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Memo

PC-SAFT and derivatives up to second order

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Contents

1 Introduction to PC-SAFT

PC-SAFT was introduced by Gross and Sadowski 2001 [1, 2], and is given by adding up various contributions to the Helmholtz energy

$$A^{\text{PC-SAFT}} = A^{\text{ideal}} + A^{\text{hard-chain}} + A^{\text{disp}} + A^{\text{assoc}} \tag{1}$$

Since the initial papers of Gross and Sadowski, there have been numerous versions of PC-SAFT published in the literature. We have chosen to implement sPC-SAFT, which stands for "simplified PC-SAFT". The sPC-SAFT model is described in [3] has the same pure-component parameters as the original PC-SAFT, has no appreciable loss of accuracy compared to the full PC-SAFT, but employs simplified mixing rules. The simplified mxing rules translates to faster and simpler code, especially when one wants to implement second order derivatives as we do. It is in our experience also more numerically robust. The three quantities that differ between sPC-SAFT and the original PC-SAFT are $\Delta^{A_iB_j}$. α^{hs} and g_{ij}; the functional forms for these quantities will be stated for both of the equations.

1.1 The term A^{assoc}

The standard association expression common to all SAFT variant is used for A^{assoc}, namely

$$\frac{A^{\text{assoc}}}{RT} = \sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{X_{A_i}}{2} + \frac{1}{2} \right) \tag{2}$$

where X_{A_i} is the fraction of molecules *not* bonded at site A_i, and is given by the nonlinear equation

$$X_{A_i} = \frac{1}{1 + (1/V) \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}}. \tag{3}$$

Here $\Delta^{A_iB_j}$ is called the bond association strength, and is given by

$$\Delta^{A_iB_j} = N_{\text{avo}} g_{ij} d_{ij}^3 \kappa^{A_iB_j} [\exp(\epsilon^{A_iB_j}/kT) - 1] \qquad \text{(PC-SAFT)} \tag{4}$$

$$\Delta^{A_iB_j} = N_{\text{avo}} g \sigma_{ij}^3 \kappa^{A_iB_j} [\exp(\epsilon^{A_iB_j}/kT) - 1] \qquad \text{(sPC-SAFT)} \tag{5}$$

The quantities σ_{ij}, $\kappa^{A_iB_j}$ and $\epsilon^{A_iB_j}$ in (5) are binary parameters obtained by using mixing rules on corresponding pure-component parameters σ_i, $\kappa^{A_iB_i}$ and $\epsilon^{A_iB_i}$. The radial distribution function g_{ij} is usually more complicated for PC-SAFT variants than for CPA. It is given by

$$g_{ij} = \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^2} \qquad \text{(PC-SAFT)} \tag{6}$$

$$g_{ij} = \frac{1-\eta/2}{(1-\eta)^3} \qquad \text{(sPC-SAFT)} \tag{7}$$

where

$$\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n, \qquad n = 0, 1, 2, 3, \qquad \eta = \zeta_3 \tag{8}$$

and

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3 \frac{\varepsilon_i}{kT} \right) \right]. \tag{9}$$

Unlike CPA, the radial distribution function in PC-SAFT and sPC-SAFT is temperature dependent, and thus has the potential of capturing more of the temperature dependence of the underlying physics.

1.2 The term $A^{\text{hard-chain}}$

The hard-chain part $A^{\text{hard-chain}}$ is given by

$$\frac{A^{\text{hard-chain}}}{nRT} = \bar{m}\alpha^{hs} - \sum_i x_i(m_i - 1)\ln g_{ii}^{hs}, \tag{10}$$

where the radial distribution function is given by eqs. (7) and (9), and $\bar{m}$ is the mean segment number in the mixture

$$\bar{m} = \sum_i x_i m_i, \tag{11}$$

and $\alpha^{hs} = \frac{A^{hs}}{N_s kT}$ is given by

$$\alpha^{hs} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_2^2} - \zeta_0\right)\ln(1-\zeta_3)\right] \qquad \text{(PC-SAFT)} \tag{12}$$

$$\alpha^{hs} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \qquad \text{(sPC-SAFT)} \tag{13}$$

1.3 The term A^{disp}

For the dispersion part A^{disp} of the Helmholtz energy, we have

$$\frac{A^{\text{disp}}}{nRT} = -2\pi\rho I_1(\eta,\bar{m})\overline{m^2\epsilon\sigma^3} - \pi\rho\bar{m}C_1 I_2(\eta,\bar{m})\overline{m^2\epsilon^2\sigma^3}, \tag{14}$$

where $\eta = \zeta_3$ (see equation (8)) and C_1 is the so-called compressibility expression, defined as

$$C_1 = \left(1 + Z^{\text{hard-chain}} + \rho\left(\frac{\partial Z^{\text{hard-chain}}}{\partial\rho}\right)\right)^{-1}. \tag{15}$$

We have furthermore used the abbreviations

$$\overline{m^2\epsilon\sigma^3} := \sum_{ij} x_i x_j m_i m_j \frac{\epsilon_{ij}}{kT}\sigma_{ij}^3 \tag{16}$$

$$\overline{m^2\epsilon^2\sigma^3} := \sum_{ij} x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT}\right)^2 \sigma_{ij}^3. \tag{17}$$

The parameters for a pair of unlike segments are determined by conventional one-fluid mixing rules:

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \qquad \epsilon_{ij} = \sqrt{\epsilon_i\epsilon_j}(1 - k_{ij}), \tag{18}$$

where the binary interaction parameters are regressed against experimental data. We note in passing that tue to the functional form of PC-SAFT, one can implement asymmetric interaction parameters. The quantities I_1 and I_2 are integrals approximated by truncated power series in reduced density η:

$$I_1(\eta,\bar{m}) = \sum_{i=0}^{6} a_i(\bar{m})\eta^i, \qquad I_2(\eta,\bar{m}) = \sum_{i=0}^{6} b_i(\bar{m})\eta^i \tag{19}$$

where the coefficients a_i and b_i are universal model constants given by

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m}-1}{\bar{m}}a_{1i} + \frac{\bar{m}-1}{\bar{m}}\frac{\bar{m}-2}{\bar{m}}a_{2i} \tag{20}$$

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m}-1}{\bar{m}}b_{1i} + \frac{\bar{m}-1}{\bar{m}}\frac{\bar{m}-2}{\bar{m}}b_{2i} \tag{21}$$

Finally, we mention that while the association contribution is essentially the same as in CPA, the dispersion contribution A^{disp} and the hard-chain contribution $A^{\text{hard-chain}}$ are nothing like the semi-empirical A^{cb} term in CPA. They are theoretically founded contributions to the Helmholtz energy, modeling a molecule i as a chain composed of m_i identical segments.

2 Derivatives of $\alpha^{\textbf{hard-chain}}(\rho, T, \mathbf{n})$ and $\alpha^{\textbf{disp}}(\rho, T, \mathbf{n})$

This section documents the derivatives of the Helmholtz contribution coming from $A^{\text{hard-chain}}$ and $A^{\text{dispersion}}$. Take note of the variable set we are using for α, namely $(\rho, T, \mathbf{n})$, where $\mathbf{n}$ are mole numbers, not mole fractions. Having established that these are the variables used, we drop subscripts on the derivatives.

