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Memo

The SAFT-VR Mie equation of state

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Contents

1 Introduction **2**

2 Model **2**
2.1 Differentials 2

3 Monomer contribution to the Mie fluid **3**
3.1 Hard-sphere diameter 3
3.1.1 Differential terms 5
3.2 First order monomer perturbation 5
3.2.1 Differential terms 7
3.3 Second order monomer perturbation 9
3.3.1 Differential terms 10
3.4 Third order monomer perturbation 14
3.4.1 Differential terms 14
3.5 Chains of monomer Mie segments 14
3.5.1 Differentials 16

4 Mixtures **21**
4.1 Mixture hard-sphere term 22
4.1.1 Differentials 23
4.2 First order term 25
4.2.1 Differentials 25
4.3 Second order term 28
4.3.1 Differentials 29
4.4 Third order term 29
4.5 Chain contribution 29
4.5.1 Differentials 30

5 Temperature dependency in σ **31**
5.1 Differentiasl with temperature dependency in σ 31

6 The non-additive hard sphere model **34**
6.1 Pure fluid hard-spere model 35
6.2 Model differentials 36

7 Pure fluid hard-spere reference **40**
7.1 Segments for the pure fluid hard-spere reference 41
7.2 Compositional dependence in hard-sphere diameter d 42

8 New term in the perturbation of mixtures **43**

9 New term **43**
9.1 The pair correlation function at contact 45
9.2 The reduced isothermal compressibillity of the mixture hard-sphere model . . 47
9.2.1 Analytical differentials 48

1 Introduction

This memo was written when implementing the SAFT-VR Mie equation of state [8], and contains SAFT-VR Mie equations and differentials. The equations used for the extension of SAFT-VR Mie to support Feynman-Hibbs quantum corrected poteitials [2, 1] as well as some equations used in the work of Hammer et al. [6] are included.

SAFT-VR Mie is a thermodynamic perturbtion theory in the Baker-Henderson [3, 4] framework.

2 Model

The Mie potential,

$$u^{\text{Mie}}(r) = \mathcal{C}\epsilon\left(\left(\frac{\sigma}{r}\right)^{\lambda_{\text{r}}} - \left(\frac{\sigma}{r}\right)^{\lambda_{\text{a}}}\right), \tag{1}$$

where,

$$\mathcal{C} = \frac{\lambda_{\text{r}}}{\lambda_{\text{r}} - \lambda_{\text{a}}}\left(\frac{\lambda_{\text{r}}}{\lambda_{\text{a}}}\right)^{\frac{\lambda_{\text{a}}}{\lambda_{\text{r}} - \lambda_{\text{a}}}}, \tag{2}$$

The resulting Helmholtz free energy function is comprised of the four main parts,

$$A = A^{\text{id}} + A^{\text{mono}} + A^{\text{chain}} + A^{\text{assoc}}, \tag{3}$$

where the ideal and association part is similar to what we have been using. In the following it is used lower caps letter for the reduced Helmholtz energy.

2.1 Differentials

As we will see, the various expressions for a, are described as functions of the packing fraction, η, and the reduced centre-centre distance for two hard spheres, x_0. There are also direct dependence to T. The differentials will be calculated based on η and x_0, and the use of the chain rule to get differentials in V etc. We use the following dependencies,

$$a = a(\eta, x_0) \tag{4}$$
$$\eta = \eta(V, T, \boldsymbol{n}) \tag{5}$$
$$x_0 = x_0(T) \tag{6}$$

giving,

$$a = a(\eta(V, T, \boldsymbol{n}), x_0(T), T). \tag{7}$$

Looking ahead to Equation 141 and 139, it is seen that some third order differentials is needed as well for a_1 and a_2.

3 Monomer contribution to the Mie fluid

The reduced monomer Helmholtz energy consists of a series expansion to third order in $\beta = 1/(k_\mathrm{B}T)$. The monomer contribution is a function of monomer number density. The monomer segment number m_s, is the number of segments per molecule. We therefore have $N_\mathrm{s} = m_\mathrm{s}N$, where N is the number of molecules. We use,

$$a^{\mathrm{mono}} = m_\mathrm{s} a^{\mathrm{m}} = m_\mathrm{s} \frac{A^{\mathrm{m}}}{N_\mathrm{s} k_\mathrm{B} T}. \tag{8}$$

