

Chain Association

To extend the analysis from dimer formation to model chain formation, the primary adjustment is to assign two sites per molecule, consistent with one proton acceptor (A) and one proton donor (D), as we might expect for an alcohol. We can easily count the number of acceptors and donors in such linear chains by noting that one unbonded acceptor is left in each bonded chain, referring to Fig. 19.9. The equations for donors are entirely symmetrical and are omitted for simplicity. Note that n^A (the mole number of acceptors *not* bonded) is something quite different from n_A (the mole number of an "A-mer"). The extent of association is then characterized in terms of the fraction of acceptor sites *not* bonded, X^A . To see the relationship, consider the mass balances we obtain,

$$n^A = \sum n_j = n_T \quad 19.67$$

But the total number of acceptors is given by noting that there are " j " total acceptors per j -mer,

$$n_0^A = \sum j n_j = n_0 \quad 19.68$$

Note that n_0 refers to the same apparent number of moles discussed previously. The fraction of unbonded sites is a ratio of 19.67 and 19.68:

$$\boxed{X^A = n^A / n_0^A = n_T / n_0} \quad (\text{pure chain-forming fluid}) \quad 19.69$$

There is a further simplification that results from treating the bonding sites instead of the bonding molecules. The fraction of sites bonded can be perceived as a simple product of the bonding probabilities. First, note that the fraction of monomers bonded, $x^{AD} = n^{AD} / n_0$, and the fraction of monomers not bonded, X^A , must sum to unity.

$$X^A + x^{AD} = 1 \quad 19.70$$

x^{AD} is the fraction of acceptors that are bonded, regardless of whether they are bonded in monomers, dimers, trimers, ... In principle, the second term is an infinite sum. From an acceptor site perspective, however, we assume that the thermodynamic change from the unbonded state to the bonded state is the same, regardless of the degree of polymerization for that i -mer. That is, adding one more monomer to the end of a chain has the same equilibrium constant regardless of the chain length. Chemically, we have

$$A_{i-1} + A = A_i \text{ and } \Delta^{AD}_i = \Delta^{AD}_{i-1} \text{ for all } i \quad 19.71$$

That transition can be represented by

$$x^{AD} = 1 - X^A = X^A \cdot \Delta^{AD} \quad 19.72$$

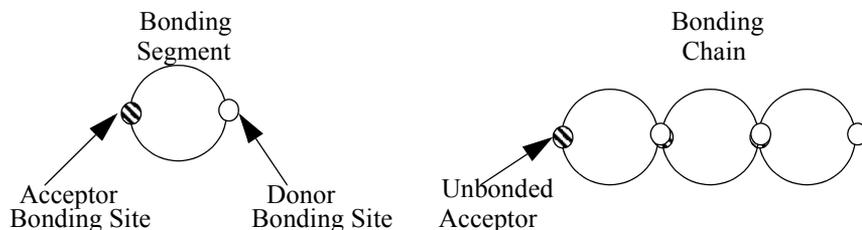


Figure 19.9 Wertheim's theory of chain association in a two-site model.

where X^D is the fraction of unbonded donors and $\Delta^{AD} = \rho g(\sigma) K^{AD} [\exp(\varepsilon^{AD}/kT) - 1]$ adapts Eqn. 19.44 to AD interactions. The term on the left is the fraction of acceptors that are bonded, and the term on the right expresses the observation that acceptors and donors must be unbonded in order to be available for bonding. By noting that one donor bonds for every acceptor, we see that $X^A = X^D$. Then we write Eqn. 19.72 in terms of X^A , $(X^A)^2$, and Δ^{AD} and we obtain $\Delta^{AD}(X^A)^2 + X^A - 1 = 0$ or

$$X^A = \frac{-1 + \sqrt{1 + 4\Delta^{AD}}}{2\Delta^{AD}} \quad (\text{pure chain-forming fluid}) \quad 19.73$$

The extension of the Helmholtz energy to chain formation simply applies the same formula developed for dimer formation. This formula accounts for the change in entropy and energy each time a bond is formed. Whether the bond is formed as part of a dimer or part of a chain, the reduction in entropy by forming a bond is the same. So is the energy released by the bond formation. In terms of acceptors and donors for a pure chain-forming fluid, Eqn. 19.54 becomes,

$$A^{chem}/RT = \ln(X^A) + (1 - X^A)/2 + \ln(X^D) + (1 - X^D)/2 = 2\ln(X^A) + (1 - X^A) \quad (\text{pure chains}) \quad 19.74$$

Eqns. 19.73, 19.74, and 19.44 characterize the chemical contribution for molecules like alcohols. Given a temperature and density, Eqn. 19.44 gives Δ^{AD} , then Eqn. 19.73 gives X^A , then Eqn. 19.74 gives A^{chem} , then Eqn. 19.1 gives $(A - A^{ig})$. Altogether, just one extra step (Eqn. 19.73) is required to compute the Helmholtz energy relative to the van der Waals model, but the rigor of the chemical perspective is greatly enhanced. In the MOSCED model, for example, the contribution involving $(\alpha_i - \alpha_j)(\beta_i - \beta_j)$ is entirely empirical. It is contrived to give the right sign when mixing acids and bases, but there is no basis for it in theory, and it does not alter the skewness of the excess Gibbs energy. On the other hand, Wertheim's theory is based on a rigorous derivation relating the molecular scale bonding volume and energy to the macroscopic properties, and fundamentally altering the behavior of the Gibbs energy.

Extension to Mixtures

Analyzing the impact of the chemical contribution on excess Gibbs energy requires extension of Wertheim's theory to mixtures. The beauty of Wertheim's perspective is that the extension of the reaction equilibrium relation (Eqn. 19.72) is entirely straightforward. One donor must bond for each bonded acceptor, whether the molecules are mixed or pure. The only issue is which molecule possesses the acceptor and which possesses the donor, but that is a notational detail. Furthermore, the fraction of bonded acceptors of type i must be in equilibrium with the all unbonded donors which can interact, including those on other types of molecules. We simply need to sum all the transition probabilities and the extension becomes:

$$1 - X_i^A = X_i^A \sum x_j N_{d,j} X_j^D \Delta_{ij}^{AD} \quad \text{or for solving use} \quad X_i^A = 1 / \left(1 + \sum x_j N_{d,j} X_j^D \Delta_{ij}^{AD} \right) \quad 19.75$$

where the sum is over donor sites, x_j is the apparent molecule mole fraction of the site host. $N_{d,j}$ is the number of identical donor sites of type j on the host, like the hydroxyl sites in polyvinyl alcohol. Analogous equations are written for each donor site, where the sum is over each interacting acceptor site and we replace Δ_{ij}^{AD} with Δ_{ij}^{DA} . Extending Eqn. 19.44 to ' AD type' association,

$$\Delta_{ij}^{AD} = \rho g_{ij}(\sigma_{ij}) K_{ij}^{AD} [\exp(\varepsilon_{ij}^{AD}/(kT)) - 1] \quad 19.76$$