We will present the derivatives in a modular, top-down approach. Any quantity is differentiated in terms of the derivatives of the functions which make up the expression, without performing the derivatives on these helper-functions. The formulas for the derivatives are complex, but the coded derivatives have been tested validated through numerical differentiation. (But even if the coded derivatives are correct, there may still be errors in the expression of this document.)

2.1 Derivatives of α^{disp}

$$\alpha^{disp} = -2\pi\rho I_1(\eta, \bar{m})\overline{m^2\epsilon\sigma^3} - \pi\rho\bar{m}C_1 I_2(\eta, \bar{m})\overline{m^2\epsilon^2\sigma^3} \tag{22}$$

$$\begin{aligned}\left(\frac{\partial\alpha^{disp}}{\partial\rho}\right) =& -2\pi\left(I_1 + \rho\left(\frac{\partial I_1}{\partial\rho}\right)\right)\overline{m^2\epsilon\sigma^3} - \\ & \pi\bar{m}\left(C_1 I_2 + \rho\left(\frac{\partial C_1}{\partial\rho}\right)I_2 + \rho C_1\left(\frac{\partial I_2}{\partial\rho}\right)\right)\overline{m^2\epsilon^2\sigma^3}\end{aligned} \tag{23}$$

$$\left(\frac{\partial\alpha^{disp}}{\partial T}\right) = -2\pi\rho\left[\left(\frac{\partial I_1}{\partial T}\right) - \frac{I_1}{T}\right]\overline{m^2\epsilon\sigma^3} - \pi\rho\bar{m}\left[\left(\frac{\partial C_1}{\partial T}\right)I_2 + C_1\left(\frac{\partial I_2}{\partial T}\right) - 2C_1\frac{I_2}{T}\right]\overline{m^2\epsilon^2\sigma^3} \tag{24}$$

$$\begin{aligned}\left(\frac{\partial\alpha^{disp}}{\partial n_k}\right) =& -2\pi\rho\left[I_{1,n_k}\overline{m^2\epsilon\sigma^3} + I_1(\overline{m^2\epsilon\sigma^3})_{n_k}\right] \\ & -\pi\rho\left[\left(\frac{\partial\bar{m}}{\partial n_k}\right)C_1 I_2 + \bar{m}C_{1,n_k}I_2 + \bar{m}C_1 I_{2,n_k}\right]\overline{m^2\epsilon^2\sigma^3} - \pi\rho\bar{m}C_1 I_2(\overline{m^2\epsilon^2\sigma^3})_{n_k}\end{aligned} \tag{25}$$

$$\begin{aligned}\left(\frac{\partial^2\alpha^{disp}}{\partial\rho^2}\right) =& -2\pi\left(2\left(\frac{\partial I_1}{\partial\rho}\right) + \rho\left(\frac{\partial^2 I_1}{\partial\rho^2}\right)\right)\overline{m^2\epsilon\sigma^3} - \\ & \left[2\left(\frac{\partial C_1}{\partial\rho}\right)I_2 + 2C_1\left(\frac{\partial I_2}{\partial\rho}\right) + 2\rho\left(\frac{\partial C_1}{\partial\rho}\right)\left(\frac{\partial I_2}{\partial\rho}\right) + \rho\left(\frac{\partial^2 C_1}{\partial\rho^2}\right)I_2 + \rho C_1\left(\frac{\partial^2 I_2}{\partial\rho^2}\right)\right] \\ & \cdot\pi\bar{m}\cdot\overline{m^2\epsilon^2\sigma^3}\end{aligned} \tag{26}$$

$$\begin{aligned}\left(\frac{\partial^2\alpha^{disp}}{\partial T\partial\rho}\right) =& -2\pi\left[\frac{1}{T}\left(I_1 + \rho\left(\frac{\partial I_1}{\partial\rho}\right)\right) + \left(\frac{\partial I_1}{\partial T}\right) + \rho\left(\frac{\partial^2 I_1}{\partial T\partial\rho}\right)\right]\overline{m^2\epsilon\sigma^3} + \\ & 2\pi\bar{m}\left(C_1 I_2 + \rho\left(\frac{\partial C_1}{\partial\rho}\right)I_2 + \rho C_1\left(\frac{\partial I_2}{\partial\rho}\right)\right)\frac{\overline{m^2\epsilon^2\sigma^3}}{T} - \\ & \pi\bar{m}\left[\left(\frac{\partial C_1}{\partial T}\right)I_2 + C_1\left(\frac{\partial I_2}{\partial T}\right) + \rho\left(\frac{\partial^2 C_1}{\partial T\partial\rho}\right)I_2 + \right. \\ & \left.\rho\left(\frac{\partial C_1}{\partial\rho}\right)\left(\frac{\partial I_2}{\partial T}\right) + \rho\left(\frac{\partial C_1}{\partial T}\right)\left(\frac{\partial I_2}{\partial\rho}\right) + \rho C_1\left(\frac{\partial^2 I_2}{\partial T\partial\rho}\right)\right]\overline{m^2\epsilon^2\sigma^3}\end{aligned} \tag{27}$$

$$
\begin{aligned}
\left(\frac{\partial^2 \alpha^{disp}}{\partial \rho \partial n_k}\right) =& -2\pi \left[I_{1,n_k}\overline{m^2\epsilon\sigma^3} + I_1(\overline{m^2\epsilon\sigma^3})_{n_k}\right] - 2\pi\rho\left[I_{1,n_k\rho}\overline{m^2\epsilon\sigma^3} + I_{1,\rho}(\overline{m^2\epsilon\sigma^3})_{n_k}\right] \\
& -\pi\left[\left(\frac{\partial \bar{m}}{\partial n_k}\right)C_1 I_2 + \bar{m}C_{1,n_k}I_2 + \bar{m}C_1 I_{2,n_k}\right]\overline{m^2\epsilon^2\sigma^3} - \pi\bar{m}C_1I_2(\overline{m^2\epsilon^2\sigma^3})_{n_k} \\
& -\pi\rho\left[\left(\frac{\partial \bar{m}}{\partial n_k}\right)C_{1,\rho}I_2 + \bar{m}C_{1,n_k\rho}I_2 + \bar{m}C_{1,\rho}I_{2,n_k} + \right. \\
& \left.\left(\frac{\partial \bar{m}}{\partial n_k}\right)C_1 I_{2,\rho} + \bar{m}C_{1,n_k}I_{2,\rho} + \bar{m}C_1 I_{2,n_k\rho}\right]\overline{m^2\epsilon^2\sigma^3} - \\
& \pi\rho\bar{m}\left(\left(\frac{\partial C_1}{\partial \rho}\right)I_2 + C_1\left(\frac{\partial I_2}{\partial \rho}\right)\right)(\overline{m^2\epsilon^2\sigma^3})_{n_k}
\end{aligned} \tag{28}
$$

$$
\begin{aligned}
\left(\frac{\partial^2 \alpha^{disp}}{\partial T^2}\right) =& -2\pi\rho\left[\left(\frac{\partial^2 I_1}{\partial T^2}\right) + 2\frac{I_1}{T^2} - 2\frac{1}{T}\left(\frac{\partial I_1}{\partial T}\right)\right]\overline{m^2\epsilon\sigma^3} - \\
& \pi\rho\bar{m}\left[-\frac{4}{T}\left(\left(\frac{\partial C_1}{\partial T}\right)I_2 + C_1\left(\frac{\partial I_2}{\partial T}\right)\right) + \frac{8C_1I_2}{T^2} + \right. \\
& \left.\left(\frac{\partial C_1}{\partial T}\right)I_2 + 2\left(\frac{\partial C_1}{\partial T}\right)\left(\frac{\partial I_2}{\partial T}\right) + C_1\left(\frac{\partial^2 I_2}{\partial T^2}\right)\right]\overline{m^2\epsilon^2\sigma^3}
\end{aligned} \tag{29}
$$