The monomer expansion becomes,

$$a^{\mathrm{m}} = a^{\mathrm{HS}} + \beta a_1 + \beta^2 a_2 + \beta^3 a_3. \tag{9}$$

3.1 Hard-sphere diameter

The hard-sphere reduced Helmholtz free energy is given by the Carnahan and Starling EOS,

$$a^{\mathrm{HS}} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}. \tag{10}$$

Where,

$$\eta = \frac{\rho_\mathrm{s} \pi \left(d^{\mathrm{HS}}\right)^3}{6} = \frac{\pi \mathrm{N_A} m_\mathrm{s} n \left(d^{\mathrm{HS}}\right)^3}{6V}, \tag{11}$$

and d^{HS} is the hard-sphere diameter. The hard-sphere diameter used by [8], is given as

$$d^{\mathrm{HS}} = \int_0^{\sigma} \left[1 - \exp\left(-\beta u^{\mathrm{Mie}}(r)\right)\right] dr. \tag{12}$$

Here $\beta = 1/(kT)$. This function is impossible to integrate analytically, and must be approximated in order to have an explicit formulation. According to Papaioannou et al. [10] a 5 point Gauss-Legendre quadrature is applied for the SAFT-VR Mie EOS, as shown by Paricaud [11]. There is a slight mismatch between the papers, Paricaud [11] evaluates 10 points, and refers to the method as ten-point, while Papaioannou et al. [10] refers to this as a 5 point quadrature. It is believed to be a 10 point quadrature.

The Gauss-Legendre quadrature is for integration in the interval [-1,1]. To fit with our problem, the quadrature would take the following form, using $x = r/\sigma$,

$$d^{\mathrm{HS}} = \frac{\sigma}{2}\int_{-1}^{1}\left[1 - \exp\left(-\beta u^{\mathrm{Mie}}\left(\frac{\sigma}{2}x + \frac{\sigma}{2}\right)\right)\right]dx \tag{13}$$

$$\approx \frac{\sigma}{2}\sum_{i=1}^{n} w_i\left[1 - \exp\left(-\beta u^{\mathrm{Mie}}\left(\frac{\sigma}{2}x_i + \frac{\sigma}{2}\right)\right)\right] \tag{14}$$

Index	x_i	w_i
1	-0.9739065285171717200780	0.0666713443086881375936
2	-0.8650633666889845107321	0.149451349150580593146
3	-0.6794095682990244062343	0.219086362515982043996
4	-0.4333953941292471907993	0.2692667193099963550912
5	-0.1488743389816312108848	0.2955242247147528701739
6	0.1488743389816312108848	0.295524224714752870174
7	0.4333953941292471907993	0.269266719309996355091
8	0.6794095682990244062343	0.2190863625159820439955
9	0.8650633666889845107321	0.1494513491505805931458
10	0.9739065285171717200780	0.0666713443086881375936

Table 1: Gauss-Legendre quadrature points

The quadrature approach was tested using methane parameters ($\lambda_{\mathrm{r}} = 12.650$, $\lambda_{\mathrm{a}} = 6.0$, $\epsilon/k_{\mathrm{B}} = 153.36$ (K), $\sigma = 3.7412$ (Å)) at $T = 300.0$ (K), revealed an error in the order 10^{-5}, using 10 point Gauss Legendre quadrature.

It is noted that the first 5 nodes all evaluate to unity, and the contribution from the exponential term is lost in numerical truncation.

3.1.1 Differential terms

Differentials of η:

$$\frac{\partial \eta}{\partial V} = -\frac{\eta}{V}, \quad (15)$$

$$\frac{\partial^2 \eta}{\partial V^2} = \frac{2\eta}{V^2}, \quad (16)$$

$$\frac{\partial^3 \eta}{\partial V^3} = -\frac{6\eta}{V^3}, \quad (17)$$

$$\frac{\partial \eta}{\partial T} = \frac{3\eta}{d}\frac{\partial d}{\partial T}, \quad (18)$$

$$\frac{\partial^2 \eta}{\partial T^2} = \frac{6\eta}{d^2}\left(\frac{\partial d}{\partial T}\right)^2 + \frac{3\eta}{d}\frac{\partial^2 d}{\partial T^2}, \quad (19)$$

$$\frac{\partial^2 \eta}{\partial V \partial T} = -\frac{1}{V}\frac{\partial \eta}{\partial T}, \quad (20)$$