The ordering of the subscripts and superscripts in Eqn. 19.76 provides the notational detail that permits accounting for which bonding site is the acceptor and which is the donor. For example, by

writing ε_{ij}^{AD} , the acceptor index is i and the donor is j . When the donor is i and the acceptor j , we write ε_{ij}^{DA} . To clarify, this distinction might be important in a mixture of alcohols and amines. An amine is usually a weak proton donor (indicated by its low acidity, α) but a strong proton acceptor (indicated by its basicity, β), whereas a typical alcohol has roughly equal acidity and basicity ($\alpha = \beta$). Numbering the acceptor and donor on the alcohol with subscript 1, and those on the amine with subscript 2, if we suppose that $\beta_{\text{alcohol}} \sim \beta_{\text{amine}}$, then $\varepsilon_{11}^{AD} \sim \varepsilon_{12}^{AD} > \varepsilon_{12}^{DA} \sim \varepsilon_{22}^{DA}$. This would mean strong solvation for the amines in alcohols, and negative deviations from Raoult's law, as observed experimentally. Eqn. 19.75 states that the bonding probability for an acceptor increases when there are donors on other molecules, and it decreases proportional to the mole fraction when the donor species are diluted by nonassociating species. The precise extent of chemical interaction is controlled by Δ_{ij}^{AD} , which could range from zero (for alkanes in water, for example) to a substantial quantity (when mixing carboxylic acids, for example). The extension of A^{chem} to any number of bonding sites or components becomes recalling that the sums are over sites,

$$\frac{A^{chem}}{RT} = \sum_{i \in A} x_i N_{d,i} [\ln X_i^A + (1 - X_i^A)/2] + \sum_{i \in D} x_i N_{d,i} [\ln X_i^D + (1 - X_i^D)/2] + \sum_{i \in C} x_i N_{d,i} [\ln X_i^C + (1 - X_i^C)/2] \quad 19.77$$

Briefly, this equation indicates that the change in Helmholtz energy due to bonding is the same regardless of how those bonds are formed. In other words, the reduction in entropy due to bond formation is universal when the packing fraction is unchanged. We know that entropy is the primary contribution because energy does not appear explicitly in Eqn. 19.77. Bonding energy affects A^{chem} implicitly through Δ , because a larger energy gives a larger value of Δ and a smaller value of X_i^B . We have included X^C here to represent dimerization (e.g., carboxylic acid bonding) as something distinct from AD interaction. A 's can only bond with D 's, and this leads to chain formation. On the other hand, C 's can only bond with C 's, confining these sites to dimerization. Although we wrote the equation for these three types of bonds, there is really no limit and Eqn. 19.77 can be extended straightforwardly to many situations. In the description here, X^C would not affect X^A because C 's can only interact with C 's. If a carboxylic acid (e.g., acetic acid) is to interact with an alcohol (e.g., water), A 's or D 's would need to be included as part of the carboxylic acid segment, in addition to the C 's, as illustrated in Fig. 19.10.¹⁸

Eqns. 19.75–19.77 provide a powerful and versatile complement to our treatment of phase equilibria. In Chapters 10–12, we might have alluded to hydrogen bonding, for example, as a reason why oil and water do not mix, but our models did not truly recognize it as bonding. The van der Waals models and local composition theories treat attractive energy as spherically symmetric, like the square-well potential. But complexation is stereospecific and this alters the description of the

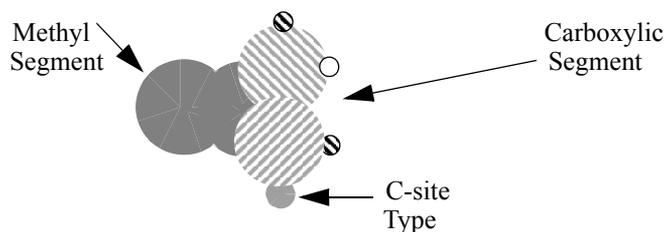


Figure 19.10 A bonding site model for acetic acid.

18. An alternative perspective would allow C to interact with A , C , or D . This would not change Eqn 19.77, but would require terms like Δ^{CA} and Δ^{CD} . cf. Muro-Suñé N, et al. 2008. *Ind. Eng. Chem. Res.* 47:5660–5668.

Helmholtz energy. The Helmholtz energy of hydrogen bonding is as different from that of the van der Waals model as Eqn. 19.77 is from $a\rho/RT$.

19.7 MASS BALANCES FOR CHAIN ASSOCIATION

The thermodynamics and phase behavior are sufficiently described by Eqns. 19.75 and 19.77, but you may be curious about the true mole fractions of the species. Furthermore, it is interesting to see how this “fraction of acceptor sites not bonded” is closely related to the fraction monomer, x_M . This turns out to be a bit subtle, and it should not distract you from the primary issue of phase behavior. If you are interested, we can use material balances to obtain two simple relations between the true number of moles in the solution, n_T , and the apparent number of moles that we would expect if there was no association,¹⁹ n_0 . Note that n_0 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 100 cm^3 of water one would estimate

$$n_0 = 100 \text{ cm}^3 \cdot 1.0 \text{ g/cm}^3 / (18 \text{ g/mole}) = 5.556 \text{ moles}$$

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 apparent 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.

For molecules with one donor and one acceptor site, the fraction of unbonded acceptors is the joint probability that the acceptors and donors are both unbonded, and since by mass balance $X^A = X^D$, then $n_M/n_0 = X^A X^D = (X^A)^2 = (n_M/n_T)(n_T/n_0) = x_M(n_T/n_0)$. We can write the equilibrium relation for i -mer formation using 19.43 as $x_i/(x_M x_{i-1}) = ((\hat{\phi}_M \hat{\phi}_{i-1})/(\hat{\phi}_i P^\circ)) PK_{a,i} = (\Delta)(n_T/n_0)$. Combining the probability and equilibrium relations, $x_i = x_{i-1}(X^A)^2 \Delta$. A recursive relation results, $x_i = x_M((X^A)^2 \Delta)^{i-1}$. Now consider the balances

$$n_0 = \sum i \cdot n_i = n_T \sum i \cdot x_i \quad 19.78$$

Substituting the recursive relation,

$$n_0 = n_T \sum i \cdot x_M ((X^A)^2 \Delta)^{i-1} = x_M n_T [1 + 2((X^A)^2 \Delta) + 3((X^A)^2 \Delta)^2 + 4((X^A)^2 \Delta)^3 + \dots]$$

This series is a common converging series. We find from a math handbook that

$$n_T x_M [1 + 2((X^A)^2 \Delta) + 3((X^A)^2 \Delta)^2 + 4((X^A)^2 \Delta)^3 + \dots] = n_T x_M [1/(1 - (X^A)^2 \Delta)^2]$$

$$\boxed{\frac{n_0}{n_T} = \frac{x_M}{(1 - (X^A)^2 \Delta)^2} = \sum_i i \cdot x_i} \quad 19.79$$

Since the mole fractions must sum to unity, we can write a second balance, for x_i ,

$$\boxed{1 = \sum_i x_i = x_M [1 + ((X^A)^2 \Delta) + ((X^A)^2 \Delta)^2 + ((X^A)^2 \Delta)^3 + \dots]} \quad 19.80$$

19. Here we choose to use subscript 0 to clearly distinguish the notation for apparent moles, even though it would be the quantity normally reported from a macroscopic experiment.

and again recognizing the series,

$$1 = x_M [1 + ((X^A)^2 \Delta) + ((X^A)^2 \Delta)^2 + ((X^A)^2 \Delta)^3 + \dots] = x_M [1/(1 - (X^A)^2 \Delta)]$$

$$\boxed{x_M = (1 - (X^A)^2 \Delta)} \quad 19.81$$

Substituting x_M for $(1 - (X^A)^2 \Delta)$ in Eqn. 19.79 results in,

$$n_0/n_T = x_M/x_M^2 = 1/x_M$$

Noting Eqn. 19.69

$$\boxed{\frac{n_T}{n_0} = X^A = x_M} ; \text{ and } \frac{n_M}{n_0} = (X^A)^2 \text{ (pure chains)} \quad 19.82$$

This equation makes clear that the properties of the mixture are closely related to the properties of the monomer.