$$
\begin{aligned}
\left(\frac{\partial^2 \alpha^{disp}}{\partial n_k \partial T}\right) =& -2\pi\rho\left[\left(\frac{\partial^2 I_1}{\partial n_k \partial T}\right) - \frac{1}{T}\left(\frac{\partial I_1}{\partial n_k}\right)\right]\overline{m^2\epsilon\sigma^3} - 2\pi\rho\left[\left(\frac{\partial I_1}{\partial T}\right) - \frac{I_1}{T}\right](\overline{m^2\epsilon\sigma^3})_{n_k} - \\
& \pi\rho\left(\left(\frac{\partial \bar{m}}{\partial n_k}\right)\cdot\overline{m^2\epsilon^2\sigma^3} + \bar{m}(\overline{m^2\epsilon^2\sigma^3})_{n_k}\right)\left[\left(\frac{\partial C_1}{\partial T}\right)I_2 + C_1\left(\frac{\partial I_2}{\partial T}\right) - 2C_1\frac{I_2}{T}\right] - \\
& \pi\rho\bar{m}\left[\left(\frac{\partial^2 C_1}{\partial n_k \partial T}\right)I_2 + \left(\frac{\partial C_1}{\partial n_k}\right)\left(\frac{\partial I_2}{\partial T}\right) - 2\left(\frac{\partial C_1}{\partial n_k}\right)\frac{I_2}{T} + \right. \\
& \left.\left(\frac{\partial C_1}{\partial T}\right)\left(\frac{\partial I_2}{\partial n_k}\right) + C_1\left(\frac{\partial^2 I_2}{\partial n_k \partial T}\right) - \frac{2}{T}C_1\left(\frac{\partial I_2}{\partial n_k}\right)\right]\overline{m^2\epsilon^2\sigma^3}
\end{aligned} \tag{30}
$$

$$
\begin{aligned}
\left(\frac{\partial^2 \alpha^{disp}}{\partial n_l \partial n_k}\right) =& -2\pi\rho\left[I_{1,n_kn_l}\overline{m^2\epsilon\sigma^3} + I_{1,n_l}(\overline{m^2\epsilon\sigma^3})_{n_k} + I_{1,n_k}(\overline{m^2\epsilon\sigma^3})_{n_l} + I_1(\overline{m^2\epsilon\sigma^3})_{n_kn_l}\right] - \\
& \pi\rho\left[\left(\frac{\partial \bar{m}}{\partial n_k}\right)C_1I_2 + \bar{m}C_{1,n_k}I_2 + \bar{m}C_1I_{2,n_k}\right](\overline{m^2\epsilon^2\sigma^3})_{n_l} - \\
& \pi\rho\left[\left(\frac{\partial \bar{m}}{\partial n_k}\right)(C_{1,n_l}I_2 + C_1I_{2,n_l}) + (\left(\frac{\partial \bar{m}}{\partial n_l}\right)C_{1,n_k}I_2 + \bar{m}C_{1,n_kn_l}I_2 + \bar{m}C_{1,n_k}I_{2,n_l}) + \right. \\
& \left.(\left(\frac{\partial \bar{m}}{\partial n_l}\right)C_1I_{2,n_k} + \bar{m}C_{1,n_l}I_{2,n_k} + \bar{m}C_1I_{2,n_kn_l})\right]\overline{m^2\epsilon^2\sigma^3} - \\
& \pi\rho\bar{m}C_1I_2(\overline{m^2\epsilon^2\sigma^3})_{n_kn_l} - \\
& \pi\rho(\left(\frac{\partial \bar{m}}{\partial n_l}\right)C_1I_2 + \bar{m}C_{1,n_l}I_2 + \bar{m}C_1I_{2,n_l})(\overline{m^2\epsilon^2\sigma^3})_{n_k}
\end{aligned} \tag{31}
$$

2.2 Derivatives of α^{hc}

$$
\alpha^{hc} = \bar{m}\alpha^{hs} - \sum_i x_i(m_i - 1)\ln g_{ii}^{hs} = \bar{m}\alpha^{hs} - G, \tag{32}
$$

where we have defined the helper function G.

$$\left(\frac{\partial \alpha^{hc}}{\partial \rho}\right) = \bar{m}\left(\frac{\partial \alpha^{hs}}{\partial \rho}\right) - \left(\frac{\partial G}{\partial \rho}\right) \tag{33}$$

$$\left(\frac{\partial \alpha^{hc}}{\partial T}\right) = \bar{m}\left(\frac{\partial \alpha^{hs}}{\partial T}\right) - \left(\frac{\partial G}{\partial T}\right) \tag{34}$$

$$\left(\frac{\partial \alpha^{hc}}{\partial n_k}\right) = \left(\frac{\partial \bar{m}}{\partial n_k}\right)\alpha^{hs} - \left(\frac{\partial G}{\partial n_k}\right) \tag{35}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial \rho^2}\right) = \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial \rho^2}\right) - \left(\frac{\partial^2 G}{\partial \rho^2}\right) \tag{36}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial \rho \partial T}\right) = \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial \rho \partial T}\right) - \left(\frac{\partial^2 G}{\partial \rho \partial T}\right) \tag{37}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial \rho \partial n_k}\right) = \left(\frac{\partial \bar{m}}{\partial n_k}\right)\left(\frac{\partial \alpha^{hs}}{\partial \rho}\right) + \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial \rho \partial n_k}\right) - \left(\frac{\partial^2 G}{\partial \rho \partial n_k}\right) \tag{38}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial T^2}\right) = \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial T^2}\right) - \left(\frac{\partial^2 G}{\partial T^2}\right) \tag{39}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial T \partial n_k}\right) = \left(\frac{\partial \bar{m}}{\partial n_k}\right)\left(\frac{\partial \alpha^{hs}}{\partial T}\right) + \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial T \partial n_k}\right) - \left(\frac{\partial^2 G}{\partial T \partial n_k}\right) \tag{40}$$

$$\left(\frac{\partial^2 \alpha^{hc}}{\partial n_l \partial n_k}\right) = \left(\frac{\partial \bar{m}}{\partial n_k}\right)\left(\frac{\partial \alpha^{hs}}{\partial n_l}\right) + \left(\frac{\partial \bar{m}}{\partial n_l}\right)\left(\frac{\partial \alpha^{hs}}{\partial n_k}\right) + \bar{m}\left(\frac{\partial^2 \alpha^{hs}}{\partial n_l \partial n_k}\right) - \left(\frac{\partial^2 G}{\partial n_l \partial n_k}\right) \tag{41}$$