$$\frac{\partial^3 \eta}{\partial V^2 \partial T} = \frac{2}{V^2}\frac{\partial \eta}{\partial T}, \quad (21)$$

$$\frac{\partial^3 \eta}{\partial T^2 \partial V} = -\frac{1}{V}\frac{\partial^2 \eta}{\partial T^2}. \quad (22)$$

$$(23)$$

Differentials for $a = \eta \tilde{a}$ simply become,

$$a_{X_i} = \eta_{X_i}\tilde{a} + \eta \tilde{a}_{X_i}, \quad (24)$$

$$a_{X_i X_j} = \eta_{X_i X_j}\tilde{a} + \eta_{X_i}\tilde{a}_{X_j} + \eta_{X_j}\tilde{a}_{X_i} + \eta \tilde{a}_{X_i X_j}, \quad (25)$$

$$a_{X_i X_j X_k} = \eta_{X_i X_j X_k}\tilde{a} + \eta_{X_i X_j}\tilde{a}_{X_k} + \eta_{X_i X_k}\tilde{a}_{X_j} + \eta_{X_i}\tilde{a}_{X_j X_k} + \eta_{X_j X_k}\tilde{a}_{X_i} + \eta_{X_j}\tilde{a}_{X_i X_k} + \eta_{X_k}\tilde{a}_{X_i X_j} + \eta \tilde{a}_{X_i X_j X_k}. \quad (26)$$

Differentials of d, allowing for a temperature dependent u^{Mie}:

$$\frac{\partial d}{\partial T} = \frac{\beta \sigma}{2}\sum_{i=1}^{n} w_i \left(\frac{\partial u_i^{\mathrm{Mie}}}{\partial T} - \frac{u_i^{\mathrm{Mie}}}{T}\right)\exp\left(-\beta u_i^{\mathrm{Mie}}\right), \quad (27)$$

$$\frac{\partial^2 d}{\partial T^2} = \frac{\beta \sigma}{2}\sum_{i=1}^{n} w_i \left[-\beta\left(\frac{\partial u_i^{\mathrm{Mie}}}{\partial T} - \frac{u_i^{\mathrm{Mie}}}{T}\right)^2 + \left(\frac{\partial^2 u_i^{\mathrm{Mie}}}{\partial T^2} - \frac{2u_i^{\mathrm{Mie}}}{T^2} - \frac{2}{T}\frac{\partial u_i^{\mathrm{Mie}}}{\partial T}\right)\right]\exp\left(-\beta u_i^{\mathrm{Mie}}\right) \quad (28)$$

Differentials of the hard-sphere term:

$$\frac{\partial a^{\mathrm{HS}}}{\partial \eta} = -\frac{2\left((\eta - 2\right)}{\left(1-\eta\right)^3}, \quad (29)$$

$$\frac{\partial^2 a^{\mathrm{HS}}}{\partial \eta^2} = \frac{10 - 4\eta}{\left(1-\eta\right)^4}. \quad (30)$$

3.2 First order monomer perturbation

The first-order perturbation term is calculated from,

$$a_1 = 2\pi \rho_{\mathrm{s}} \int_{\sigma}^{\infty} g_{\mathrm{d}}^{\mathrm{HS}}\left(r\right) u^{\mathrm{Mie}}\left(r\right) r^2 dr. \quad (31)$$

Here g_d^HS is the reference hard-sphere radial-distribution-function (RDF), approximated as

$$g_\mathrm{d}^\mathrm{HS}\left(d\right) = \frac{1-\eta/2}{\left(1-\eta\right)^3}. \tag{32}$$

Lafitte et al. [8] developed an algebraic approximation to a_1,

$$a_1 = \mathcal{C}\left[x_0^{\lambda_\mathrm{a}}\left(a_1^\mathrm{S}\left(\eta;\lambda_\mathrm{a}\right) + B\left(\eta;\lambda_\mathrm{a}\right)\right) - x_0^{\lambda_\mathrm{r}}\left(a_1^\mathrm{S}\left(\eta;\lambda_\mathrm{r}\right) + B\left(\eta;\lambda_\mathrm{r}\right)\right)\right]. \tag{33}$$

