}}{\hat{\varphi}_i}$. To evaluate this expression, we must next solve for the fugacity coefficient of a component in a mixture in accordance with our new EOS. Then we can substitute the expression back into the reaction equilibrium equation and solve for x_M. As a specific example of the formula, consider the conversion of monomer to dimer, the first step in the oligomerization, represented by $\frac{\hat{\varphi}_M\hat{\varphi}_M}{\hat{\varphi}_D}$.

Writing the true fugacity coefficients in terms of logarithms,

$$\begin{aligned} 2\ln\hat{\varphi}_M - \ln\hat{\varphi}_D = {} & 2\left[-\ln(1-b_M\rho) + \frac{b_M\rho_T}{1-b_M\rho} - \frac{2\rho_T}{RT}\sum_j x_j a_{Mj} - \ln Z_T\right] \\ & -\left[-\ln(1-b_M\rho) + \frac{b_D\rho_T}{1-b_M\rho} - \frac{2\rho_T}{RT}\sum_j x_j a_{Dj} - \ln Z_T\right] \end{aligned} \qquad \text{S-19.28}$$

The repulsive term is the important term in determining the fugacity coefficient ratios.

Recall that $b_D = 2\,b_M$ by Eqn. S-19.12 and $a_{Dj} = 2ja_M$, and $a_{Mj} = ja_M$ by Eqn. S-19.16. Therefore

$$2\ln\hat{\varphi}_M - \ln\hat{\varphi}_D = \ln\left[\frac{n_TRT}{P\underline{V}(1-b_M\rho)}\right] \qquad \text{S-19.29}$$

$$\frac{\hat{\varphi}_M\hat{\varphi}_M}{\hat{\varphi}_D} = \frac{n_TRT}{P\underline{V}(1-b_M\rho)} \qquad \text{S-19.30}$$

An analogous derivation for other oligomers gives

$$\frac{\hat{\varphi}_M\hat{\varphi}_{i-1}}{\hat{\varphi}_i} = \frac{n_T RT}{P\underline{V}(1-b_M\rho)} \qquad \text{S-19.31}$$

Since this expression of fugacity coefficients is independent of *i*, referring back to Eqn. S-19.4, K_a is the same for all species.

$$\text{Finally } \Delta\cdot q = \frac{\hat{\varphi}_M\hat{\varphi}_{i-1}}{\hat{\varphi}_i}\frac{PK_a}{P°} = \frac{n_T RT}{P\underline{V}(1-b_M\rho)}\frac{PK_a}{P°} = \frac{RTK_a}{(1-b_M\rho)P°\underline{V}}\frac{n_o}{n_o}\frac{n_T}{n_o} = \frac{RTK_a\rho}{(1-b_M\rho)P°}x_M \qquad \text{S-19.32}$$

Now we split our definition of $\Delta\cdot q$, by defining

$$\Delta = \frac{RTK_a\rho}{(1-b_M\rho)P°} \qquad \text{and} \qquad q = x_M \qquad \text{S-19.33}$$

Δ is a function of *T*, ρ. $\Delta\cdot q$ can now be substituted back into Eqn. S-19.9, while recognizing that $q = x_M$.

$$x_M = 1 - \Delta x_M^2$$

Solving the quadratic for the only reasonable root gives

$$\boxed{x_M = \frac{-1+\sqrt{1+4\Delta}}{2\Delta}} \text{ (pure chain-forming fluid)} \qquad \text{S-19.34}$$

In principle, our problem is now solved. Note that the only difference between Eqn. S-19.20 and the original van der Waals equation is the factor of x_M in the repulsive term, and we now have an equation to determine x_M at a given temperature and density. Two new parameters must be introduced, however, to characterize Δ and its dependency on temperature. Since Δ is closely related to K_a, we will need to consider the van't Hoff relation to characterize the dependence of K_a on *T*. The temperature dependence of the hydrogen bonding may be given by the form of the van't Hoff equation, which is simplified to be

$$\boxed{K_a = \frac{(K_a)_c}{T_r}\exp\left[H\left(1-\frac{1}{T_r}\right)\right]} \qquad \text{S-19.35}$$

where $(K_a)_c$ is the value of the equilibrium constant at the critical point, and the constant *H* is found by fitting the vapor pressure curve. The explanation for this form of the equation is given in Section S-19.4 but it is easy to see that the value approaches zero at infinite temperature and is equal to the critical value at the critical temperature. Substitution into Eqn. S-19.33 gives

$$\boxed{\Delta = \left(\frac{RT_c(K_a)_c}{P°b_M}\right)\left(\frac{b_M\rho}{(1-b_M\rho)}\right)\exp\left[H\left(1-\frac{1}{T_r}\right)\right] = K_a'\left(\frac{b_M\rho}{(1-b_M\rho)}\right)\exp\left[H\left(1-\frac{1}{T_r}\right)\right]} \qquad \text{S-19.36}$$

$K_a' = RT_cK_{ac}/(P°\, b_M)$ is the dimensionless form of $(K_a)_c$.

Solving the Equation of State for Density

We can see that Eqn. S-19.23 is not truly a cubic in density because x_M depends on density. Also, its functional dependence is nonlinear, which makes implementation more difficult. However, Δ is a monotonic function of density, and successive substitution of density has been found to quickly yield converged values for density. The algorithm is given in Fig. S-19.7.