Derivatives of the helper function G

$$G = \sum_i x_i(m_i - 1)\ln g_{ii}^{hs} \tag{42}$$

$$\left(\frac{\partial G}{\partial \rho}\right) = \sum_i x_i(m_i - 1)\frac{1}{g_{ii}^{hs}}\left(\frac{\partial g_{ii}^{hs}}{\partial \rho}\right) \tag{43}$$

$$\left(\frac{\partial G}{\partial T}\right) = \sum_i x_i(m_i - 1)\frac{1}{g_{ii}^{hs}}\left(\frac{\partial g_{ii}^{hs}}{\partial T}\right) \tag{44}$$

$$\left(\frac{\partial G}{\partial n_k}\right) = \frac{m_k - 1}{n}\ln g_{kk}^{hs} + \sum_i x_i(m_i - 1)\frac{1}{g_{ii}^{hs}}\left(\frac{\partial g_{ii}}{\partial n_k}\right) - \frac{G}{n} \tag{45}$$

$$\left(\frac{\partial^2 G}{\partial \rho^2}\right) = \sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial \rho}\right)^2 + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial \rho^2}\right)\right] \tag{46}$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right) = \sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial T}\right)^2 + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial T^2}\right)\right] \tag{47}$$

$$\left(\frac{\partial^2 G}{\partial \rho \partial T}\right) = \sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial \rho}\right)\left(\frac{\partial g_{ii}^{hs}}{\partial T}\right) + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial \rho \partial T}\right)\right] \tag{48}$$

$$\left(\frac{\partial^2 G}{\partial \rho \partial n_k}\right) = \frac{m_k - 1}{n g_{kk}^{hs}} \left(\frac{\partial g_{kk}^{hs}}{\partial \rho}\right) + \tag{49}$$

$$\sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial \rho}\right)\left(\frac{\partial g_{ii}^{hs}}{\partial n_k}\right) + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial \rho \partial n_k}\right)\right] - \frac{1}{n}\left(\frac{\partial G}{\partial \rho}\right) \tag{50}$$

$$\begin{aligned}\left(\frac{\partial^2 G}{\partial T \partial n_k}\right) =& \frac{m_k - 1}{n g_{kk}^{hs}} \left(\frac{\partial g_{kk}^{hs}}{\partial T}\right) + \\ & \sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial T}\right)\left(\frac{\partial g_{ii}^{hs}}{\partial n_k}\right) + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial T \partial n_k}\right)\right] - \frac{1}{n}\left(\frac{\partial G}{\partial T}\right)\end{aligned} \tag{51}$$

$$\begin{aligned}\left(\frac{\partial^2 G}{\partial n_l \partial n_k}\right) =& \frac{m_k - 1}{n g_{kk}^{hs}} \left(\frac{\partial g_{kk}^{hs}}{\partial n_l}\right) + \frac{m_l - 1}{n g_{ll}^{hs}} \left(\frac{\partial g_{ll}}{\partial n_k}\right) \\ & + \sum_i x_i(m_i - 1)\left[-\frac{1}{(g_{ii}^{hs})^2}\left(\frac{\partial g_{ii}^{hs}}{\partial n_l}\right)\left(\frac{\partial g_{ii}^{hs}}{\partial n_k}\right) + \frac{1}{g_{ii}^{hs}}\left(\frac{\partial^2 g_{ii}^{hs}}{\partial n_l \partial n_k}\right)\right] \\ & - \frac{1}{n}\left(\frac{\partial G}{\partial n_k}\right) - \frac{1}{n}\left(\frac{\partial G}{\partial n_l}\right)\end{aligned} \tag{52}$$

2.3 Derivatives of α^{hs}

$$\alpha^{hs} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{53}$$

$$\left(\frac{\partial \alpha^{hs}}{\partial \eta}\right) = \frac{2(\eta - 2)}{(1-\eta)^2} \tag{54}$$

$$\left(\frac{\partial^2 \alpha^{hs}}{\partial \eta^2}\right) = \frac{2(5 - 2\eta)}{(1-\eta)^4} \tag{55}$$

2.4 Derivatives of g_{ij}

$$g_{ij} = \frac{1 - \eta/2}{(1-\eta)^3} \tag{56}$$

$$\left(\frac{\partial g_{ij}}{\partial \eta}\right) = \frac{5 - 2\eta}{(2(1-\eta))^4} \tag{57}$$

$$\left(\frac{\partial^2 g_{ij}}{\partial \eta^2}\right) = \frac{3(\eta - 3)}{(\eta - 1)^5} \tag{58}$$

2.5 Derivatives of $\overline{m^2\epsilon\sigma^3}$

Define the constant $D_{ij} = m_i m_j \frac{\epsilon_{ij}}{k}\sigma_{ij}^3$. Note that $D_{ij} \neq D_{ji}$ if $k_{ij} \neq k_{ji}$.

$$\overline{m^2\epsilon\sigma^3} = \sum_{i,j} x_i x_j D_{ij}/T \tag{59}$$

$$(\overline{m^2\epsilon\sigma^3})_T = -\frac{\overline{m^2\epsilon\sigma^3}}{T} \tag{60}$$

$$(\overline{m^2\epsilon\sigma^3})_{n_k} = \frac{-2(\overline{m^2\epsilon\sigma^3})}{n} + \sum_i \frac{n_i}{n^2}\frac{D_{ik}+D_{ki}}{T} \tag{61}$$

$$(\overline{m^2\epsilon\sigma^3})_{TT} = 2\frac{\overline{m^2\epsilon\sigma^3}}{T^2} \tag{62}$$

$$(\overline{m^2\epsilon\sigma^3})_{T,n_k} = (\overline{m^2\epsilon\sigma^3})_{n_k}/T \tag{63}$$

$$(\overline{m^2\epsilon\sigma^3})_{n_k,n_l} = \frac{2(\overline{m^2\epsilon\sigma^3})}{n^2} - \frac{2(\overline{m^2\epsilon\sigma^3})_{n_l}}{n} - \sum_i \frac{2n_i}{n^3}\frac{D_{ik}+D_{ki}}{T} + \frac{1}{n^2}\frac{D_{lk}+D_{kl}}{T} \tag{64}$$

2.6 Derivatives of $\overline{m^2\epsilon^2\sigma^3}$

Define the constant $E_{ij} = m_i m_j \left(\frac{\epsilon_{ij}}{k}\right)^2 \sigma_{ij}^3$. Note that $E_{ij} \neq E_{ji}$ if $k_{ij} \neq k_{ji}$.

$$\overline{m^2\epsilon^2\sigma^3} = \sum_{i,j} x_i x_j E_{ij}/T^2 \tag{65}$$

$$(\overline{m^2\epsilon^2\sigma^3})_T = -2\frac{\overline{m^2\epsilon^2\sigma^3}}{T} \tag{66}$$

$$(\overline{m^2\epsilon\sigma^3})_{n_k} = \frac{-2(\overline{m^2\epsilon^2\sigma^3})}{n} + \sum_i \frac{n_i}{n^2}\frac{E_{ik}+E_{ki}}{T^2} \tag{67}$$

$$(\overline{m^2\epsilon\sigma^3})_{TT} = 6\frac{\overline{m^2\epsilon\sigma^3}}{T^3} \tag{68}$$

$$(\overline{m^2\epsilon\sigma^3})_{T,n_k} = (\overline{m^2\epsilon\sigma^3})_{n_k}/T \tag{69}$$

$$(\overline{m^2\epsilon\sigma^3})_{n_k,n_l} = \frac{2(\overline{m^2\epsilon\sigma^3})}{n^2} - \frac{2(\overline{m^2\epsilon\sigma^3})_{n_l}}{n} - \sum_i \frac{2n_i}{n^3}\frac{D_{ik}+D_{ki}}{T^2} + \frac{1}{n^2}\frac{D_{lk}+D_{kl}}{T^2} \tag{70}$$