Example 19.5 Molecules of H₂O in a 100 ml beaker

Modeling water as chains, assuming Δ is about 100 at room temperature and $\rho = 1 \text{ g/cm}^3$, estimate the moles of H₂O monomer in a 100 ml beaker of liquid water.

Solution: Note that the problem statement requests moles of H₂O, not (H₂O)₂ or (H₂O)₃, and so on, so we are interested in the true number of H₂O monomer moles. We know $n_0 = 5.556$ by applying the monomer molecular weight, but the number of monomer moles $n_M = x_M n_T$ will be significantly less. Proceeding, using Eqn. 19.73,

$$X^A = [-1 + \sqrt{1 + 4\Delta}] / 2\Delta = 0.095 = n^A/n_0 = n_T/n_0 = x_M = 0.095 = n_T/n_0$$

$$\Rightarrow n_M = 0.095 \cdot (n_T/n_0) \cdot n_0 = 0.095^2 \cdot n_0 = 0.05 \text{ moles}$$

Therefore, the true number of moles is 100 times less than the apparent number of moles.

19.8 THE CHEMICAL CONTRIBUTION TO THE FUGACITY COEFFICIENT AND COMPRESSIBILITY FACTOR

The solution to phase equilibrium problems can be achieved in the manner of Chapter 15 (Eqn 15.20), where Eqns. 19.1 and 19.2 describe the enhanced equation of state. Eqns. 19.75–19.77 completely characterize the temperature, density, and composition dependence of the chemical contribution to Helmholtz energy. The Z^{chem} contribution is implied, but requires differentiation as in $RT \cdot Z^{chem} = -V(\partial A^{chem}/\partial V)_T$. Similarly, the fugacity coefficient is implicitly determined through differentiation. Nevertheless, the differentiation can be complicated relative to the fugacity coefficient of the van der Waals model. The summation of Eqn. 19.77 means that terms like $\partial X_i/\partial n_j$ contribute and Eqn. 19.75 implies a nonlinear system of equations that must be solved to determine these con-

tributions. For example, consider a mixture of three alcohols, with $X_i^A = X_i^D$ and $N_{d_i} = 1$ for all i . Numbering the acceptors and donors with the same subscript as their host, Eqn. 19.75 implies that

$$-\partial X_1^A / \partial n_1 = X_1^A \left[x_1 X_1^A \Delta_{11}^{AD} \partial X_1^A / \partial n_1 + x_2 X_2^A \Delta_{12}^{AD} \partial X_1^A / \partial n_2 + x_3 X_3^A \Delta_{13}^{AD} \partial X_1^A / \partial n_3 \right] \quad 19.83$$

The only way to fully determine all $\partial X_i / \partial n_j$ is to apply Eqn. 19.75 eight more times to obtain nine equations for the nine unknown values implied by $\partial X_i / \partial n_j$. Once again, Wertheim's theory seems to become impractical.

Fortunately, this particular nonlinear system of equations possesses subtle but advantageous properties. Briefly, there are many symmetries in the calculus that lead to surprising simplifications when cleverly manipulated. Michelsen and Hendriks showed that $A^{chem}/(RT)$ can be rewritten as the stationary point of a generalized function \underline{Q} where $A^{chem}/(RT)$ is minimized and \underline{Q} is maximized.²⁰ A result of the chemical equilibria is that $\partial \underline{Q} / \partial X_i^B = 0$, for all i and B , where B is an acceptor or donor. The beauty of the generalized function is that derivatives with respect to X_i^B can be separated from derivatives with respect to \underline{V} or n_j . Applying the expansion rule to $\underline{Q}(T, \underline{V}, n, X)$, and using $(\partial \underline{Q} / (\partial X_i^B))_{T, \underline{V}, n_j \neq k} = 0$ at the stationary point,

$$\left(\frac{\partial \underline{Q}_{sp}}{\partial \underline{V}} \right)_{T, n} = \left(\frac{\partial \underline{Q}}{\partial \underline{V}} \right)_{T, n, X} + \sum_{i \in B} \left(\frac{\partial \underline{Q}}{\partial X_i^B} \right)_{T, n, \underline{V}} \left(\frac{\partial X_i^B}{\partial \underline{V}} \right) = \left(\frac{\partial \underline{Q}}{\partial \underline{V}} \right)_{T, n, X} + \sum_{i \in B} (0) \left(\frac{\partial X_i^B}{\partial \underline{V}} \right) = \left(\frac{\partial \underline{Q}}{\partial \underline{V}} \right)_{T, n, X} \quad 19.84$$

Similarly,

$$\left(\frac{\partial \underline{Q}_{sp}}{\partial n_k} \right)_{T, \underline{V}, n_j \neq k} = \left(\frac{\partial \underline{Q}}{\partial n_k} \right)_{T, \underline{V}, X, n_j \neq k} + \sum_{i \in B} \left(\frac{\partial \underline{Q}}{\partial X_i^B} \right)_{T, \underline{V}, n_j \neq k} \left(\frac{\partial X_i^B}{\partial n_k} \right) = \left(\frac{\partial \underline{Q}}{\partial n_k} \right)_{T, \underline{V}, X, n_j \neq k} \quad 19.85$$

The generalized function, \underline{Q} , is intentionally created by shifting $A^{chem}/(RT)$ a manner such that derivatives with respect to X_i^B will cancel and that $\underline{Q} = A^{chem}/(RT)$ at the stationary point. Ignoring C-type sites of Eqn. 19.77 for this discussion, summing over sites using x_i as in Eqn. 19.75

$$\underline{Q}(T, \underline{V}, n, X) = \sum x_i N_{d_i} [\ln(X_i^A) + (1 - X_i^A)] + \sum x_i N_{d_i} [\ln(X_i^D) + (1 - X_i^D)] - h/2 \quad 19.86$$

Each site summation has been shifted by $\sum x_i N_{d_i} (1 - X_i^B)/2$. The term h is constructed to cancel this shift at the stationary point (equilibrium) by using the right hand side of Eqn. 19.75 for each x_i .