Fitting the Constants in the Equation of State

So far, we have assumed that the constants needed for a fluid are available. However, the associating fluid model must be used to obtain the parameter values. To obtain approximate hydrogen bonding parameters,[7] we can use the same approach applied for nonassociating systems. Rearranging Eqn. S-19.23 in terms of the compressibility factor.

$$Z^3 - (x_M + B)Z^2 + AZ - AB = 0 \tag{S-19.37}$$

Writing out $(Z - Z_c)^3$, which equals 0 at the calculated critical point:

$$Z^3 - (3Z_c)Z^2 + (3Z_c^2)Z - (Z_c^3) = 0 \tag{S-19.38}$$

Comparing term-by-term with the previous equation, we find at the critical point:

$$x_M + B_c = 3Z_c^{EOS} \tag{S-19.39}$$

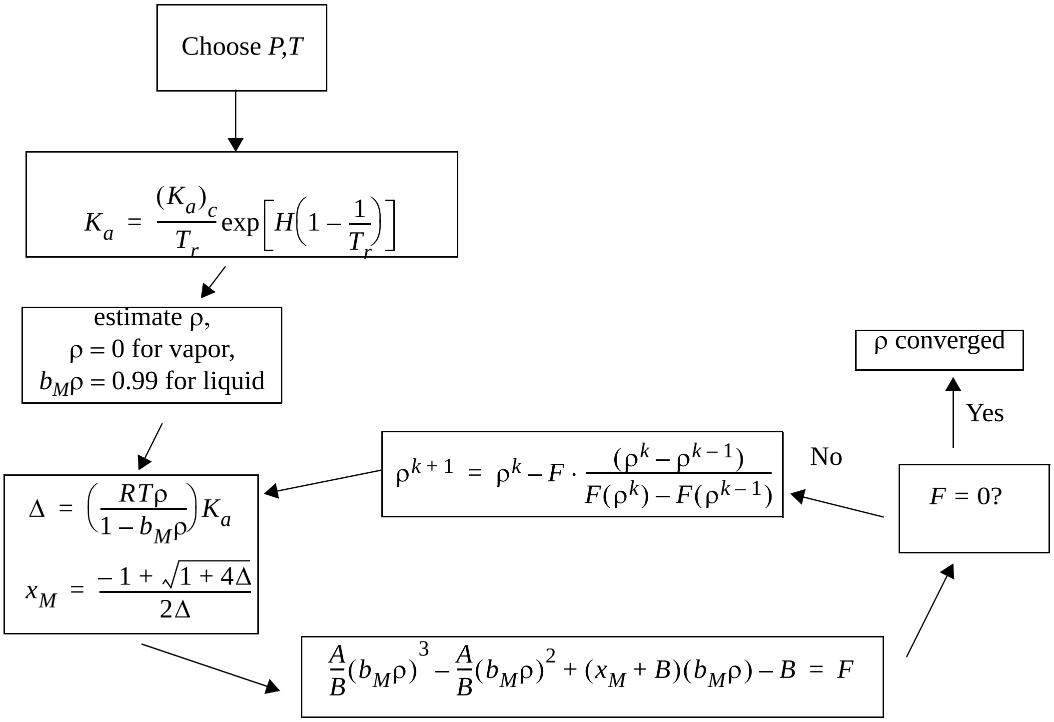

Figure S-19.7 *Flowsheet for calculating density by the van der Waals pure associating chain fluid model.*

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[7] Note: Rigorously matching the critical point requires recognizing that x_M is a function of density, so the above method is only approximate in terms of matching the critical point. On the other hand, the characterization obtained in this way provides reasonable accuracy for an introduction. Problem 19.13 describes the route to rigorously matching the critical point.

$$A_c = 3(Z_c^{EOS})^2 \qquad \text{S-19.40}$$

$$A_cB_c = (Z_c^{EOS})^3 \qquad \text{S-19.41}$$

where the superscript *EOS* has been added to explicitly show that this is the value predicted by the equation of state. These three equations differ from the original van der Waals equation only by the x_M appearing in Eqn. S-19.39. Plugging S-19.40 into S-19.41, we find

$$B_c = \frac{Z_c^{EOS}}{3} \qquad \text{S-19.42}$$

Using this result in Eqn. S-19.39,

$$Z_c^{EOS} = \frac{3}{8}(x_M)_c \qquad \text{S-19.43}$$

where x_M would have a value of unity in a nonassociating system. Plugging this into S-19.42, we find

$$\boxed{b_M = \frac{RT_c}{8P_c}(x_M)_c} \qquad \text{S-19.44}$$

and into S-19.40,

$$\boxed{a_M = \frac{27}{64}\frac{(RT_c)^2}{P_c}(x_M)_c^2} \qquad \text{S-19.45}$$

Finding x_M from Z_c

Experimental values of Z_c cannot be used directly in Eqn. S-19.43, because we know that the value of Z_c = 0.375 predicted by the van der Waals equation is significantly in error for nonassociating species. For argon, krypton, and xenon, Z_c is approximately 0.29. Therefore, this equation is systematically in error even for spherical nonassociating fluids. To account for the systematic error of the equation, one can assume the form of Eqn. S-19.43 is correct, but the coefficient is incorrect; thus, we could preserve the proportionality $Z_c \propto (x_M)_c$. This implies that the ratio of the experimental Z_c to Z_c^{homo}, the critical compressibility factor of a nonassociating homomorph[8] gives $(x_M)_c$,

$$\boxed{\frac{Z_c^{exp}}{Z_c^{homo}} = (x_M)_c} \qquad \text{S-19.46}$$

where several common species and homomophs are listed in Table S-19.1.

From $(x_M)_c$ we can use Eqns. S-19.44 and S-19.45 to determine a_M and b_M. We also can use Eqn. S-19.9, and noting that $q = x_M$,

$$\Delta_c = \left(\frac{1-x_M}{qx_M}\right)_c = \left(\frac{1-x_M}{x_M^2}\right)_c \qquad \text{S-19.47}$$

since

---

[8] Homomorph means having the same shape. In this context it refers to a hydrocarbon having the same size and branching (e.g., isobutane is a homomorph of isopropanol).

$$\Delta_c = \left(\frac{RT\rho}{1-b_M\rho}\right)_c \frac{(K_a)_c}{P^\circ} = \left(\frac{b_M\rho}{1-b_M\rho}\right)\left(\frac{RT_cK_{ac}}{P^\circ b_M}\right) = \left(\frac{b_M\rho}{1-b_M\rho}\right)K_a' \qquad \text{S-19.48}$$

where $K_a' = RT_cK_{ac}/(P^\circ\, b)$. Noting from Eqn. S-19.42 that $b_M\rho_c = B_c/Z_c = {}^1/_3$ for the van der Waals EOS gives:

$$2\Delta_c = K_a' = 2\left(\frac{1-x_{Mc}}{x_{Mc}^2}\right) \qquad \text{S-19.49}$$