2.7 Derivatives of I_1 and I_2

$$I_1(\eta,\bar{m}) = \sum_{i=0}^{6} a_i(\bar{m})\eta^i, \qquad I_2(\eta,\bar{m}) = \sum_{i=0}^{6} b_i(\bar{m})\eta^i \tag{71}$$

$$I_{1,\rho} = I_{1,\rho}\eta_\rho \tag{72}$$
$$I_{2,\rho} = I_{2,\rho}\eta_\rho \tag{73}$$

$$I_{1,T} = I_{1,\eta}\eta_T \tag{74}$$
$$I_{2,T} = I_{2,\eta}\eta_T \tag{75}$$

$$I_{1,n_k} = \sum_{i=0}^{6} a_{i,n_k}\eta^i + I_{1,\eta}\eta_{n_k} \tag{76}$$
$$I_{2,n_k} = \sum_{i=0}^{6} b_{i,n_k}\eta^i + I_{2,\eta}\eta_{n_k} \tag{77}$$

$$I_{1,\rho\rho} = I_{1,\rho\rho}\eta_\rho^2 + I_{1,\rho}\eta_{\rho\rho} \tag{78}$$
$$I_{2,\rho\rho} = I_{2,\rho\rho}\eta_\rho^2 + I_{2,\rho}\eta_{\rho\rho} \tag{79}$$

$$I_{1,\rho T} = I_{1,\rho\eta}\eta_\rho\eta_T + I_{1,\eta}\eta_{\rho T} \tag{80}$$
$$I_{2,\rho T} = I_{2,\rho\eta}\eta_\rho\eta_T + I_{2,\eta}\eta_{\rho T} \tag{81}$$

$$I_{1,\rho n_k} = \sum_{i=0}^{6} a_{i,n_k} i\eta^{i-1}\eta_\rho + I_{1,\eta\eta}\eta_{n_k}\eta_\rho + I_{1,\eta}\eta_{\rho n_k} \tag{82}$$
$$I_{2,\rho n_k} = \sum_{i=0}^{6} b_{i,n_k} i\eta^{i-1}\eta_\rho + I_{2,\eta\eta}\eta_{n_k}\eta_\rho + I_{2,\eta}\eta_{\rho n_k} \tag{83}$$

$$I_{1,TT} = I_{1,TT}\eta_T^2 + I_{1,T}\eta_{TT} \tag{84}$$
$$I_{2,TT} = I_{2,TT}\eta_T^2 + I_{2,T}\eta_{TT} \tag{85}$$

$$I_{1,Tn_k} = \sum_{i=0}^{6} a_{i,n_k} i\eta^{i-1}\eta_T + I_{1,\eta\eta}\eta_{n_k}\eta_T + I_{1,\eta}\eta_{Tn_k} \tag{86}$$
$$I_{2,Tn_k} = \sum_{i=0}^{6} b_{i,n_k} i\eta^{i-1}\eta_T + I_{2,\eta\eta}\eta_{n_k}\eta_T + I_{2,\eta}\eta_{Tn_k} \tag{87}$$

$$I_{1,n_l n_k} = \sum_{i=0}^{6} (a_{i,n_l n_k}\eta^i + i\eta^{i-1}[a_{i,n_k}\eta_{n_l} + a_{i,n_l}\eta_{n_k}]) + I_{1,\eta\eta}\eta_{n_k}\eta_{n_l} \tag{88}$$
$$I_{2,n_l n_k} = \sum_{i=0}^{6} (b_{i,n_l n_k}\eta^i + i\eta^{i-1}[b_{i,n_k}\eta_{n_l} + b_{i,n_l}\eta_{n_k}]) + I_{2,\eta\eta}\eta_{n_k}\eta_{n_l} \tag{89}$$

Auxiliary derivatives

$$I_{1,\eta} = \sum_{i=1}^{6} i a_i \eta^{i-1}, \qquad I_{2,\eta} = \sum_{i=1}^{6} i b_i \eta^{i-1} \tag{90}$$

$$I_{1,\eta\eta} = \sum_{i=2}^{6} i(i-1) a_i \eta^{i-2}, \qquad I_{2,\eta\eta} = \sum_{i=2}^{6} i(i-1) b_i \eta^{i-2} \tag{91}$$

2.8 Derivatives of a_i and b_i

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m}-1}{\bar{m}} a_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2i} \tag{92}$$

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m}-1}{\bar{m}} b_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} b_{2i} \tag{93}$$

$$a_{i,n_k} = \frac{\bar{m}_{n_k}}{\bar{m}^2} a_{1i} + \frac{\bar{m}_{n_k}}{\bar{m}^2} \left(3 - \frac{4}{\bar{m}}\right) a_{2i} \tag{94}$$

$$b_{i,n_k} = \frac{\bar{m}_{n_k}}{\bar{m}^2} b_{1i} + \frac{\bar{m}_{n_k}}{\bar{m}^2} \left(3 - \frac{4}{\bar{m}}\right) b_{2i} \tag{95}$$

$$a_{i,n_k n_l} = \frac{\bar{m}_{n_k} \bar{m}_{n_l}}{\bar{m}^3} \left(-2a_{1i} - 6a_{2i} + \frac{12}{\bar{m}} a_{2i}\right) \tag{96}$$

$$b_{i,n_k n_l} = \frac{\bar{m}_{n_k} \bar{m}_{n_l}}{\bar{m}^3} \left(-2b_{1i} - 6b_{2i} + \frac{12}{\bar{m}} b_{2i}\right) \tag{97}$$

All other derivatives are zero.

2.9 Derivatives of C_1

$$C_1 = \left(1 + \bar{m} \frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-\bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{(1-\eta)^2 (2-\eta)^2}\right)^{-1} \tag{98}$$

$$\left(\frac{\partial C_1}{\partial \rho}\right) = \left(\frac{\partial C_1}{\partial \eta}\right) \eta_\rho \tag{99}$$

$$\left(\frac{\partial C_1}{\partial T}\right) = \left(\frac{\partial C_1}{\partial \eta}\right) \eta_T \tag{100}$$

$$\left(\frac{\partial^2 C_1}{\partial \rho^2}\right) = \left(\frac{\partial^2 C_1}{\partial \eta^2}\right) \eta_\rho^2 + \left(\frac{\partial C_1}{\partial \eta}\right) \eta_{\rho\rho} \tag{101}$$

$$\left(\frac{\partial^2 C_1}{\partial \rho \partial T}\right) = \left(\frac{\partial^2 C_1}{\partial \eta^2}\right) \eta_\rho \eta_T + \left(\frac{\partial C_1}{\partial \eta}\right) \eta_{\rho T} \tag{102}$$

$$\left(\frac{\partial^2 C_1}{\partial T^2}\right) = \left(\frac{\partial^2 C_1}{\partial \eta^2}\right) \eta_T^2 + \left(\frac{\partial C_1}{\partial \eta}\right) \eta_{TT} \tag{103}$$