$$\begin{aligned} h &= \sum_{i \in A} \sum_{j \in D} x_i x_j N_{d_i} N_{d_j} X_i^A X_j^D \Delta_{ij}^{AD} + \sum_{i \in D} \sum_{j \in A} x_i x_j N_{d_i} N_{d_j} X_i^D X_j^A \Delta_{ij}^{DA} \\ \underline{h} &= \sum_{i \in A} \sum_{j \in D} n_i n_j N_{d_i} N_{d_j} X_i^A X_j^D (\Delta_{ij}^{AD}/n) + \sum_{i \in D} \sum_{j \in A} n_i n_j N_{d_i} N_{d_j} X_i^D X_j^A (\Delta_{ij}^{DA}/n) \end{aligned} \quad 19.87$$

where all x and n are for apparent moles. We can write the extensive expression of Eqn. 19.86, \underline{Q}

$$\underline{Q}(T, \underline{V}, n, X) = \sum_{i \in A} n_i N_{d_i} [\ln(X_i^A) + (1 - X_i^A)] + \sum_{i \in D} n_i N_{d_i} [\ln(X_i^D) + (1 - X_i^D)] - \underline{h}/2 \quad 19.88$$

The balance Eqn. 19.75 should not be inserted except at the stationary point. Even though the right and left side of this equation were used to create \underline{Q} , the equality holds only at the stationary point. Because $\underline{Q}_{sp} = A^{chem}/(RT)$ at the stationary point compositions determined by Eqn. 19.75, we can take advantage of Eqns. 19.84 and 19.86 to obtain,

20. Michelsen, M.L., Hendriks, E.M. 2001. *Fluid Phase Equil.* 180:165.

$$RT \cdot Z^{chem} = -V \partial(A^{chem}/\partial V) = \eta_P RT (\partial Q/\partial \eta_P)_X = -0.5 RT \eta_P (\partial h/\partial \eta_P)_X$$

Note that Q and \underline{Q} are not manipulated before differentiation, and remember that only h is density dependent. Differentiating Eqn. 19.87,

$$\begin{aligned} -2Z^{chem} = \eta_P (\partial h/\partial \eta_P)_X &= \sum_{i \in A} \sum_{j \in D} x_i x_j N_{d,i} N_{d,j} X_i^A X_j^D (\eta_P \partial \Delta_{ij}^{AD}/\partial \eta_P) \\ &+ \sum_{i \in D} \sum_{j \in A} x_i x_j N_{d,i} N_{d,j} X_i^D X_j^A (\eta_P \partial \Delta_{ij}^{DA}/\partial \eta_P) \end{aligned} \quad 19.89$$

Condensing notation for 19.77, $\Delta = \rho g(\sigma) K^{AD\dagger}$ where $K^{AD\dagger} = K^{AD} [\exp(\varepsilon/(kT)) - 1]$. To simply Eqn. 19.89, consider the derivative,

$$\eta_P \frac{\partial \Delta_{ij}}{\partial \eta_P} = \frac{\eta_P K_{ij}^{AD\dagger} \partial(\eta_P g(\sigma))}{b \partial \eta_P} = \rho K_{ij}^{AD\dagger} (g(r) + \eta_P \frac{\partial g(\sigma)}{\partial \eta_P}) = \Delta_{ij} \left(1 + \frac{\partial \ln g(\sigma)}{\partial \ln \eta_P}\right)$$

Inserting into 19.89 and recognizing that we can insert 19.75 at the stationary point,

$$Z^{chem} = -0.5 \left(1 + \frac{\partial \ln g(\sigma)}{\partial \ln \eta_P}\right) \left(\sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D) \right) \quad 19.90$$

$$\ln(\hat{\phi}_k^{chem}) = (\partial \underline{Q}/\partial n_k)_X = \sum N_{d,k} [\ln(X_k^A) + (1 - X_k^A)] + \sum N_{d,k} [\ln(X_k^D) + (1 - X_k^D)] - 0.5 (\partial h/\partial n_k)_X \quad 19.91$$

$$\begin{aligned} (\partial h/\partial n_k)_X &= 2 \sum x_j (N_{d,k} N_{d,j} X_k^A X_j^D \Delta_{kj}^{AD} + N_{d,k} N_{d,j} X_k^D X_j^A \Delta_{kj}^{DA}) \\ &+ \sum \sum x_i x_j N_{d,i} N_{d,j} [X_i^A X_j^D n^2 \partial(\Delta_{ij}^{AD}/n)/\partial n_k + X_i^D X_j^A n^2 \partial(\Delta_{ij}^{DA}/n)/\partial n_k] \end{aligned} \quad 19.92$$

where all x and n are for apparent moles. Cancellation of terms by Eqn. 19.75 results in

$$\begin{aligned} \ln(\hat{\phi}_k^{chem}) &= \sum N_{d,k} \ln(X_k^A) + \sum N_{d,k} \ln(X_k^D) - 0.5 \sum \sum x_i x_j N_{d,i} N_{d,j} [X_i^A X_j^D n^2 \partial(\Delta_{ij}^{AD}/n)/\partial n_k + \\ &X_i^D X_j^A n^2 \partial(\Delta_{ij}^{DA}/n)/\partial n_k] \end{aligned} \quad 19.93$$

The derivative can be simplified

$$\frac{n^2 \partial(\Delta_{ij}/n)}{\partial n_k} = \frac{n^2 K_{ij}^{AD\dagger} \partial g(\sigma)}{V \partial n_k} = \frac{n \rho K_{ij}^{AD\dagger} g(\sigma) \partial g(\sigma)}{g(\sigma) \partial n_k} = (\Delta_{ij}) n \frac{\partial \ln g(\sigma)}{\partial n_k}$$

Inserting into 19.93 and recognizing $h_{sp} = \sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D)$ can replace the quadratic sum,

$$\begin{aligned} \ln(\hat{\phi}_k^{chem}) &= \sum_{i \text{ on } k} (N_{d,i} \ln(X_i^A) + N_{d,i} \ln(X_i^D)) - \\ &0.5 \left(n \frac{\partial \ln g(r)}{\partial n_k} \right) \left(\sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D) \right) \end{aligned} \quad 19.94$$

The computational complexity of Eqns. 19.75–19.77 is reduced for the case with one acceptor and one donor per molecule assuming $\Delta_{(molec\ i)(molec\ j)}^{AD} = (\Delta_{(molec\ i)(molec\ i)}^{AD} \Delta_{(molec\ j)(molec\ j)}^{AD})^{1/2}$, which we refer to as the square root combining rule (SRCR). The SRCR is suitable for Δ_{ij} of alco-

hols + aldehydes + water, but not for alcohols + amines. In general, Eqns. 19.75–19.77 require an iterative solution, as illustrated in Example 19.7. An initial guess for any j, B adapts the SRCR method²¹

$$\frac{1}{X_j^B} \approx 1 + \sqrt{\Delta_{(\text{molec } j)(\text{molec } j)}^{AD}} \sum_{\text{molec } i} \{ (x_i \sqrt{\Delta_{(\text{molec } i)(\text{molec } i)}^{AD}}) / [1 + \sqrt{\Delta_{(\text{molec } i)(\text{molec } i)}^{AD}}] \} \quad 19.95$$

When the SRCR rule is not valid (e.g. alcohols + amines), Eqn. 19.95 can be adapted by replacing $\sqrt{\Delta_{(\text{molec } i)(\text{molec } i)}^{AD}} \Delta_{(\text{molec } j)(\text{molec } j)}^{AD}$ in the numerator with $\Delta_{(\text{molec } i)(\text{molec } j)}^{AD}$.