Here $x_0 = \sigma/d$, and a_1^S is the Helmholtz free energy of the hard-core Sutherland particle,

$$a_1^\mathrm{S}\left(\eta;\lambda\right) = -12\epsilon\eta\left(\frac{1}{\lambda-3}\right)\frac{1-\eta_\mathrm{eff}\left(\eta;\lambda\right)/2}{\left(1-\eta_\mathrm{eff}\left(\eta;\lambda\right)\right)^3}, \tag{34}$$

where,

$$\eta_\mathrm{eff}\left(\eta;\lambda\right) = c_1\left(\lambda\right)\eta + c_2\left(\lambda\right)\eta^2 + c_3\left(\lambda\right)\eta^3 + c_4\left(\lambda\right)\eta^4, \tag{35}$$

is a correlation valid for $5 < \lambda \leq 100$. The coefficients are given from,

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0.81096 & 1.7888 & -37.578 & 92.284 \\ 1.0205 & -19.341 & 151.26 & -463.50 \\ -1.9057 & 22.845 & -228.14 & 973.92 \\ 1.0885 & -6.1962 & 106.98 & -677.64 \end{pmatrix}\begin{pmatrix} 1 \\ 1/\lambda \\ 1/\lambda^2 \\ 1/\lambda^3 \end{pmatrix}. \tag{36}$$

B is calculated as follows,

$$B\left(\eta;\lambda\right) = 12\eta\epsilon\left(\frac{1-\eta/2}{\left(1-\eta\right)^3}I_\lambda\left(\lambda\right) - \frac{9\eta\left(1+\eta\right)}{2\left(1-\eta\right)^3}J_\lambda\left(\lambda\right)\right), \tag{37}$$

$$= 6\eta\epsilon\left(k_I\left(\eta\right)I_\lambda\left(\lambda\right) + k_J\left(\eta\right)J_\lambda\left(\lambda\right)\right). \tag{38}$$

Here,

$$I_\lambda\left(\lambda\right) = -\frac{x_0^{\left(3-\lambda\right)} - 1}{\lambda-3}, \tag{39}$$

$$J_\lambda\left(\lambda\right) = -\frac{x_0^{\left(4-\lambda\right)}\left(\lambda-3\right) - x_0^{\left(3-\lambda\right)}\left(\lambda-4\right) - 1}{\left(\lambda-3\right)\left(\lambda-4\right)}, \tag{40}$$

and,

$$k_I\left(\eta\right) = \frac{2-\eta}{\left(1-\eta\right)^3}, \tag{41}$$

$$k_J\left(\eta\right) = -\frac{9\eta\left(1+\eta\right)}{\left(1-\eta\right)^3}. \tag{42}$$

Looking ahead to the mixture formulation, a reduced property is defined,

$$\tilde{a} = \frac{a}{\eta}. \tag{43}$$

This gives,

$$\tilde{a}_1 = \mathcal{C}\left[x_0^{\lambda_\mathrm{a}}\left(\tilde{a}_1^\mathrm{S}\left(\eta;\lambda_\mathrm{a}\right) + \tilde{B}\left(\eta;\lambda_\mathrm{a}\right)\right) - x_0^{\lambda_\mathrm{r}}\left(\tilde{a}_1^\mathrm{S}\left(\eta;\lambda_\mathrm{r}\right) + \tilde{B}\left(\eta;\lambda_\mathrm{r}\right)\right)\right]. \tag{44}$$

3.2.1 Differential terms

Differentials of η_{eff}:

$$\frac{\partial \eta_{\mathrm{eff}}}{\partial \eta} = c_{1,\lambda} + 2c_{2,\lambda}\eta + 3c_{3,\lambda}\eta^2 + 4c_{4,\lambda}\eta^3, \tag{45}$$

$$\frac{\partial^2 \eta_{\mathrm{eff}}}{\partial \eta^2} = 2c_{2,\lambda} + 6c_{3,\lambda}\eta + 12c_{4,\lambda}\eta^2, \tag{46}$$

$$\frac{\partial^3 \eta_{\mathrm{eff}}}{\partial \eta^3} = 6c_{3,\lambda} + 24c_{4,\lambda}\eta. \tag{47}$$