Table 19.1 *Homomorphs for several associating compounds, and* $(x_M)_c$ *for the associating van der Waals model.*

Specie	Z_c	**Homomorph**	Z_c^{homo}	$(x_M)_c$
ethanol	0.248	propane	0.281	0.883
methanol	0.224	ethane	0.284	0.789
water	0.233	methane	0.288	0.809

This allows K_a' to be determined. The temperature dependence of the hydrogen bonding is given by the van’t Hoff equation with $\Delta C_P = -R$, which is simplified to give Eqn. S-19.35 above. The last constant, H in Eqn. S-19.35, is found by fitting the vapor pressure curve. The justification for the form of the equation is given in Section S-19.4. nonpolar fluids tend to have a slight downward curvature to the plot of ln P^{sat} versus $1/T$. Associating fluids actually have a little less curvature, and by fitting the vapor pressure curve, a parameter value for H can be obtained.

Helmholtz Energy and the Fugacity Coefficient for van der Waals

There is a connection between Helmholtz energy and the fugacity coefficient that we introduced in Eqns. 19.1-19.3. We will use these relations to identify the chemical contribution to the Helmholtz energy.

To see the desired relation for the association term, we need to rearrange Eqn. S-19.27 to identify all the terms except association, and thus identify the relationship between the Helmholtz departure and the association. Adding and subtracting x_M in the form $x_M(1 - b_M\rho)/(1 - b_M\rho) - x_M$,

$$\begin{aligned}\ln\varphi &= -\ln(1-b_M\rho) + \frac{b_M\rho x_M}{1-b_M\rho} + x_M\frac{(1-b_M\rho)}{(1-b_M\rho)} - \frac{2\rho a_M}{RT} - \ln Z + - x_M + 2\ln x_M \qquad \text{S-19.50}\\ &= -\ln(1-b_M\rho) + \frac{x_M}{1-b_M\rho} - \frac{2\rho a_M}{RT} - \ln Z - x_M + 2\ln x_M\end{aligned}$$

Adding and subtracting one, in the form $1 - (1 - b_M\rho)/(1 - b_M\rho)$,

$$\begin{aligned}\ln\varphi &= -\ln(1-b_M\rho) + \frac{x_M}{1-b_M\rho} - \frac{(1-b_M\rho)}{(1-b_M\rho)} - \frac{2\rho a_M}{RT} - \ln Z + 1 - x_M + 2\ln x_M \qquad \text{S-19.51}\\ &= -\ln(1-b_M\rho) - \frac{\rho a_M}{RT} + \frac{b_M\rho}{(1-b_M\rho)} - \frac{\rho a_M}{RT} - \frac{1-x_M}{1-b_M\rho} + 1 - x_M + 2\ln x_M - \ln Z\end{aligned}$$

Then matching the terms one-to-one with their origin:

$$\ln\varphi = \frac{\underline{A}^{rep}}{n_oRT} + \frac{\underline{A}^{att}}{n_oRT} + Z^{rep} + Z^{att} + Z^{chem} + 1 - x_M + 2\ln x_M - \ln Z$$

Therefore, the unmatched terms are the contribution to Helmholtz departure due to association,

The contribution of hydrogen bonding to the residual Helmholtz energy.

$$\boxed{\frac{\underline{A}^{chem}}{n_o RT} = 1 - x_M + 2\ln x_M} \qquad \text{S-19.52}$$

This derivation has been tedious, but the extension to mixtures and the adaptation to other equations of state should now be straightforward.

Applications to Pure Fluids

Table S-19.2 summarizes results of Eqns. 15.72–15.76 for three compounds. Note that 0.300/0.375 = 0.233/0.291 maintaining the ratio of Eqn. 15.74. All that remains is to specify a value for the parameter H in Eqn. 15.63. One reasonable approach would be to set the energy of hydrogen bonding equal to a typical value like 20 kJ/mole. For water, this would result in $H = 3.716$. Other approaches to characterizing H are discussed in the homework problems. Given the values for these parameters, you should be able to implement the algorithm of Fig. 15.7 with no difficulty.

S19.4 THE ESD EQUATION FOR ASSOCIATING FLUIDS

The van der Waals model has served well to introduce the methods used in developing a model for associating fluids, however, it has several shortcomings when considering quantitative modeling. One alternative would be to adapt the Peng-Robinson equation. This option is developed as a homework problem. That approach can provide improved accuracy for vapor-liquid equilibria, but a consistent extension to liquid-liquid equilibria in systems like hydrocarbons with water has been difficult to develop.[9] Part of the problem with the Peng-Robinson equation is the inaccurate form of the van der Waals repulsive term. Heidemann and Prausnitz[10] corrected this shortcoming in their analysis of associating fluids, but their analysis applied only to pure fluids. A number of other authors have pursued adaptations which correct the repulsive term or address consistent models for vapor-liquid-liquid equilibria, but we will limit our discussion to two: the ESD equation,[11] and the SAFT equation.[12] In this section we introduce the ESD equation. The ESD equation has the following features:

Table 19.2 *Role of association in depressing Z_c according to the vdW-HB EOS*

Component	$K_a' = K_{ac}RT_c/(bP°)$	x_{Mc}	a/bRT_c	Z_c **(calculated)**	Z_c **(experiment)**
Argon	0	1.000	3.375	0.375	0.291
Water	0.620	0.801	2.703	0.300	0.233
Acetonitrile	1.843	0.632	2.134	0.237	0.184

ESD.exe

1. The equation of state is cubic, which permits us to retain the principles we have developed for solving and applying the equation of state.
2. The equation of state explicitly represents the effect of shape for nonpolar molecules. This means that extension of the equation to polymers is straightforward. This additional flexibility requires an additional characteristic parameter; however the shape parameter has been correlated in terms of the acentric factor for nonassociating fluids, much like the parameter κ in the Peng-Robinson equation.