This concludes the theoretical development for the chemical contributions to phase equilibrium. Eqns. 19.75–19.77 and 19.90 and 19.94 permit solution of Eqns. 19.1 and 19.2 for mixtures as well as pure fluids and computation of the fugacity coefficients to perform any phase equilibrium determination. Wertheim's theory of solution thermodynamics is more challenging than that of van der Waals or local compositions, but it replaces the empirical conjectures of those models with rigorous analysis that has been verified with molecular simulations. The perspective offered by Wertheim's theory will be extended to nonspherical molecules in the following section.

Example 19.6 Complex fugacity for the van der Waals model

A sample calculation with a specific reference equation of state will clarify application for trimethylamine(t) + methanol(m). With A_t on component t , and A_m and D_m on component m , let $K_{tm}^{AD} = K_{mm}^{AD} = 0.72 \text{ cm}^3/\text{mol}$ and $\varepsilon_{tm}^{AD} = \varepsilon_{mm}^{AD} = 20 \text{ kJ/mol}$, $b_t = 27.5$ and $b_m = 20.4 \text{ cm}^3/\text{mol}$. For the associating van der Waals equation, assuming chains form,

(a) Derive Z^{chem} and $\ln(\hat{\phi}_k^{chem})$ adapting the definition of Δ from Eqn. 19.44.

(b) Evaluate the expressions at $x_t = 0.5$, $\rho = 0.0141 \text{ mol/cm}^3$, and $T = 300\text{K}$.

Solution: (a) For Z^{chem} , we need

$$1 + \frac{\partial \ln g(\sigma)}{\partial \ln \eta_p} = 1 + \frac{\eta_p}{g(\sigma)} \frac{(\partial(1 - \eta_p)^{-1})}{\partial \eta_p} = 1 + \frac{\eta_p}{g(r)(1 - \eta_p)^2} = \frac{1}{(1 - \eta_p)} \quad 19.96$$

$$Z^{chem} = \frac{-0.5}{(1 - \eta_p)} \left(\sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D) \right) \quad 19.97$$

For $(\hat{\phi}_k^{chem})$ we need

$$n \frac{\partial \ln g(\sigma)}{\partial n_k} = \frac{n}{g(\sigma)} \frac{\partial(1 - \eta_p)^{-1}}{\partial n_k} = \frac{n}{g(\sigma)} \frac{(\partial \eta_p) / (\partial n_k)}{(1 - \eta_p)^2} = \frac{b_k \rho}{(1 - \eta_p)} \quad 19.98$$

$$\begin{aligned} \ln(\hat{\phi}_k^{chem}) &= \sum_{i \text{ on } k} (N_{d,i} \ln(X_i^A) + N_{d,i} \ln(X_i^D)) \\ &- \frac{0.5 b_k \rho}{(1 - \eta_p)} \left(\sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D) \right) \end{aligned} \quad 19.99$$

21. Elliott, J.R. 1996. *Ind. Eng. Chem. Res.* 35:1624. To relate Elliott's variable F to the h used here, $F^2 = h/2 = [\sum x_j X_j^A (\Delta_{jj}^{DA})^{1/2}]^2$.

Example 19.6 Complex fugacity for the van der Waals model (Continued)

b) Because only one acceptor/donor value exists for the specified interactions, $\Delta_{ij}^{AD} = \rho K^{AD}(\exp(\beta\varepsilon_{ij}^{AD}) - 1)/(1 - \eta_P) = \Delta$.

$$b = 0.5 \cdot 27.5 + 0.5 \cdot 20.4 = 24.0; \quad \eta_P = 0.0141 \cdot 24.0 = 0.338 \quad 19.100$$

$$\Delta_{im}^{AD} = \Delta_{mm}^{AD} = 0.338/(1 - 0.338) \cdot (0.72/24.0) \cdot (\exp(20000/8.314/300) - 1) = 46.4 \quad 19.101$$

To solve Eqns. 19.92 for X_i^A , X_m^A , and X_m^D ,

$$1 - X_i^A = 0.5 X_i^A X_m^D \Delta \quad 19.102$$

$$1 - X_m^D = 0.5 X_i^A X_m^D \Delta + 0.5 X_m^A X_m^D \Delta \quad 19.103$$

$$1 - X_m^A = 0.5 X_m^A X_m^D \Delta \quad 19.104$$

This gives three equations. Note that $X_i^A = X_m^A$ for this case. We use these in Eqn. 19.103 to obtain a quadratic equation in terms of X_m^D . Usually, we would need to iterate to solve for X_i^B .

$$X_i^A = X_m^A = 1/(1 + 0.5 X_m^D \Delta) \quad 19.105$$

$$X_m^D = 1/(1 + 0.5 X_i^A \Delta + 0.5 X_m^A \Delta) = 1/(1 + X_m^A \Delta) = 1/(1 + \Delta/(1 + 0.5 X_m^D \Delta)) \quad 19.106$$

$$X_m^D = (1 + 0.5 X_m^D \Delta)/(1 + (1 + 0.5 X_m^D \Delta) \Delta)$$

$$X_m^D + X_m^D \Delta + 0.5 (X_m^D)^2 \Delta = 1 + 0.5 X_m^D \Delta$$

$$X_m^D = [- (1 + \Delta/2) + \sqrt{(1 + \Delta/2)^2 + 2\Delta}] / \Delta = 0.0397 \quad 19.107$$

$$X_m^A = X_i^A = 1/(1 + 0.5 \cdot 0.0397 \cdot 46.4) = 0.520 \quad 19.108$$

This shows that D_m is almost completely bonded. Calculating the sum in Z^{chem} of 19.97, $h_{sp} = 0.5(1 - 0.52) + 0.5(1 - 0.52) + 0.5(1 - 0.0397) = 0.960$

$$Z^{chem} = -0.5 h_{sp} / (1 - \eta_P) = -0.480 / (1 - 0.338) = -0.725$$

By Eqn. 19.99, recognizing Z^{chem} within the last term of each

$$\ln(\hat{\phi}_i^{chem}) = \ln(X_i^A) - 0.5 h_{sp} b_i \rho / (1 - \eta_P) = -0.6539 - 0.725(27.5)(0.0141) = -0.935$$

$$\begin{aligned} \ln(\hat{\phi}_m^{chem}) &= \ln(X_m^A) + \ln(X_m^D) - 0.5 h_{sp} b_m \rho / (1 - \eta_P) \\ &= -0.6539 - 3.226 - 0.725(20.4)(0.0141) = -4.09 \end{aligned}$$

There are several points of interest in this result. The acceptors in this mixture outnumber donors by two to one. Therefore, it is impossible that $X_i^A < 0.5$, and, in fact, $X_m^D \sim 2 \cdot (X_i^A - 0.5)$ because the lack of donor saturation is reflected twice, in X_i^A and X_m^A . The compressibility factor is depressed in a simple way that sums over all donors and acceptors, but the fugacity is depressed more for the alcohol than for the amine. There are two ways for the alcohol to interact, but only one for the amine, so the depression of the fugacity is much greater. On the other hand, the fugacity of the alcohol is depressed less in the mixture than in the pure fluid because relatively fewer acceptors are bonded ($\ln(\hat{\phi}_m^{chem}) = -6.105$ at $x_m = 1$). So the mixture activity for the alcohol is enhanced by less hydrogen bonding relative to the pure component, while the activity of the amine is depressed by more hydrogen bonding at all compositions relative to the pure component.