Auxiliary derivatives

$$\left(\frac{\partial C_1}{\partial \eta}\right) = -C_1^2\left(\bar{m}\frac{-4\eta^2+20\eta+8}{(1-\eta)^5} + (1-\bar{m})\frac{2\eta^3+12\eta^2-48\eta+40}{(1-\eta)^3(2-\eta)^3}\right) \tag{104}$$

$$\begin{aligned}\left(\frac{\partial^2 C_1}{\partial \eta^2}\right) &= \frac{2}{C_1}\left(\frac{\partial C_1}{\partial \eta}\right)^2 \\ &- C_1^2\bar{m}\frac{(-8\eta+20)(1-\eta)+(-4\eta^2+20\eta+8)5}{(1-\eta)^6} \\ &- C_1^2(1-\bar{m})\frac{(6\eta^2+24\eta-48)(1-\eta)(2-\eta)+(2\eta^3+12\eta^2-48\eta+40)[3(2-\eta)+3(1-\eta)]}{(1-\eta)^4(2-\eta)^4}\end{aligned} \tag{105}$$

2.10 Derivatives of ζ_n

$$\zeta_n = \frac{\pi}{6}\rho\sum_i x_i m_i d_i^n \tag{106}$$

$$\zeta_{n,\rho} = \frac{\pi}{6}\sum_i x_i m_i d_i^n \tag{107}$$

$$\zeta_{n,T} = \begin{cases} 0 & n=0 \\ \frac{\pi}{6}\rho n \sum_i x_i m_i d_i^{n-1} d_{i,T} & n=1,2,3 \end{cases} \tag{108}$$

$$\zeta_{n,n_k} = \frac{1}{n}\frac{\pi}{6}\rho m_k d_k^n - \frac{\zeta_n}{n} \tag{109}$$

$$\zeta_{n,\rho\rho} = 0 \tag{110}$$

$$\zeta_{n,\rho T} = \zeta_{n,T}/\rho \tag{111}$$

$$\zeta_{n,\rho n_k} = \zeta_{n,n_k}/\rho \tag{112}$$

$$\zeta_{n,TT} = \begin{cases} 0 & n=0 \\ \frac{\pi}{6}\rho n \sum_i x_i m_i d_{i,TT} & n=1 \\ \frac{\pi}{6}\rho n \sum_i x_i m_i \left[(n-1)d_i^{n-2}d_{i,T}^2 + d_i^{n-1}d_{i,TT}\right] & n=2,3 \end{cases} \tag{113}$$

$$\zeta_{n,Tn_k} = \begin{cases} 0 & n=0 \\ \frac{\pi}{6}\rho n\left(\frac{1}{n} - \frac{x_k}{n}\right) m_k d_k^{n-1} d_{k,T} & n=1,2,3 \end{cases} \tag{114}$$

$$\zeta_{n,n_k n_l} = -\frac{\zeta_{n,n_k}+\zeta_{n,n_l}}{n} + \frac{\zeta_n}{n^2} \tag{115}$$

2.11 Derivatives of d_i

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3\frac{\varepsilon_i}{kT}\right)\right]. \tag{116}$$

$$\left(\frac{\partial d_i}{\partial T}\right) = -\frac{0.36\varepsilon_i}{kT^2}\sigma_i \exp\left(-3\frac{\varepsilon_i}{kT}\right) \tag{117}$$

$$\left(\frac{\partial^2 d_i}{\partial T^2}\right) = \sigma_i \exp\left(-3\frac{\varepsilon_i}{kT}\right)\left(\frac{0.72\varepsilon_i}{kT^3} - \frac{1.08\varepsilon_i^2}{k^2T^4}\right) \tag{118}$$

The other derivatives of d_i are zero.

3 Derivatives of A^{assoc}

In the following we will document the derivatives of $F^{\mathrm{assoc}}(T, V, \mathbf{n}) = A^{\mathrm{assoc}}(T, V, \mathbf{n})/RT$ up to second order.

3.1 The Q function and its relation to F^{assoc}

Define the function

$$Q(\mathbf{n}, T, V, \mathbf{X}) = \sum_i \sum_{A_i} n_i \left(\ln X_{A_i} - X_{A_i} + 1\right) - \frac{1}{2V} \sum_{i,j} \sum_{A_i, B_j} n_i n_j X_{A_i} X_{B_j} \Delta^{A_i B_j}. \tag{119}$$

Here $\Delta^{A_i B_j} = \Delta^{A_i B_j}(T, V, \mathbf{n})$ is the bond association strength. If $\mathbf{X}$ solves the equations

$$\left(\frac{\partial Q}{\partial \mathbf{X}}\right)(T, V, \mathbf{n}, X) = \mathbf{0}, \quad \text{i.e.} \quad \frac{1}{X_{A_i}} - 1 - \frac{1}{V}\sum_j \sum_{B_j} n_j X_{B_j} \Delta^{A_i B_j} = 0 \quad \forall\ X_{A_i}. \tag{120}$$

then the resulting solution $\mathbf{X} = \mathbf{X}(T, V, \mathbf{n})$ is such that[1]

$$F^{\mathrm{assoc}}(T, V, \mathbf{n}) = Q(T, V, \mathbf{n}, \mathbf{X}(T, V, \mathbf{n})). \tag{121}$$

We now clarify the notation used below in the expressions for the derivatives. Given a differential operator ∂, we will in the following use ∂Q_{sp} to mean $(\partial Q)(T, V, \mathbf{n}, \mathbf{X}(T, V, \mathbf{n}))$. For example, $\left(\frac{\partial Q_{sp}}{\partial V}\right) = \left(\frac{\partial Q}{\partial V}\right)(T, V, \mathbf{n}, \mathbf{X}(T, V, \mathbf{n}))$. Moreover, to avoid subscripting every partial derivative to show which variables are fixed, we agree once and for all that F^{assoc} has $(T, V, \mathbf{n})$ as independent variables, while Q has $(T, V, \mathbf{n}, \mathbf{X})$ as independent variables. The equality (121) can also be stated as $F^{\mathrm{assoc}} = Q|_{\mathbf{X}=\mathbf{X}(T,V,\mathbf{n})}$.

3.2 First-order derivatives of F^{assoc}

We find that

$$\begin{aligned}\left(\frac{\partial F^{\mathrm{assoc}}}{\partial V}\right) &= \left(\frac{\partial Q_{sp}}{\partial V}\right) + \sum_i \sum_{A_i} \left(\frac{\partial Q_{sp}}{\partial X_{A_i}}\right)\left(\frac{\partial X_{A_i}}{\partial V}\right) \\ &= \left(\frac{\partial Q_{sp}}{\partial V}\right),\end{aligned}$$

since $\left(\frac{\partial Q_{sp}}{\partial X_{A_i}}\right) = 0$. Similarly, we have

$$\left(\frac{\partial F^{\mathrm{assoc}}}{\partial T}\right) = \left(\frac{\partial Q_{sp}}{\partial T}\right) \quad \text{and} \quad \left(\frac{\partial F^{\mathrm{assoc}}}{\partial n_k}\right) = \left(\frac{\partial Q_{sp}}{\partial n_k}\right).$$

[1] Where $F^{\mathrm{assoc}}(T, V, \mathbf{n}) = A^R(T, V, \mathbf{n})/RT$ and A^R is the association contribution to the residual Helmholtz energy.