---

[9] Raymond, M. B. Ph.D. Thesis, University of Akron, 1998.

[10] Heidemann, R. A. and Prausnitz, J. M. *Proc Nat Acad Sci*, 73:17773 (1976).

[11] Elliott, J. R., Suresh, S. J., Donohue, M. D. *Ind. Eng. Chem. Res.*, 29:1476 (1990).

[12] Chapman, W. G., Jackson, G., Gubbins, K. E., Radosz, M., *Ind. Eng. Chem. Res.* 29:1709 (1990).

3. The equation of state has been developed by modeling computer simulations, and thus should capture the essential physics of size, shape, and hydrogen bonding.

Noting the detailed development for the van der Waals equation provided above, we will rapidly move through the adaptation to the ESD equation. All of the steps are essentially equivalent to those for the van der Waals equation. The one additional complication is that the shape parameter and H cannot be determined independently for an associating fluid. This is because the experimental acentric factor is a measure of both shape and hydrogen bonding for associating systems,[13] and thus the acentric factor is insufficient for determining the shape parameter. Other features include improvement of the assumption of a temperature-independent value for H in the van't Hoff Eqn. S-19.35, which ignores the change in heat capacity due to temperature-dependent association, and the possibility of branching and its impact on the assumptions about $q\Delta$ and a_{ij}.

The equation proposed by Elliott et al. (1990) is:

$$\frac{PV}{RT} = 1 + \frac{4\langle c\eta\rangle}{1-1.9\eta} - \frac{9.5\langle qY\eta\rangle}{1+1.7745\langle Y\eta\rangle} \tag{S-19.53}$$

where

$$b = \sum_i x_i b_i \text{, therefore, } \eta = b\rho = \left(\sum_i x_i b_i\right)\rho$$

$c = \sum_i x_i c_i$, a "shape factor" which represents the effect of nonsphericity on the repulsive term.

$q = 1 + 1.90476(c - 1) = q = \sum_i x_i q_i$ is a shape factor which represents the effect of nonsphericity on the attractive term.

$$<c\eta> = c \cdot b \cdot \rho = \left(\sum_i x_i c_i\right) \cdot \left(\sum_j x_j b_j\right) \cdot \rho = \rho \sum_i \sum_j (x_i x_j (b_i c_j + b_j c_i))/2$$

$$Y_{ij} = \exp(\varepsilon_{ij}/kT) - 1.0617$$

$$<qY\eta> = \rho<qYb> = \rho \sum_i \sum_j (x_i x_j Y_{ij} (b_i q_j + b_j q_i))/2$$

$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij})$ the energy of disperse attraction (equivalent to well-depth of a square-well potential). As before k_{ij} is zero for monomer-oligomer interactions.

$$<Y\eta> = \rho<Yb> = \rho \sum_i x_i b_i Y_i$$

The most important modification over the van der Waals equation is the inclusion of the shape factor, c, in the repulsive term of the EOS. Elliott et al. illustrated that this form for the repulsive term significantly improves agreement with molecular simulation data for hard spheres[14] and chains[15] relative to the repulsive term assumed in the van der Waals or Peng-Robinson equations, as shown in Fig. 19.8. Note that the van der Waals and Peng-Robinson estimates are the same regardless of chain length whereas the ESD equation sets

---

[13] Recall that the acentric factor is a measure of the slope of the vapor pressure line. For nonpolar substances this is determined by shape. For associating species, the association is also a function of temperature, so it also changes along the vapor pressure curve, also affecting the slope.

[14] Erpenpeck, J. J., Wood, W. W., *J.Stat. Phys.* 35:321 (1984).

[15] Dickman, R., Hall, C. K., *J.Chem.Phys.* 89:3168 (1988)

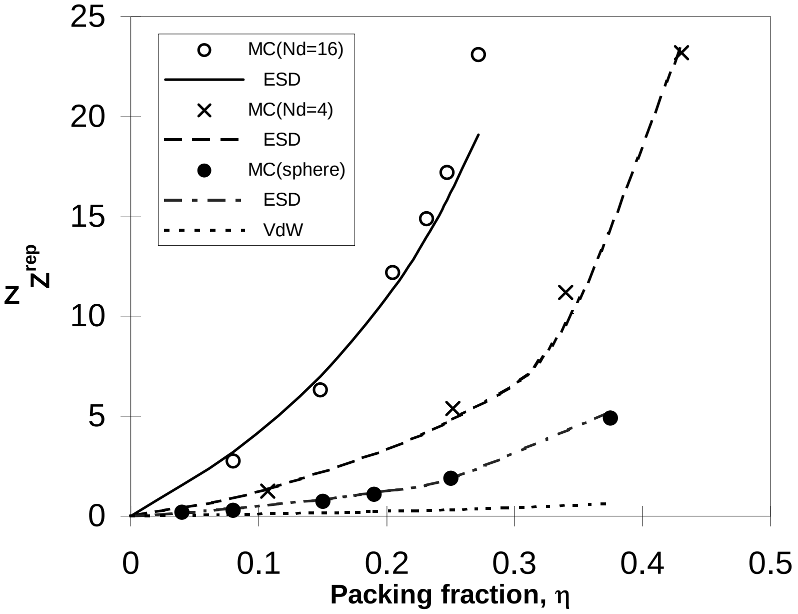

Figure S-19.8 *Comparison of molecular simulations, the van der Waals equation, and the ESD equation of state for* Z^{rep}. *Nd is the number of spheres in a chain.*

$c = 1 + (N_d - 1)/2$, where N_d is the chain length. In practice, the shape factor is actually correlated with the acentric factor obtained from experimental data. The attractive term of the ESD equation was derived from similar comparisons to square-well spheres.[16] Note that the effect of nonsphericity is stronger for the attractive term than the repulsive term by the factor of 1.90476.