Example 19.7 More complex fugacity for the van der Waals model

Evaluate the expressions for Z^{chem} and $\ln(\hat{\phi}_k^{chem})$ of trimethylamine(*t*) + methanol(*m*) at $x_t = 0.4$, $\rho = 0.0141$ mol/cm³, and $T = 300$ K. With A_t on component *t*, and A_m and D_m on component *m*, let $K_{tm}^{AD} = K_{mm}^{AD} = 0.72$ cm³/mol and $1.25\varepsilon_{tm}^{AD} = \varepsilon_{mm}^{AD} = 20$ kJ/mol, $b_t = 27.5$, and $b_m = 20.4$ cm³/mol.

Solution: The difference between this example and the previous is that $\varepsilon_{tm}^{AD} \neq \varepsilon_{mm}^{AD}$, indicating that the amine + alcohol is slightly weaker than the alcohol + alcohol association. Because of this lack of symmetry, an iterative solution for X_t^B is required.

Substituting the mole fractions and solving for Δ 's,

$b = 0.4 \cdot 27.5 + 0.6 \cdot 20.4 = 23.4$; $\eta_p = 0.0141 \cdot 23.4 = 0.328$. This is slightly less than Eqn 19.100.

$$\Delta_{mm}^{AD} = \rho K_{mm}^{AD} (\exp(\beta \varepsilon_{mm}^{AD}) - 1) / (1 - \eta_p) = 45.8; \Delta_{tm}^{AD} = 9.21; \Delta_{tt}^{DA} = \Delta_{tm}^{DA} = 0.$$

$$1 - X_t^A = 0.6 X_t^A X_m^D \Delta_{tm}^{AD}; \quad 1 - X_m^D = 0.4 X_m^D X_t^A \Delta_{tm}^{AD} + 0.6 X_m^D X_m^A \Delta_{mm}^{AD};$$

$$1 - X_m^A = 0.6 X_m^A X_m^D \Delta_{mm}^{AD}; \quad \text{rearranging all three:}$$

$$X_t^A = 1 / (1 + 0.6 X_m^D \Delta_{tm}^{AD}); \quad X_m^A = 1 / (1 + 0.6 X_m^D \Delta_{mm}^{AD});$$

$$X_m^D = 1 / (1 + 0.4 X_t^A \Delta_{tm}^{AD} + 0.6 X_m^A \Delta_{mm}^{AD});$$

Unlike the previous example, an explicit solution is not found. The previous example was contrived to achieve an exact solution, but this is rarely possible. Normally, we must iterate to achieve a numerical solution. It is convenient to guess X_m^D , then compute X_t^A and X_m^A , then use successive substitution to converge all X_t^B . Adapting Eqn. 19.95 for the non-SRCR case,

$$1/X_m^D \approx 1 + 0.4(9.2)/(1 + \sqrt{0}) + 0.6(45.8)/(1 + \sqrt{45.8}) = 8.218 \Rightarrow X_m^D = 0.122;$$

$$X_t^A = 0.597; \quad X_m^A = 0.230; \quad X_m^D = 0.105;$$

Eleven more iterations gives $X_t^A = 0.677$; $X_m^A = 0.296$; $X_m^D = 0.0864$. The large number of iterations is necessary because this particular mixture deviates substantially from the SRCR.

$$X_t^A = 1 / (1 + 0.6 \cdot 0.0864 \cdot 9.21) = 0.677$$

$$X_m^A = 1 / (1 + 0.6 \cdot 0.0864 \cdot 45.8) = 0.296$$

$$X_m^D = 1 / (1 + 0.4 \cdot 0.677 \cdot 9.21 + 0.6 \cdot 0.296 \cdot 45.8) = 0.086$$

Calculating the sum in Z^{chem} of 19.97,

$$h_{sp} = 0.4(1 - 0.677) + 0.6(1 - 0.296) + 0.6(1 - 0.086) = 1.100$$

$$Z^{chem} = -0.5 h_{sp} / (1 - \eta_p) = -0.55 / (1 - 0.328) = -0.818$$

$$\ln(\hat{\phi}_t^{chem}) = \ln(X_t^A) - 0.5 h_{sp} b_t \rho / (1 - \eta_p) = -0.390 - 0.55(27.5)(0.0141) / (0.672) = -0.707$$

$$\ln(\hat{\phi}_m^{chem}) = \ln(X_m^A) + \ln(X_m^D) - 0.5 h_{sp} b_m \rho / (1 - \eta_p) = -3.91$$

These results show that a 20% decrease in ε_{tm}^{AD} compared to Example 19.6 gives a 80% decrease in Δ_{tm}^{AD} . That is fairly sensitive. This change in Δ_{tm}^{AD} is primarily responsible for the increase in X_t^A from 0.52 to 0.68 and the decrease of X_m^A from 0.520 to 0.30.

19.9 WERTHEIM'S THEORY OF POLYMERIZATION

Now that we have an accounting for the thermodynamics of bond formation, it is natural to wonder what happens to the thermodynamics as the bond energy approaches infinity. This would be a natu-

ral limit for covalent bond formation. Having a theoretical basis for nonspherical molecules would be a big step forward, considering that all theories discussed until now have been based on spherical molecules. Of course, we added correction terms like $\alpha(T, \omega)$ to the Peng-Robinson model, but this was done with no theoretical basis. Wertheim's theory provides an opportunity to develop meaningful guidelines for shape effects.