Differentials of $\tilde{a}_1^{\mathrm{S}}$:

$$\frac{\partial \tilde{a}_1^{\mathrm{S}}}{\partial \eta} = \left(\frac{6\epsilon}{\lambda - 3}\right) \frac{(2\eta_{\mathrm{eff}} - 5)}{(1-\eta_{\mathrm{eff}})^4} \frac{\partial \eta_{\mathrm{eff}}}{\partial \eta}, \tag{48}$$

$$\frac{\partial^2 \tilde{a}_1^{\mathrm{S}}}{\partial \eta^2} = \left(\frac{6\epsilon}{\lambda - 3}\right) \left[\frac{2\eta_{\mathrm{eff}} - 5}{(1-\eta_{\mathrm{eff}})^4} \frac{\partial^2 \eta_{\mathrm{eff}}}{\partial \eta^2} + \frac{6\left(\eta_{\mathrm{eff}} - 3\right)}{(1-\eta_{\mathrm{eff}})^5} \left(\frac{\partial \eta_{\mathrm{eff}}}{\partial \eta}\right)^2\right], \tag{49}$$

$$\frac{\partial^3 \tilde{a}_1^{\mathrm{S}}}{\partial \eta^3} = \left(\frac{6\epsilon}{\lambda - 3}\right) \left[\frac{(2\eta_{\mathrm{eff}} - 5)}{(1-\eta_{\mathrm{eff}})^4} \frac{\partial^3 \eta_{\mathrm{eff}}}{\partial \eta^3} + \frac{12\left(7 - 2\eta_{\mathrm{eff}}\right)}{(1-\eta_{\mathrm{eff}})^6} \left(\frac{\partial \eta_{\mathrm{eff}}}{\partial \eta}\right)^3 + \frac{18\left(\eta_{\mathrm{eff}} - 3\right)}{(1-\eta_{\mathrm{eff}})^5} \frac{\partial \eta_{\mathrm{eff}}}{\partial \eta} \frac{\partial^2 \eta_{\mathrm{eff}}}{\partial \eta^2}\right]. \tag{50}$$

Differentials of $\tilde{B}$:

$$\frac{\partial^{i+j} \tilde{B}}{\partial \eta^i \partial x_0^j} = 6\epsilon \left(\frac{\partial^i k_I}{\partial \eta^i} \frac{\partial^j I_\lambda}{\partial {x_0}^j} + \frac{\partial^i k_J}{\partial \eta^i} \frac{\partial^j J_\lambda}{\partial {x_0}^j}\right). \tag{51}$$

Differentials of k_I and k_J:

$$\frac{\partial k_I}{\partial \eta} = \frac{5 - 2\eta}{(1-\eta)^4}, \tag{52}$$

$$\frac{\partial^2 k_I}{\partial \eta^2} = \frac{6\left(3 - \eta\right)}{(1-\eta)^5}, \tag{53}$$

$$\frac{\partial^3 k_I}{\partial \eta^3} = \frac{12\left(7 - 2\eta\right)}{(1-\eta)^6}, \tag{54}$$

$$\frac{\partial k_J}{\partial \eta} = -\frac{9\left(\eta^2 + 4\eta + 1\right)}{(1-\eta)^4}, \tag{55}$$

$$\frac{\partial^2 k_J}{\partial \eta^2} = -\frac{18\left(\eta^2 + 7\eta + 4\right)}{(1-\eta)^5}, \tag{56}$$

$$\frac{\partial^3 k_J}{\partial \eta^3} = -\frac{54\left(\eta^2 + 10\eta + 9\right)}{(1-\eta)^6}. \tag{57}$$

Differentials of I_λ:

$$\frac{\partial I_\lambda}{\partial x_0} = x_0^{(2-\lambda)}, \tag{58}$$

$$\frac{\partial^2 I_\lambda}{\partial {x_0}^2} = \left(2 - \lambda\right) x_0^{(1-\lambda)}. \tag{59}$$

Differentials of J_λ:

$$\frac{\partial J_\lambda}{\partial x_0} = x_0^{(3-\lambda)} - x_0^{(2-\lambda)}, \tag{60}$$

$$\frac{\partial^2 J_\lambda}{\partial {x_0}^2} = (3-\lambda)\, x_0^{(2-\lambda)} - (2-\lambda)\, x_0^{(1-\lambda)}. \tag{61}$$