Fugacity Coefficient

The fugacity coefficient is evaluated using Eqn. S-19.1. The first step is to derive the Helmholtz departure,

$$\frac{(\underline{A}-\underline{A}^{ig})_{TV}}{RT} = n\int_0^\rho \frac{4cb}{1-1.9b\rho}d\rho - n\int_0^\rho \frac{9.5\langle qYb\rangle}{1+1.7745\langle Yb\rangle\rho}d\rho \qquad \text{S-19.54}$$

$$= \frac{-4nc}{1.9}\ln(1-1.9\eta) - \frac{9.5n\langle qYb\rangle}{1.7745\langle Yb\rangle}\ln(1+1.7745\langle Y\eta\rangle)$$

Differentiating,

$$\left(\frac{\partial\left(\frac{\underline{A}-\underline{A}^{ig}}{RT}\right)_{TV}}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} = \frac{-4}{1.9}\ln(1-1.9\eta)\left(\frac{\partial(nc)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} + \frac{4nc}{(1-1.9\eta)}\left(\frac{\partial\eta}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} \qquad \text{S-19.55}$$

$$-\frac{9.5}{1.7745}\ln(1+1.7745\langle Y\eta\rangle)\left(\frac{\partial\left(\frac{n\langle qYb\rangle}{\langle Yb\rangle}\right)}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}}$$

$$-\frac{9.5n\langle qYb\rangle}{\langle Yb\rangle(1+1.7745\langle Y\eta\rangle)}\left(\frac{\partial\langle Y\eta\rangle}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}}$$

---

16. Sandler, S. I., Lee, K. H., *Fluid Phase Equil.* 30:135 (1986)

Determining the intermediate derivatives,

$$
\begin{aligned}
&\left(\frac{\partial(nc)}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = c_i\\
&\left(\frac{\partial\eta}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = \left(\frac{\partial(bn\underline{\rho})}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = b_i\underline{\rho}\\
&\left(\frac{\partial\langle Y\eta\rangle}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = b_iY_i\underline{\rho}
\end{aligned}
\qquad \text{S-19.56}
$$

$$
\begin{aligned}
&\left(\frac{\partial\left(\frac{n\langle qYb\rangle}{\langle Yb\rangle}\right)}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = \left(\frac{\partial\left(\frac{n^2\langle qYb\rangle}{n\langle Yb\rangle}\right)}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} = \\
&\frac{1}{n\langle Yb\rangle}\left(\frac{\partial(n^2\langle qYb\rangle)}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}} - \frac{n^2\langle qYb\rangle}{n^2\langle Yb\rangle^2}\left(\frac{\partial(n\langle Yb\rangle)}{\partial n_i}\right)_{T,\,\underline{V},\,n_{j\neq i}}
\end{aligned}
\qquad \text{S-19.57}
$$

The first of the derivatives in the right-most expression of Eqn. S-19.57 is of the form of Eqn. S-19.57, and the second is of the form of Eqn. 15.23, and they can be written by inspection. Combining,

$$
\begin{aligned}
\ln\hat{\varphi}_i = {}& -\frac{4}{1.9}c_i\ln(1-1.9\eta) + \frac{4cb_i\rho}{1-1.9\eta}\\
& -\frac{9.5}{1.7745}\frac{\ln(1+1.7745\langle Y\eta\rangle)}{\langle Yb\rangle}\left(\sum_j x_jY_{ij}(b_iq_j+b_jq_i) - \frac{\langle qYb\rangle}{\langle Yb\rangle}Y_ib_i\right)\\
& -\frac{9.5\langle qYb\rangle}{\langle Yb\rangle}\frac{Y_ib_i\rho}{1+1.7745\langle Y\eta\rangle} - \ln Z
\end{aligned}
\qquad \text{S-19.58}
$$

❗ Fugacity coefficient for a component in a nonassociating mixture.

For a pure fluid, this simplifies to

$$
\begin{aligned}
\ln\varphi = {}& -\frac{4}{1.9}c\ln(1-1.9\eta) + \frac{4cb\rho}{1-1.9\eta}\\
& -\frac{9.5q}{1.7745}\ln(1+1.7745\langle Y\eta\rangle) - \frac{9.5qYb\rho}{1+1.7745\langle Y\eta\rangle} - \ln Z
\end{aligned}
\qquad \text{S-19.59}
$$

❗ Fugacity coefficient for a pure, nonassociating fluid.

Extension to Associating Fluids

The extension to associating mixtures is analogous to the discussion above for the van der Waals equation; we start with the equation for nonassociating fluids, and adapt it by multiplying by x_M, and writing the density in terms of true density.

$$
Z_T = x_M + \frac{4x_M\langle c\eta_T\rangle}{1-1.9\eta} - \frac{9.5x_M\langle qY\eta_T\rangle}{1+1.7745\langle Y\eta_T\rangle} \qquad \text{S-19.60}
$$

where only the denominator of the second term is clearly unaffected; the other terms will be evaluated. We apply the same mixing rules for the size parameter, $b_i = i \cdot b_M$; so, like the van der Waals equation, $b = b_M/x_M$, and $b\rho_T = b_M\rho$.

For linear associating species, we assume[17]

$$c_i = c_M + (i-1)\cdot(c_M - 0.475) = i(c_M - 0.475) + 0.475 \qquad \text{S-19.61}$$

For the repulsive term in the EOS, the value of $\langle c\eta_T \rangle = \left(\sum_i x_i c_i\right) \cdot \left(\sum_j x_j b_j\right) \cdot \rho_T$. Therefore,

$$4\langle c\eta_T \rangle = 4\left(\sum_i x_i c_i\right) \cdot \left(\sum_j x_j b_j\right) \cdot \rho_T = 4\left(\sum_i x_i c_i\right)\eta_P$$