The key step is to find the contribution to the equation of state from forming a bond in the limit of infinite bond energy. The result for dimerization, Eqn. 19.54, is convenient to illustrate the key points. At first glance, the limit may not seem obvious, because the X term in A^{chem} must approach zero and the log term would then be undefined. This issue can be resolved by substituting, $1 - X = X^2\Delta$. We use A^{bond} to denote the covalent nature of the bonds and take the limit of no monomer.

$$\boxed{\frac{A^{bond}}{n_o RT} = \ln(X) - \left(\frac{1-X}{2}\right) = 0.5 \ln\left(\frac{1-X}{\Delta}\right) - \left(\frac{1-X}{2}\right) \rightarrow \lim_{X \rightarrow 0} \frac{A^{bond}}{n_o RT} = -0.5 \ln(\Delta) - 0.5} \quad 19.109$$

Eqn. 19.109 is helpful when $\Delta \rightarrow \infty$ because Z^{bond} can be obtained by differentiation of A^{bond} . Referring to Eqns. 19.44 and 19.49 and taking the derivative,

$$\boxed{\frac{P^{bond} V}{n_T RT} = \frac{n_o \rho}{n_T} \frac{\partial}{\partial \rho} \left(\frac{A^{bond}}{n_o RT} \right) = \frac{-2\rho}{2\Delta} \frac{\partial}{\partial \rho} (\rho g(\sigma) K_a) = - \left[1 + \frac{\rho \partial g(\sigma)}{g \partial \rho} \right] \equiv Z^{bond}} \quad 19.110$$

From a model for $g(\sigma)$, the bonding contribution to the EOS results. For example, if $g(\sigma)$ is given by the van der Waals model,

$$Z^{bond}(\text{vdW, dimer}) = - \left[1 + \frac{\eta_P}{g_{vdW} \partial \eta_P} (g_{vdW}) \right] = - \left[1 + \frac{\eta_P}{(1 - \eta_P)} \right] = \frac{-1}{(1 - \eta_P)} \quad 19.111$$

Generalizing this result to a polymer chain with m segments, there are $(m-1)$ bonds per chain. For example, continuing with the vdW model,

$$Z^{polybond}(\text{vdW, } m\text{-mer}) = -(m-1) \left[1 + \frac{\eta_P}{(1 - \eta_P)} \right] = \frac{-(m-1)}{(1 - \eta_P)} \quad 19.112$$

This is essentially Wertheim's theory of polymerization, although Wertheim specifically treated the case resulting in a mixture with a range of molecular weights and average degree of polymerization of $\langle m \rangle$.²²

19.10 STATISTICAL ASSOCIATING FLUID THEORY (THE SAFT MODEL)

Shortly after Wertheim's work appeared, Chapman et al. formulated an equation of state that incorporated the bonding contribution and complexation as well as the disperse repulsive and attractive terms. Their perspective was to treat any solution in the conventional way as a fluid of independent spheres, then to add the bonding contribution required to assemble the spheres into chains. Then the equation of state becomes

$$Z = mZ^{HS} + (m-1)Z^{bond} + mZ^{att} + Z^{chem} \quad 19.113$$

22. Wertheim, M.S. 1986. *J. Stat. Phys.* 42:459.

Adding and subtracting $(1 - m)$ to isolate the ideal gas limit,

$$Z = mZ^{HS} + (1 - m) + (m - 1) + (m - 1)Z^{bond} + mZ^{att} + Z^{chem}$$

$$Z = 1 + m(Z^{HS} - 1) + (m - 1)(1 + Z^{bond}) + mZ^{att} + Z^{chem}$$

$$Z = 1 + m(Z^{HS} - 1) - (m - 1)\rho\partial\ln g/\partial\rho + mZ^{att} + Z^{chem} = 1 + m(Z^{HS} - 1) + Z^{chain} + mZ^{att} + Z^{chem} \quad 19.114$$

Recognizing the significance of Wertheim's statistical mechanical theory for associating (and solvating) systems, Chapman et al. named their model SAFT. In principle, any equation of state can be applied for the dispersion interactions, but Chapman et al. adopted the Carnahan-Starling model for the hard-sphere systems, including the Mansoori-Carnahan-Starling-Leland (MCSL) model for hard-sphere mixtures.²³ That choice has remained consistent in most variations of the SAFT model, but several alternatives have been adopted to describe the attractive dispersion interactions, Z^{att} . The original version suggested using second order perturbation contributions of the Lennard-Jones fluid for Z^{att} .²⁴ Huang and Radosz adopted a 20-parameter equation of state for argon (HR-SAFT).²⁵ More recently, Gross and Sadowski took a slightly different approach.²⁶ They treated the hard-sphere and chain contributions in the usual manner of SAFT, but treated Z^{att} by a second order perturbation theory that takes the tangent-sphere-chain as the reference fluid, instead of the tangent spheres themselves. They refer to their method as Perturbed Chain SAFT (PC-SAFT). In the conventional SAFT approach, Z^{att} would be a universal curve, but PC-SAFT shows a mild variation in this quantity with chain length. We focus our discussion on PC-SAFT for the most part.

Example 19.8 The SAFT model

Chapman et al. (1990)^a suggested that second order perturbation theory could be applied for the segment term of the SAFT model, with the hard-sphere contribution described by the Carnahan-Starling (CS) equation and the A^{att} given by:

$$A^{att}/RT = A_1\beta\varepsilon + A_2(\beta\varepsilon)^2$$

$$A_1 = -11.61\eta_p - 8.28\eta_p^2 - 5.24\eta_p^3 + 34.21\eta_p^4$$

$$A_2 = -25.76\eta_p + 181.87\eta_p^2 - 547.17\eta_p^3 + 529.00\eta_p^4$$

Express this model as an equation of state for alcohols, including Z^{chain} , that is $Z = Z(m, \eta_p, \beta\varepsilon)$.

Solution: The CS equation is given by $Z^{HS} - 1 = 4\eta_p(1 - \eta_p/2)/(1 - \eta_p)^3$. This corresponds to $g(\sigma) = (1 - \eta_p/2)/(1 - \eta_p)^3$ and, by Eqn. 19.44, $\Delta = \rho(1 - \eta_p/2)K^{AD}(\exp(\beta\varepsilon_{ij}^{AD}) - 1)/(1 - \eta_p)^3$.

Then, $\eta_p\partial\ln g/\partial\eta_p = \eta_p\{-0.5/(1 - \eta_p)^3 + 3(1 - \eta_p/2)/(1 - \eta_p)^4\}/g = \eta_p[-0.5/(1 - \eta_p/2) + 3/(1 - \eta_p)]$

Rearranging,

$$Z^{chain} = -(m - 1)(5\eta_p - 2\eta_p^2)/[(2 - \eta_p)(1 - \eta_p)]$$

$Z^{chem} = -0.5h\partial\ln\Delta/\partial\ln\eta_p = -(1 - X^4)\partial\ln\Delta/\partial\ln\eta_p = -(1 - X^4)\{1 + (5\eta_p - 2\eta_p^2)/[(2 - \eta_p)(1 - \eta_p)]\}$; and $Z^{att} = Z_1\beta\varepsilon + Z_2(\beta\varepsilon)^2$, where $Z_1 = -11.61\eta_p - 16.56\eta_p^2 - 15.72\eta_p^3 + 136.84\eta_p^4$ and $Z_2 = -25.76\eta_p + 363.74\eta_p^2 - 1641.51\eta_p^3 + 2116.00\eta_p^4$.