3.2.1 Volume derivative

$$\left(\frac{\partial F^{\text{assoc}}}{\partial V}\right) = \left(\frac{\partial Q_{sp}}{\partial V}\right) \tag{122}$$
$$= \frac{1}{2V} \sum_{i,j} \sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j} \left[\frac{\Delta^{A_i B_j}}{V} - \left(\frac{\partial \Delta^{A_i B_j}}{\partial V}\right)\right].$$

3.2.2 Temperature derivative

$$\left(\frac{\partial F^{\text{assoc}}}{\partial T}\right) = \left(\frac{\partial Q_{sp}}{\partial T}\right) \tag{123}$$
$$= -\frac{1}{2V} \sum_{i,j} \sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j} \left(\frac{\partial \Delta^{A_i B_j}}{\partial T}\right).$$

3.2.3 Composition derivative

$$\left(\frac{\partial F^{\text{assoc}}}{\partial n_k}\right) = \left(\frac{\partial Q_{sp}}{\partial n_k}\right)$$
$$= \sum_{A_k} (\ln X_{A_k} - X_{A_k} + 1) - \frac{1}{V} \sum_{j} \sum_{A_k,B_j} n_j X_{A_k} X_{B_j} \Delta^{A_k B_j} \tag{124}$$
$$- \frac{1}{2V} \sum_{i,j} \sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j} \left(\frac{\partial \Delta^{A_i B_j}}{\partial n_k}\right) \tag{125}$$
$$= \sum_{A_k} \ln X_{A_k} - \frac{1}{2V} \sum_{i,j} \sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j} \left(\frac{\partial \Delta^{A_i B_j}}{\partial n_k}\right). \tag{126}$$

3.3 Second-order derivatives of F^{assoc}

Let the variables ζ_1, ζ_2 each equal one of the scalar variables in $(T, V, \mathbf{n})$. Recalling that

$$\left(\frac{\partial F^{assoc}}{\partial \zeta_1}\right)(T, V, \mathbf{n}) = \left(\frac{\partial Q}{\partial \zeta_1}\right)(T, V, \mathbf{n}, \mathbf{X}(T, V, \mathbf{n})),$$

we get

$$\left(\frac{\partial^2 F^{\text{assoc}}}{\partial \zeta_2 \partial \zeta_1}\right) = \frac{\partial}{\partial \zeta_2}\left(\frac{\partial F^{\text{assoc}}}{\partial \zeta_1}\right) \tag{127}$$
$$= \left(\frac{\partial^2 Q_{sp}}{\partial \zeta_2 \partial \zeta_1}\right) + \left(\frac{\partial^2 Q_{sp}}{\partial \zeta_1 \partial \mathbf{X}}\right)\left(\frac{\partial \mathbf{X}}{\partial \zeta_2}\right). \tag{128}$$

We once again stress the meaning of our notation: in the first term of (128), $\mathbf{X}$ is to be treated as a constant when the cross-derivative is taken. Now, the expression (128) involves the derivative $\partial \mathbf{X}/\partial \zeta_2$. To find this derivative, we differentiate the defining relation for $X(T, V, \mathbf{n})$, namely $\left(\frac{\partial Q}{\partial \mathbf{X}}\right) = \mathbf{0}$. Doing this (and taking care to transpose vectors correctly), we get

$$\mathbf{0} = \frac{\partial}{\partial \zeta_2}\left(\frac{\partial Q_{sp}}{\partial \mathbf{X}}\right) = \left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X} \partial \zeta_2}\right) + \left(\frac{\partial \mathbf{X}}{\partial \zeta_2}\right)^t \left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}^2}\right), \tag{129}$$

yielding

$$\left(\frac{\partial \mathbf{X}}{\partial \zeta_2}\right) = -\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}^2}\right)^{-1}\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}\partial \zeta_2}\right)^t. \tag{130}$$

In conclusion, the formula for the second derivative is obtained by combining (128) and (130):

$$\left(\frac{\partial^2 F^{\text{assoc}}}{\partial \zeta_2\partial \zeta_1}\right) = \left(\frac{\partial^2 Q_{sp}}{\partial \zeta_2\partial \zeta_1}\right) - \left(\frac{\partial^2 Q_{sp}}{\partial \zeta_1\partial \mathbf{X}}\right)\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}^2}\right)^{-1}\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}\partial \zeta_2}\right)^t. \tag{131}$$

Or, if one prefers summation notation:

$$\left(\frac{\partial^2 F^{\text{assoc}}}{\partial \zeta_2\partial \zeta_1}\right) = \left(\frac{\partial^2 Q_{sp}}{\partial \zeta_2\partial \zeta_1}\right) - \sum_{i,j}\sum_{A_i,B_j}\left(\frac{\partial^2 Q_{sp}}{\partial \zeta_1\partial X_{A_i}}\right)\left(\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}^2}\right)^{-1}\right)_{ij}\left(\frac{\partial^2 Q_{sp}}{\partial X_{B_j}\partial \zeta_2}\right). \tag{132}$$

3.3.1 Formulas for $\left(\frac{\partial^2 Q_{sp}}{\partial \zeta_2\partial \zeta_1}\right)$

$$\left(\frac{\partial^2 Q_{sp}}{\partial T^2}\right) = -\frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial T^2}\right).$$

$$\left(\frac{\partial^2 Q_{sp}}{\partial T\partial V}\right) = \frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left[\frac{1}{V}\left(\frac{\partial \Delta^{A_iB_j}}{\partial T}\right) - \left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial T\partial V}\right)\right]$$

$$\begin{aligned}\left(\frac{\partial^2 Q_{sp}}{\partial T\partial n_k}\right) = &-\frac{1}{V}\sum_{j}\sum_{A_k,B_j} n_j X_{A_k} X_{B_j}\left(\frac{\partial \Delta^{A_kB_j}}{\partial T}\right)\\ &-\frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial T\partial n_k}\right)\end{aligned}$$

$$\left(\frac{\partial^2 Q_{sp}}{\partial V^2}\right) = \frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left[-\frac{2\Delta^{A_iB_j}}{V^2} + \frac{2}{V}\left(\frac{\partial \Delta^{A_iB_j}}{\partial V}\right) - \left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial V^2}\right)\right]$$

$$\begin{aligned}\left(\frac{\partial^2 Q_{sp}}{\partial V\partial n_k}\right) = &\sum_{j}\sum_{A_k,B_j} n_j X_{A_k} X_{B_j}\left[\frac{\Delta^{A_kB_j}}{V^2} - \frac{1}{V}\left(\frac{\partial \Delta^{A_kB_j}}{\partial V}\right)\right]\\ &+\frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left[\frac{1}{V}\left(\frac{\partial \Delta^{A_iB_j}}{\partial n_k}\right) - \left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial V\partial n_k}\right)\right].\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial^2 Q_{sp}}{\partial n_l\partial n_k}\right) = &-\frac{1}{V}\sum_{A_k,B_l} X_{A_k} X_{B_l}\Delta^{A_kB_l} - \frac{1}{V}\sum_{j}\sum_{A_l,B_j} n_j X_{A_l} X_{B_j}\left(\frac{\partial \Delta^{A_lB_j}}{\partial n_k}\right)\\ &-\frac{1}{V}\sum_{j}\sum_{A_k,B_j} n_j X_{A_k} X_{B_j}\left(\frac{\partial \Delta^{A_kB_j}}{\partial n_l}\right) - \frac{1}{2V}\sum_{i,j}\sum_{A_i,B_j} n_i n_j X_{A_i} X_{B_j}\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial n_l\partial n_k}\right)\end{aligned}$$

These derivatives are all found by performing one more differentiation on the first-order derivatives we found in section 3.2. However, when taking an additional derivative of $\left(\frac{\partial Q_{sp}}{\partial n_k}\right)$, we have to take care to differentiate the expressions on (124) and (125), and not the simplified expression (126). This is because the supscript sp means that $X(T, V, \mathbf{n})$ should be substituted in *after* all the derivatives have been performed.