However,

$$\sum_i x_i c_i = \sum_i x_i\,[i\cdot(c_M - 0.475) + 0.475] = (c_M - 0.475)/x_M + 0.475 = c_M/x_M - 0.475(1/x_M - 1) \qquad \text{S-19.62}$$

$$4c = 4c_M/x_M - 1.9(1/x_M - 1) \qquad \text{S-19.63}$$

The value we need for the numerator of the second term of Eqn. S-19.60 is $x_M\langle 4c\eta \rangle$

$$x_M\langle 4c\eta \rangle = 4\eta\, c_M - 1.9\,\eta(1 - x_M)$$

For the ESD equation, $Y_{ij} = Y$ for the monomer. Considering the attractive term, we will also need to evaluate q_i, which we will show equals $i \cdot q_M$. We keep the definition of $q_i = 1 + 1.90476\,(c_i - 1)$, which may be written $q_i = 1 + k_3\,(c_i - 1)$, where, $k_3 = 1.90476$. Note that $0.475 = (k_3 - 1)/\,k_3$, and inserting c from Eqn. S-19.61

$$q_i = 1 + k_3\,\{c_i - 1\} = 1 + k_3 \cdot \{i(c_M - (k_3 - 1)/\,k_3) + (k_3 - 1)/\,k_3 - 1\} =$$

$$1 + \{ic_M k_3 - k_3 i + i + k_3 - 1 - k_3\} = i\cdot[1 + k_3(c_M - 1)] = i\cdot q_M$$

Using these results,

$$\langle qYb \rangle = \sum_i \sum_j x_i x_j Y_{ij} \frac{(ib_M j q_M + j b_M i q_M)}{2} = q_M b_M Y_M \sum_i \sum_j x_i x_j ij = \frac{q_M b_M Y_M}{x_M^2}$$

$$\langle qY\eta_T \rangle = \langle qYb \rangle \rho_T = \frac{q_M b_M Y_M}{x_M^2} \rho x_M = \frac{q_M b_M Y_M}{x_M}$$

and the numerator of the attractive term becomes

$$9.5 x_M \langle qY\eta \rangle = 9.5 q_M Y_M \eta$$

The term $\langle Y\eta \rangle$ in the denominator is independent of association,

$$\langle Yb \rangle = Y_M \sum_i x_i b_i = \frac{Y_M b_M}{x_M},\ \langle Y\eta \rangle = Y_M\left(\sum_i x_i b_i\right)\rho_T = \frac{Y_M b_M}{x_M}\rho_T = Y_M b_M \rho = Y_M \eta$$

The final result is of the form $Z = 1 + Z^{rep} + Z^{att} + Z^{chem}$.

---

[17] The motivation for this assumption is discussed in relation to Eqn. S-19.68.

$$\boxed{Z = 1 + \frac{4c_M\eta}{1-1.9\eta} - \frac{9.5q_MY_M\eta}{1+1.7745\langle Y\eta\rangle} - \left(\frac{1.9\eta(1-x_M)}{1-1.9\eta} + 1 - x_M\right)} \tag{S-19.64}$$

We can clearly identify

$$\boxed{Z^{chem} = \frac{-1.9\,\eta_P(1-x_M)}{(1-1.9\,\eta_P)} - (1-x_M) = \frac{-(1-x_M)}{(1-1.9\,\eta_P)}} \tag{S-19.65}$$

Pure Associating-Fluid Fugacity

For the fugacity of a true monomer, we adapt Eqn. S-19.58,

$$\begin{aligned}\ln\hat{\varphi}_M &= -\frac{4}{1.9}c_M\ln(1-1.9\eta) + \frac{4cb_M\rho_T}{1-1.9\eta}\\ &-\frac{9.5}{1.7745}\frac{\ln(1+1.7745\langle Y\eta\rangle)}{\langle Yb\rangle}\left(Y_M\sum_j x_j(b_Mq_j+b_jq_M) - \frac{\langle qYb\rangle}{\langle Yb\rangle}Y_Mb_M\right)\\ &-\frac{9.5\langle qYb\rangle}{\langle Yb\rangle}\frac{Y_Mb_M\rho_T}{1+1.7745\langle Y\eta\rangle} - \ln Z_T\end{aligned} \tag{S-19.66}$$

The summation term becomes $Y_Mb_M\sum_i x_iq_M + Y_Mq_M\sum_i ib_M = 2Y_Mb_Mq_M/x_M$. Substituting $4c$ from Eqn. S-19.63,

$$\begin{aligned}\ln\hat{\varphi}_M &= -\frac{4}{1.9}c_M\ln(1-1.9\eta) + \frac{4c_Mb_M\rho}{1-1.9\eta}\\ &-\frac{9.5}{1.7745}\ln(1+1.7745\langle Y\eta\rangle)(q_M)\\ &-\frac{9.5\langle qYb\rangle}{\langle Yb\rangle}\frac{Y_Mb_M\rho}{1+1.7745\langle Y\eta\rangle} - \frac{1.9\eta(1-x_M)}{1-1.9\eta} - \ln Z + \ln x_M\end{aligned} \tag{S-19.67}$$

❗ True fugacity coefficient for monomer in a pure associating fluid.

Determination of x_M for the ESD Equation

Given the equation of state, we must next solve for the fugacity coefficient of a component in a mixture. Recalling the definitions of Eqn. S-19.2, and noting that contributions to ln φ_D^{att} cancel with those of ln φ_M^{att},[18]

$$\ln\hat{\varphi}_i = -\frac{4c_i}{1.9}\ln(1-1.9\eta) + \frac{4cb_i}{1-1.9\eta} - \ln Z_T \tag{S-19.68}$$

Considering the monomer to dimer step,

$$\begin{aligned}2\ln\hat{\varphi}_M - \ln\hat{\varphi}_D &= 2\left[-\frac{4c_M}{1.9}\ln(1-1.9\eta) + \frac{4cb_M}{1-1.9\eta} - \ln Z_T\right]\\ &-\left[-\frac{4c_D}{1.9}\ln(1-1.9\eta) + \frac{4cb_D}{1-1.9\eta} - \ln Z_T\right]\end{aligned} \tag{S-19.69}$$

Recalling that $b_D = 2b_M$ and further assuming that $c_i = c_M + (i-1)\cdot(c_M - 0.475)$, we obtain

$$2\ln\hat{\varphi}_M - \ln\hat{\varphi}_D = -\frac{4(2c_M - c_D)}{1.9}\ln(1-1.9\eta) - \ln Z_T$$

---

[18] In fact, the motivation for Eqn. S-19.61 was to anticipate and ensure cancellation of ln φ_i^{att}, and Eqn. S-19.61 in turn motivated $k_3 = 1.90476$.