Putting it all together,

23. Mansoori, G.A., Carnahan, N.F., Starling, K.E., Leland, T.W. 1971. *J. Chem. Phys.* 54:1523.

24. Chapman, W.G., Gubbins, K.E., Jackson, G., Radosz, M. 1990. *Ind. Eng. Chem. Res.* 29:1709.

25. Huang, S.H., Radosz, M. 1990. *Ind. Eng. Chem. Res.* 29:2284.

26. Gross, J., Sadowski, G. 2001. *Ind. Eng. Chem. Res.* 40:1244.

Example 19.8 The SAFT model (Continued)

$$Z(m, \eta_P, T_r) = 1 + m[4\eta_P(1 - \eta_P/2)/(1 - \eta_P)^3 + Z_1\beta\varepsilon + Z_2(\beta\varepsilon)^2] \\ - (m - 1)(5\eta_P - 2\eta_P^2)/[(2 - \eta_P)(1 - \eta_P)] - (1 - X^A)\{1 + (5\eta_P - 2\eta_P^2)/[(2 - \eta_P)(1 - \eta_P)]\}$$

where $X^A = [-1 + (1 + 4\Delta)^{1/2}]/(2\Delta)$, $\Delta = \eta_P(1 - \eta_P/2)(K^{AD}/b)(\exp(H\beta\varepsilon) - 1)/(1 - \eta_P)^3$, $H = \varepsilon_{ij}^{AD}/\varepsilon$. Since all the terms can be computed based on $m, \eta_P, \beta\varepsilon$, the equation of state is complete.

a. Chapman, W.G., Gubbins, K.E., Jackson, G., Radosz, M. 1990. *Ind. Eng. Chem. Res.* 29:1709.

The tangent-sphere-chain that lays the foundation of all SAFT models is well defined and relatively simple to treat by molecular simulation. This makes it possible to evaluate the accuracy of Wertheim's theory for the hard chain reference system. With only slightly more effort we can also evaluate the accuracy for a reference fluid of fused sphere chains with 110° bond angles, as in n -alkane chains. As shown in Fig. 19.11, the comparison is quite favorable for tangent sphere chains, showing that Wertheim's theory and the related SAFT models have a solid theoretical foundation that is validated by molecular simulation.

The PC-SAFT model has the same form as Example 19.8 except for A^{att} .

$$(A - A^{ig})/RT = mA^{HS} + A^{chain} + mA^{att} + A^{chem} \quad 19.115$$

$$A^{att} = -12\eta_P I_1 \beta\varepsilon - 6\eta_P (\beta\varepsilon)^2 I_2 / D_2 \quad 19.116$$

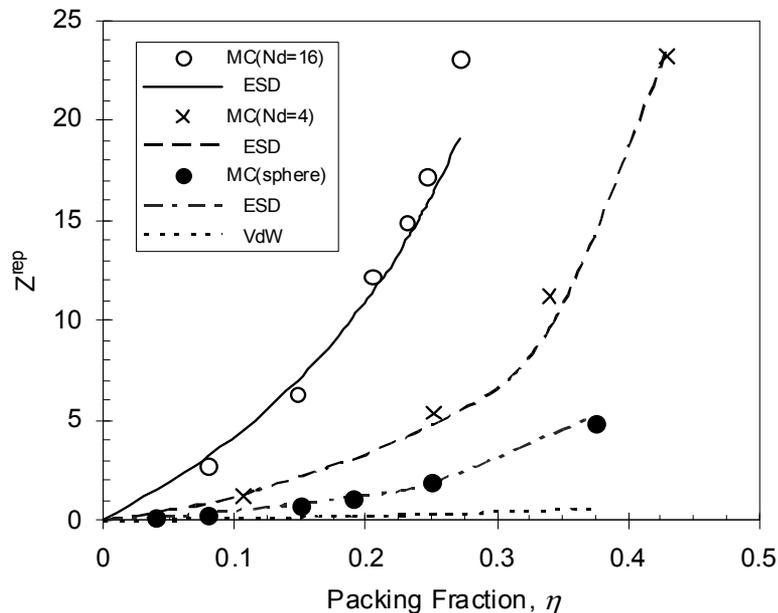


Figure 19.11 Comparison of molecular simulations, the van der Waals equation, and the ESD equation of state for Z^{rep} , where $Z^{rep} = m(Z^{HS} - 1) + Z^{chain}$. N_d is the number of spheres in a chain.

$$I_n = \sum_{j=0}^6 a_{j,n}(m) \eta_P^j \quad 19.117$$

$$a_{j,n}(m) = a_{0j,n} + a_{1j,n} \frac{(m-1)}{m} + a_{2j,n} \frac{(m-1)(m-2)}{m} \quad 19.118$$

$$D_2 = \frac{8\eta_P - 4\eta_P^2}{(1-\eta_P)^4} - \frac{(m-1)20\eta_P - 27\eta_P^2 + 12\eta_P^3 - 2\eta_P^4}{m[(1-\eta_P)(2-\eta_P)]^2} + \frac{1}{m} \quad 19.119$$

Eqns. 19.117 and 19.118 include 42 coefficients listed in the original reference.

You might wonder whether there is a simpler form of the SAFT model that is more sophisticated than the van der Waals model, but not as complicated as the PC-SAFT model. Such a model would be convenient for illustrating the key advantages of an association model without losing the simplicity of a cubic model like the PR model. One alternative is simply to add the association contribution of Example 15.8 to the PR model. This is the basis of the CPA model of Kontogeorgis et al.²⁷ This is a feasible model and it has been applied in many practical settings, but it is not entirely faithful to the Wertheim perspective in that it uses $g(\sigma)$ from one model and Z^{HS} from another, while ignoring Z^{chain} completely. Another alternative is to reconsider the ESD model in light of the SAFT analysis. Then we can rewrite the ESD model as a “simplified SAFT” model:²⁸

$$Z = 1 + q(Z^{HS} - 1 + Z^{att}) - (q-1) \frac{1.9\eta_P}{(1-1.9\eta_P)} - \frac{(1-X^A)}{(1-1.9\eta_P)} \quad 19.120$$

In this form, recognizing that $g(\sigma)=1/(1-1.9\eta_P)$ provides consistency as a SAFT model. Then,

$$Z^{HS} = 1 + \frac{4\eta_P}{(1-1.9\eta_P)}; \quad Z^{att} = \frac{(-9.5)Y\eta_P}{1+1.7745Y\eta_P} \quad 19.121$$

$$Z^{chain} = -(q-1) \frac{1.9\eta_P}{(1-1.9\eta_P)} \quad 19.122$$

$$Z^{chem} = \frac{-(1-X^A)}{(1-1.9\eta_P)} \quad (\text{pure chains}) \quad 19.123$$

19.11 FITTING THE CONSTANTS FOR AN ASSOCIATING EQUATION OF STATE

To this point in the discussion, we have assumed that the constants needed for a fluid are available. However, association models add complexity in the sense that two association parameters must be characterized in addition to the usual size (b), energy (a or ϵ), and shape (k , m , q , or c). One simple

27. Kontogeorgis, G.M., Michelsen, M.M., Folas, G.K., Derawi, S., von Solms, N., Stenby, E.H. 2006. *Ind. Eng. Chem. Res.*, 45:4855.

28. See problem 7.19, $q = 1 + 1.90476(c - 1)$. Algebraically, $4 \cdot 0.90476 / 1.90476 = 1.900$. The coefficient 1.90476 was inferred originally in a very different way, but it is entirely consistent with Wertheim's theory when $g(\sigma) = 1/(1-1.9\eta_P)$.