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

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

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, Werthiem'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 $\underline{A}^{chem}/(RT)$ can be rewritten as the stationary point of a generalized function \underline{Q} where $\underline{A}^{chem}/(RT)$ is minimized and \underline{Q} is maximized.²¹ 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 $\underline{A}^{chem}/(RT)$ a manner such that derivatives with respect to X_i^B will cancel and that $\underline{Q} = \underline{A}^{chem}/(RT)$ 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

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

Each site summation has been shifted by $\sum x_i N_{di} (1 - X_i^B)/2$. 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 .

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

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

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

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 $\underline{Q}_{sp} = \underline{A}^{chem}/(RT)$ at the stationary point compositions determined by Eqn. 19.75, we can take advantage of Eqns. 19.84 and 19.86 to obtain,

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

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

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

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

Combining Eqns. 19.44 and 19.49, $\Delta = \rho g(r) K^{AD\dagger}$ where $K^{AD\dagger} = K^{AD} [\exp(\varepsilon/(kT)) - 1]$. To simply Eqn. 19.89, consider the derivative,

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

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

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

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

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

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

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

The derivative can be simplified

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

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 $\Delta_{(\text{molec } i)(\text{molec } j)}^{AD} = (\Delta_{(\text{molec } i)(\text{molec } i)}^{AD} \Delta_{(\text{molec } j)(\text{molec } j)}^{AD})^{1/2}$, which we refer to as the square root combining rule (SRCR). The SRCR is suitable for Δ_{ij} of alcohols + aldehydes + water, but not for alcohols + amines. In general, Eqns. 19.75–19.77 require an

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iterative solution, as illustrated in Example 19.7. An initial guess for any j, B adapts the SRCR method²²

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

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

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

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

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

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

$$\ln(\hat{\phi}_k^{chem}) = \sum_{i \text{ on } k} (N_{d,i} \ln(X_i^A) + N_{d,i} \ln(X_i^D)) \quad 19.99$$

$$- \frac{0.5 b_k \rho}{(1 - \eta_p)} \left(\sum_{i \in A} x_i N_{d,i} (1 - X_i^A) + \sum_{i \in D} x_i N_{d,i} (1 - X_i^D) \right)$$

22. 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, $\Delta_{ij}^{AD} = \rho K^{AD}(\exp(\beta \varepsilon_{ij}^{AD}) - 1)/(1 - \eta_P) = \Delta$.

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

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

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

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

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

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

This gives three equations. Note that $X_t^A = X_m^A$ 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_t^B .

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

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

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

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

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

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

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

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

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

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

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

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 $X_t^A < 0.5$, and, in fact, $X_m^D \sim 2 \cdot (X_t^A - 0.5)$ because the lack of donor saturation is reflected twice, in X_t^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 $K_{mm}^{AD} = K_{mm}^{AD} = 0.72$ 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_i^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.

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

$$1 - X_t^A = 0.6 X_t^A X_m^D \Delta_{12}^{AD}; \quad 1 - X_m^D = 0.4 X_m^D X_t^A \Delta_{tm}^{AD} + 0.6 X_m^D X_m^A \Delta_{mm}^{AD};$$

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

$$X_t^A = 1 / (1 + 0.6 X_m^D \Delta_{12}^{AD}); \quad X_m^A = 1 / (1 + 0.6 X_m^D \Delta_{mm}^{AD});$$

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

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_i^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_{mm}^{AD} compared to Example 19.6 gives a 80% decrease in Δ_{mm}^{AD} . That is fairly sensitive. This change in Δ_{mm}^{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.

$$\frac{A^{bond}}{n_0RT} = \ln(X) - \left(\frac{1-X}{2}\right) = 0.5 \ln\left(\frac{1-X}{\Delta}\right) - \left(\frac{1-X}{2}\right) \rightarrow \lim_{X \rightarrow 0} \frac{A^{bond}}{n_0RT} = -0.5 \ln(\Delta) - 0.5 \quad 19.109$$

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,

$$\frac{P^{bond}V}{n_TRT} = \frac{n_0\rho}{n_T} \frac{\partial}{\partial \rho} \left(\frac{A^{bond}}{n_0RT} \right) = \frac{-2\rho}{2\Delta} \frac{\partial}{\partial \rho} (\rho g(r) K_a) = - \left[1 + \frac{\rho \partial g(r)}{g \partial \rho} \right] \equiv Z^{bond} \quad 19.110$$

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

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

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

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

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 $\langle m \rangle$.²³

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

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

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