But, $c_D - 2\,c_M = 2\,c_M - 0.475 - 2\,c_M = -0.475$ and $-4\cdot(-0.475)/1.9 = 1$.

$$\boxed{\frac{\hat{\varphi}_M^2}{\hat{\varphi}_D} = \frac{1}{Z_T(1-1.9\eta)}} \qquad \text{S-19.70}$$

Noting that Eqn. S-19.70 is analogous to Eqn. S-19.30 then,

$$\boxed{x_M = \frac{-1+\sqrt{1+4\Delta}}{2\Delta}} \qquad \text{S-19.71}$$

Simplified form of Δ using the van’t Hoff expression. The ESD program uses the form given by Eqn. S-19.83.

$$\Delta = \frac{\eta K_a'}{(1-1.9\eta)}\exp\left(H\left(1-\frac{1}{T_r}\right)\right) \qquad \text{S-19.72}$$

Helmholtz Energy and the Fugacity Coefficient for the ESD Equation

As with van der Waals equation, we can seek the relationship between the hydrogen bonding and the Helmholtz departure. Writing Eqn. S-19.67 for the superficial fugacity coefficient

$$\begin{aligned}\ln\varphi = \ln\hat{\varphi}_M x_M = {} & -\frac{4}{1.9}c_M\ln(1-1.9\eta) + \frac{4c_M b_M\rho}{1-1.9\eta} \\ & -\frac{9.5}{1.7745}\ln(1+1.7745\langle Y\eta\rangle)(q_M) \\ & -\frac{9.5\langle qYb\rangle}{\langle Yb\rangle}\frac{Y_M b_M\rho}{1+1.7745\langle Y\eta\rangle} - \frac{1.9\eta(1-x_M)}{1-1.9\eta} - \ln Z + 2\ln x_M\end{aligned} \qquad \text{S-19.73}$$

To obtain Z^{chem} in the equation, we must subtract and add $(1 - x_M)$

Superficial fugacity coefficient of pure associating species.

$$\begin{aligned}\ln\varphi = \ln\hat{\varphi}_M x_M = {} & -\frac{4}{1.9}c_M\ln(1-1.9\eta) + \frac{4c_M b_M\rho}{1-1.9\eta} \\ & -\frac{9.5}{1.7745}\ln(1+1.7745\langle Y\eta\rangle)(q_M) \\ & -\frac{9.5\langle qYb\rangle}{\langle Yb\rangle}\frac{Y_M b_M\rho}{1+1.7745\langle Y\eta\rangle} + \left(\frac{-1.9\eta(1-x_M)}{1-1.9\eta} - (1-x_M)\right) \\ & + ((1-x_M) + 2\ln x_M) - \ln Z\end{aligned} \qquad \text{S-19.74}$$

From this equation, we find that the contribution to Helmholtz energy from association is the same as the van der Waals equation.

$$\boxed{\frac{A^{chem}}{n_o RT} = 2\ln x_M + (1-x_M)} \qquad \text{S-19.75}$$

The Temperature Dependence of Δ

Hydrogen bonding is basically a simple exothermic reaction. As such, its behavior is described by the van’t Hoff equation. As the temperature goes up, conversion decreases. Since it is a relatively weak reaction, hydrogen bonding can become very weak at elevated temperatures. To develop more quantitative expressions, we must analyze K_a in detail. We begin by assuming that the term ΔC_P is constant with respect to temperature. Then,

$$\ln K_a = \frac{-\Delta G_T^o}{RT} = \frac{-\Delta H_R^o - \Delta C_P(T-T_R)}{RT} + \frac{\Delta S_R^o + \Delta C_P\ln(T/T_R)}{R} \qquad \text{S-19.76}$$

We are free to choose $T_R = T_c$. Then we have

$$\ln K_a = \frac{-\Delta G^o_{T_c}}{RT_c} + \frac{-\Delta H^o_{T_c}}{R}\left(\frac{1}{T} - \frac{1}{T_c}\right) - \frac{\Delta C_P(1 - 1/T_r)}{R} + \frac{\Delta C_P \ln T_r}{R} \qquad \text{S-19.77}$$

$$\ln K_a = \ln K_{ac} + \left(\frac{\Delta H^o_{T_c}}{RT_c} - \frac{\Delta C_P}{R}\right)\left(1 - \frac{1}{T_r}\right) + \frac{\Delta C_P \ln T_r}{R} \qquad \text{S-19.78}$$

$$\ln\left(\frac{K_a}{K_{ac}}\right) = \ln(T_r)^{\Delta C_P/R} + \left(\frac{\Delta H^o_{T_c}}{RT_c} - \frac{\Delta C_P}{R}\right)\left(1 - \frac{1}{T_r}\right) \qquad \text{S-19.79}$$

Setting $\Delta C_P / R = -1$ and defining a quantity $H = \left(\frac{\Delta H^o_{T_c}}{RT_c} - \frac{\Delta C_P}{R}\right)$, we have

$$\frac{T_r K_a}{K_{ac}} = \exp\left[H\left(1 - \frac{1}{T_r}\right)\right] \qquad \text{S-19.80}$$

The ESD equation provides the following form of Δ, which after some minor rearrangements, we have

$$\Delta = \frac{\rho}{1 - 1.9\eta}\frac{K_a RT}{P^\circ} = \frac{\eta}{1 - 1.9\eta}\frac{K_a RT}{P^\circ b_M} = \frac{\eta}{1 - 1.9\eta}K_a'\frac{T_r K_a}{K_{ac}}$$

Where we have defined $K_a' = \frac{K_{ac} RT_c}{P^\circ b_M}$. Substituting in the expression for $\frac{T_r K_a}{K_{ac}}$ from Eqn. S-19.80, we obtain

$$\Delta = \frac{\eta}{1 - 1.9\eta}K_a' \exp\left[H\left(1 - \frac{1}{T_r}\right)\right] \qquad \text{S-19.81}$$

Δ is thus characterized by the two parameters K_a' and H. These parameters can be determined by optimizing the fit to the critical properties and vapor pressure curve of the associating compound. For example K_a' can be determined from Z_c as given in Eqn. S-19.46. Z_c, and H can be determined to fit the shape of the vapor pressure curve. The presence of association tends to raise the vapor pressure at low temperatures relative to a nonassociating component of the same acentric factor. As an alternative, the values may be determined by optimizing the fit to other phase equilibrium data. Suresh and Elliott[19] showed that the sensitivity of LLE calculations to the volumetric parameter, b_M, can be applied to optimize the fit of LLE for one binary pair then those parameters for c, ε/k, b_M, H, and K_a' can be applied to a large number of systems. Puhala and Elliott[20] illustrated the point by applying it to 320 binary systems, all correlated to less than 10% error.