3.3.2 Formulas for $\left(\frac{\partial^2 Q_{sp}}{\partial X_{A_i}\partial \zeta_1}\right)$

We have

$$\left(\frac{\partial Q}{\partial X_{A_i}}\right) = \frac{n_i}{X_{A_i}} - n_i - \frac{n_i}{V}\sum_j \sum_{B_j} n_j X_{B_j} \Delta^{A_i B_j}, \tag{133}$$

and thus

$$\left(\frac{\partial^2 Q_{sp}}{\partial T \partial X_{A_i}}\right) = -\frac{n_i}{V}\sum_j \sum_{B_j} n_j X_{B_j} \left(\frac{\partial \Delta^{A_i B_j}}{\partial T}\right)$$

$$\left(\frac{\partial^2 Q_{sp}}{\partial V \partial X_{A_i}}\right) = n_i \sum_j \sum_{B_j} n_j X_{B_j} \left[\frac{1}{V^2}\Delta^{A_i B_j} - \frac{1}{V}\left(\frac{\partial \Delta^{A_i B_j}}{\partial V}\right)\right]$$

$$\left(\frac{\partial^2 Q_{sp}}{\partial n_l \partial X_{A_i}}\right) = -\frac{n_i}{V}\sum_{B_l} X_{B_l}\Delta^{A_i B_l} - \frac{1}{V}\sum_j \sum_{B_j} n_j X_{B_j} n_i \left(\frac{\partial \Delta^{A_i B_j}}{\partial n_l}\right).$$

3.3.3 Solving for $\left(\frac{\partial \mathbf{X}}{\partial V}\right)$ and $\left(\frac{\partial^2 Q_{sp}}{\partial V^2}\right)$ simultaneously

The derivatives $\left(\frac{\partial \mathbf{X}}{\partial V}\right)$ and $\left(\frac{\partial^2 Q_{sp}}{\partial V^2}\right)$ are needed in the Newton iteration when solving for volume given pressure, temperature and composition. When both of these are needed, one wants to first solve for $\left(\frac{\partial \mathbf{X}}{\partial V}\right)$ from (130), and then use (128) to find $\left(\frac{\partial^2 Q_{sp}}{\partial V^2}\right)$, and therefore a dedicated routine for this has been implemented. To obtain $\left(\frac{\partial \mathbf{X}}{\partial V}\right)$, we solve the linear system

$$\left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}^2}\right)\left(\frac{\partial \mathbf{X}}{\partial V}\right) = -\left(\frac{\partial^2 Q_{sp}}{\partial V \partial \mathbf{X}}\right)^t. \tag{134}$$

where[2]

$$\left(\frac{\partial^2 Q}{\partial X_{A_i}\partial X_{B_j}}\right) = -\frac{n_i}{X_{A_i}^2}\delta_{A_i B_j} - \frac{n_i n_j}{V}\Delta^{A_i B_j}. \tag{135}$$

Having found this derivative, we find $\left(\frac{\partial P}{\partial V}\right)$ from (128):

$$\left(\frac{\partial^2 F^{\text{assoc}}}{\partial V^2}\right) = \left(\frac{\partial^2 Q_{sp}}{\partial V^2}\right) + \left(\frac{\partial^2 Q_{sp}}{\partial \mathbf{X}\partial V}\right)\left(\frac{\partial \mathbf{X}}{\partial V}\right). \tag{136}$$

3.4 Derivatives for $\Delta^{A_i B_j}(T, V, \mathbf{n})$

We now address the association part of PC-SAFT. In this section, we will use the notation $\beta^{A_i B_j}$ instead of $\kappa^{A_i B_j}$.

$$\Delta^{A_i B_j}(T, V, \mathbf{n}) = g(T, V, \mathbf{n}) \cdot [\exp(\epsilon^{A_i B_j}/RT) - 1](\sigma_{ij})^3 \beta^{A_i B_j} \tag{137}$$

$$= g(T, V, \mathbf{n}) h(T) \tag{138}$$

[2]Note that only the diagonal of $\left(\frac{\partial^2 Q}{\partial X_{A_i}\partial X_{B_j}}\right)$ is dependent on $\mathbf{X}$.

where $\epsilon^{A_iB_j}$, σ_{ij} and $\beta^{A_iB_j}$ are constants. The first derivatives are thus given by

$$\left(\frac{\partial \Delta^{A_iB_j}}{\partial T}\right) = g(T,V,\mathbf{n})h'(T) + \left(\frac{\partial \ln g(T,V,\mathbf{n})}{\partial T}\right)\Delta^{A_iB_j} \tag{139}$$

$$\left(\frac{\partial \Delta^{A_iB_j}}{\partial V}\right) = \left(\frac{\partial \ln g(V,\mathbf{n})}{\partial V}\right)\Delta^{A_iB_j} \tag{140}$$

$$\left(\frac{\partial \Delta^{A_iB_j}}{\partial n_k}\right) = \left(\frac{\partial \ln g(V,\mathbf{n})}{\partial n_k}\right)\Delta^{A_iB_j} \tag{141}$$

while the second derivatives are given by

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial T^2}\right) = g(T,V,\mathbf{n})h''(T) + 2\left(\frac{\partial g(T,V,\mathbf{n})}{\partial T}\right)h'(T) + \left(\frac{\partial^2 g(T,V,\mathbf{n})}{\partial T^2}\right)h(T) \tag{142}$$

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial V \partial T}\right) = \left(\frac{\partial g(T,V,\mathbf{n})}{\partial V}\right)h'(T) + \left(\frac{\partial^2 g(T,V,\mathbf{n})}{\partial T \partial V}\right) \tag{143}$$

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial n_l \partial T}\right) = \left(\frac{\partial g(T,V,\mathbf{n})}{\partial n_l}\right)h'(T) + \left(\frac{\partial^2 g(T,V,\mathbf{n})}{\partial T \partial n_l}\right) \tag{144}$$

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial V^2}\right) = \left(\frac{\partial^2 g(V,\mathbf{n})}{\partial V^2}\right)\frac{\Delta^{A_iB_j}}{g(T,V,\mathbf{n})} \tag{145}$$

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial n_l \partial V}\right) = \left(\frac{\partial^2 g(V,\mathbf{n})}{\partial n_l \partial V}\right)\frac{\Delta^{A_iB_j}}{g(T,V,\mathbf{n})} \tag{146}$$

$$\left(\frac{\partial^2 \Delta^{A_iB_j}}{\partial n_l \partial n_k}\right) = \left(\frac{\partial^2 g(V,\mathbf{n})}{\partial n_l \partial n_k}\right)\frac{\Delta^{A_iB_j}}{g(T,V,\mathbf{n})} \tag{147}$$

Moreover,

$$h(T) = [\exp(\epsilon^{A_iB_j}/RT) - 1](\sigma_{ij})^3\beta^{A_iB_j} \tag{148}$$

$$h'(T) = -\frac{\epsilon^{A_iB_j}}{RT^2}\exp(\epsilon^{A_iB_j}/RT)(\sigma_{ij})^3\beta^{A_iB_j} \tag{149}$$

$$h''(T) = \left(2 + \frac{\epsilon^{A_iB_j}}{RT}\right)\frac{\epsilon^{A_iB_j}}{RT^3}\exp(\epsilon^{A_iB_j}/RT)(\sigma_{ij})^3\beta^{A_iB_j} \tag{150}$$

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