Differentials of $\tilde{a}_1$ then becomes:

$$\frac{\partial \tilde{a}_1}{\partial x_0} = \mathcal{C}\left[\lambda_\mathrm{a} x_0^{(\lambda_\mathrm{a}-1)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}} + \tilde{B}_{\lambda_\mathrm{a}}\right) - \lambda_\mathrm{r} x_0^{(\lambda_\mathrm{r}-1)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}} + \tilde{B}_{\lambda_\mathrm{r}}\right) + x_0^{\lambda_\mathrm{a}}\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0} - x_0^{\lambda_\mathrm{r}}\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0}\right], \tag{62}$$

$$\frac{\partial^2 \tilde{a}_1}{\partial {x_0}^2} = \mathcal{C}\left[\lambda_\mathrm{a}(\lambda_\mathrm{a}-1) x_0^{(\lambda_\mathrm{a}-2)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}} + \tilde{B}_{\lambda_\mathrm{a}}\right) - \lambda_\mathrm{r}(\lambda_\mathrm{r}-1) x_0^{(\lambda_\mathrm{r}-2)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}} + \tilde{B}_{\lambda_\mathrm{r}}\right) + 2\lambda_\mathrm{a} x_0^{(\lambda_\mathrm{a}-1)}\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0} - 2\lambda_\mathrm{r} x_0^{(\lambda_\mathrm{r}-1)}\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0} + x_0^{\lambda_\mathrm{a}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial {x_0}^2} - x_0^{\lambda_\mathrm{r}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial {x_0}^2}\right], \tag{63}$$

$$\frac{\partial \tilde{a}_1}{\partial \eta} = \mathcal{C}\left[x_0^{\lambda_\mathrm{a}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right) - x_0^{\lambda_\mathrm{r}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right)\right], \tag{64}$$

$$\frac{\partial^2 \tilde{a}_1}{\partial \eta^2} = \mathcal{C}\left[x_0^{\lambda_\mathrm{a}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta^2} + \frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta^2}\right) - x_0^{\lambda_\mathrm{r}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta^2} + \frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta^2}\right)\right], \tag{65}$$

$$\frac{\partial^3 \tilde{a}_1}{\partial \eta^3} = \mathcal{C}\left[x_0^{\lambda_\mathrm{a}}\left(\frac{\partial^3 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta^3} + \frac{\partial^3 \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta^3}\right) - x_0^{\lambda_\mathrm{r}}\left(\frac{\partial^3 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta^3} + \frac{\partial^3 \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta^3}\right)\right], \tag{66}$$

$$\frac{\partial^2 \tilde{a}_1}{\partial \eta \partial x_0} = \mathcal{C}\left[\lambda_\mathrm{a} x_0^{(\lambda_\mathrm{a}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right) - \lambda_\mathrm{r} x_0^{(\lambda_\mathrm{r}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right) + x_0^{\lambda_\mathrm{a}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0 \partial \eta} - x_0^{\lambda_\mathrm{r}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0 \partial \eta}\right], \tag{67}$$

$$\frac{\partial^3 \tilde{a}_1}{\partial \eta^2 \partial x_0} = \mathcal{C}\left[\lambda_\mathrm{a} x_0^{(\lambda_\mathrm{a}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right) - \lambda_\mathrm{r} x_0^{(\lambda_\mathrm{r}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right) + x_0^{\lambda_\mathrm{a}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0 \partial \eta} - x_0^{\lambda_\mathrm{r}}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0 \partial \eta}\right], \tag{68}$$

$$\frac{\partial^3 \tilde{a}_1}{\partial {x_0}^2 \partial \eta} = \mathcal{C}\left[\lambda_\mathrm{a}(\lambda_\mathrm{a}-1) x_0^{(\lambda_\mathrm{a}-2)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right) - \lambda_\mathrm{r}(\lambda_\mathrm{r}-1) x_0^{(\lambda_\mathrm{r}-2)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta} + \frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right) + 2\lambda_\mathrm{a} x_0^{(\lambda_\mathrm{a}-1)}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0 \partial \eta} - 2\lambda_\mathrm{r} x_0^{(\lambda_\mathrm{r}-1)}\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0 \partial \eta} + x_0^{\lambda_\mathrm{a}}\frac{\partial^3 \tilde{B}_{\lambda_\mathrm{a}}}{\partial {x_0}^2 \partial \eta} - x_0^{\lambda_\mathrm{r}}\frac{\partial^3 \tilde{B}_{\lambda_\mathrm{r}}}{\partial {x_0}^2 \partial \eta}\right]. \tag{69}$$

Differentials of x_0,

$$\frac{\partial x_0}{\partial T} = -\frac{x_0}{d}\frac{\partial d}{\partial T}, \tag{70}$$

$$\frac{\partial^2 x_0}{\partial T^2} = -\frac{2}{d}\frac{\partial x_0}{\partial T}\frac{\partial d}{\partial T} - \frac{x_0}{d}\frac{\partial^2 d}{\partial T^2}. \tag{71}$$