There was a slight evolution in the assumed temperature dependence of Δ between 1990 and 1992. A closely related theory based on the statistical mechanics of intermolecular potentials designed to model hydrogen bonding[21] was investigated which suggested an alternative route to describing the thermodynamics of associating mixtures. Wertheim's theory offers especially powerful routes to relating the microscopic and macroscopic perspectives. We can build a bridge from the chemical theory to Wertheim's by examining the form assumed for $\Delta C_P / R$. Recall that we previously assumed $\Delta C_P / R = -1$ for the van der Waals-associating fluid and ESD equations. For a molecule which only possesses 2 bonding sites, Wertheim's theory is exactly equivalent to the chemical theory if we assume a somewhat more complicated form for $\Delta C_P / R$. Using $-(\Delta H^o_{T_c})/R = \varepsilon_{HB}/k$, the Wertheim formula is:

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[19] Suresh, S. J., Elliott, J.R. *Ind. Eng. Chem. Res.* 31:2783 (1992).

[20] Puhala, A. S., Elliott, J. R. *Ind Eng. Chem Res.* 32:3174 (1993).

[21] Wertheim, M. S. *J. Stat. Phys.* 42:477 (1986) and references therein.

$$\frac{\Delta C_P}{R} = \frac{\ln[\exp(\varepsilon_{HB}/(kT)) - 1] + (\varepsilon_{HB}/(kT_c))(1 - 1/T_r) - \ln(T_r)}{\ln(T_r) - (1 - 1/T_r)} \qquad \text{S-19.82}$$

whereby the formula for Δ takes on a remarkably subtle change.

The ESD program uses this formula for Δ.

$$\boxed{\Delta = \frac{\eta}{(1 - 1.9\eta)} K^{AD}\left[\exp\left(\frac{\varepsilon_{HB}}{kT}\right) - 1\right]} \qquad \text{S-19.83}$$

The superscript "*AD*" indicates bond formation between a proton acceptor and a donor in the form of a linear chain. From an engineering perspective, there is little to distinguish the two forms of Δ other than analyzing which provides the basis for the most accurate correlations and predictions of engineering phase equilibrium data. Suresh and Elliott carried out extensive evaluations for hydrocarbon + water and hydrocarbon + alcohol systems including LLE as well as VLE. They found that the Wertheim form provided slightly greater accuracy.

Pure Component Parameters for the ESD Equation

The pure component parameters for a number of associating components are given in Table S-19.3, and many more are given in the computer file esdparms.txt. For any component which does not self-associate (e.g. ethers, esters, most ketones, and halocarbons as well as hydrocarbons), the equation of state parameters may be estimated from T_c, P_c, and ω in much the same manner as applied in the Peng-Robinson equation:

$$c = 1.0 + 3.535\omega + 0.533\omega^2 \qquad \text{S-19.84}$$

$$Z_c = (1 + 0.115/c^{1/2} - 0.186/c + 0.217/c^{3/2} - 0.173/c^2)/3 \qquad \text{S-19.85}$$

$$b = \frac{RT_c}{P_c}\frac{Z_c^2[-(1.9k_1Z_c + 3a) + \sqrt{(1.9k_1Z_c + 3a)^2 + 4a(4c - 1.9)(9.5q - k_1)/Z_c}]}{2a(4c - 1.9)} \qquad \text{S-19.86}$$

$$Y_c = \frac{Z_c^3}{a}\left(\frac{RT_c}{bP_c}\right)^2 \qquad \text{S-19.87}$$

$$\frac{\varepsilon}{k} = T_c \ln(Y_c + 1.0617) \qquad \text{S-19.88}$$

where $a = 1.9(9.5q - k_1) + 4ck_1$ and $k_1 = 1.7745$

In cases of associating compounds, the ESD equation typically imposes the constraint that the critical temperature be matched and the error in vapor pressure be minimized. For some especially important compounds, like water, the optimization of pure component parameters is broadened to recognize that predictions for mixtures can be sensitive to the choice of pure component parameters. For example, predictions of water + hydrocarbon liquid-liquid equilibria are very sensitive to the volume parameter for water, *b*, but many values of *b* can give similar accuracy for the vapor pressure of water. Therefore, the value chosen for the *b* parameter is the one which optimizes both vapor pressure correlation and liquid-liquid equilibria correlation.

Table 19.3 *Pure component parameters for a number of associating components according to the ESD equation. More parameters are available in the file* esdparms.txt *available on the Internet.*

Component	**ε/k (K)**	**b(cm^3/mole)**	**c**	**ε_{HB}/RT_c**	**K_{AB}'**
water	427.25	9.412	1.0053	4.00	0.1000
H2S	333.84	11.677	1.0416	2.00	0.0442

Table 19.3 *Pure component parameters for a number of associating components according to the ESD equation. More parameters are available in the file* esdparms.txt *available on the Internet.*

methanol	326.06	20.366	1.1202	5.17	0.0226
ethanol	269.72	23.540	1.5655	4.86	0.0283
1-propanol	242.51	25.124	2.7681	2.50	0.1000
2-propanol	236.54	27.701	2.3148	3.75	0.0500
phenol	354.33	29.996	2.0972	2.14	0.1220
acetone	247.70	30.273	2.1001	0.51	0.1000