Using e for η, and x for x_0, and simplifying the differential notation ($a_T = \partial a/\partial T$), the η and x_0 differential can be converted to TV differentials. If we have $a(e(T,V), x(T))$, the differentials become,

$$a_T = a_e e_T + a_x x_T, \tag{72}$$
$$a_{TT} = a_{ee} e_T^2 + 2a_{ex} e_T x_T + a_e e_{TT} + a_{xx} x_T^2 + a_x x_{TT}, \tag{73}$$
$$a_V = a_e e_V, \tag{74}$$
$$a_{VV} = a_{ee} e_V^2 + a_e e_{VV}, \tag{75}$$
$$a_{VVV} = a_{eee} e_V^3 + 3a_{ee} e_V e_{VV} + a_e e_{VVV}, \tag{76}$$
$$a_{VT} = a_{ee} e_V e_T + a_e e_{VT} + a_{ex} e_V x_T, \tag{77}$$
$$a_{VVT} = a_{eee} e_V^2 e_T + a_{ee} e_{VV} e_T + 2a_{ee} e_V e_{VT} + a_e e_{VVT} + a_{eex} e_V^2 x_T + a_{ex} e_{VV} x_T, \tag{78}$$
$$a_{VTT} = a_{eee} e_V e_T^2 + 2a_{ee} e_T e_{VT} + 2a_{eex} e_V e_T x_T + 2a_{ex} e_{VT} x_T + a_{ee} e_{TT} + a_e e_{VTT} + a_{exx} e_V x_T^2 + a_{ex} e_V x_{TT}. \tag{79}$$

3.3 Second order monomer perturbation

The second order monomer perturbation is given as,

$$a_2 = \frac{1}{2} K^{\mathrm{HS}} (1+\chi) \epsilon \mathcal{C}^2 \left[x_0^{2\lambda_\mathrm{a}} \left(a_1^\mathrm{S} (\eta; 2\lambda_\mathrm{a}) + B(\eta; 2\lambda_\mathrm{a}) \right) \right. \tag{80}$$
$$- 2x_0^{\lambda_\mathrm{a}+\lambda_\mathrm{r}} \left(a_1^\mathrm{S} (\eta; \lambda_\mathrm{a}+\lambda_\mathrm{r}) + B(\eta; \lambda_\mathrm{a}+\lambda_\mathrm{r}) \right) \tag{81}$$
$$\left. + x_0^{2\lambda_\mathrm{r}} \left(a_1^\mathrm{S} (\eta; 2\lambda_\mathrm{r}) + B(\eta; 2\lambda_\mathrm{r}) \right) \right]. \tag{82}$$

Here,

$$K^{\mathrm{HS}} = \frac{(1-\eta)^4}{1+4\eta+4\eta^2-4\eta^3+\eta^4}, \tag{83}$$

and,

$$\chi = f_1(\alpha) \bar{\zeta}_x + f_2(\alpha) \left(\bar{\zeta}_x\right)^5 + f_3(\alpha) \left(\bar{\zeta}_x\right)^8. \tag{84}$$

Here $\bar{\zeta}_x$ is temperature independent and defined as,

$$\bar{\zeta}_x = \eta x_0^3 = \frac{\pi \mathrm{N_A} m_\mathrm{s} \sigma^3}{6V}. \tag{85}$$

α is given as,

$$\alpha = \mathcal{C} \left(\frac{1}{\lambda_\mathrm{a}-3} - \frac{1}{\lambda_\mathrm{r}-3} \right), \tag{86}$$

and $f_i(\alpha)$ is given from,

$$f_i(\alpha) = \frac{\sum_{n=0}^{n=3} \phi_{i,n} \alpha^n}{1+\sum_{n=4}^{n=6} \phi_{i,n} \alpha^{n-3}} \quad i \in 1, \ldots, 6. \tag{87}$$

n	$\phi_{1,n}$	$\phi_{2,n}$	$\phi_{3,n}$	$\phi_{4,n}$	$\phi_{5,n}$	$\phi_{6,n}$	$\phi_{7,n}$
0	7.5365557	-359.44	1550.9	-1.19932	-1911.28	9236.9	10
1	-37.60463	1825.6	-5070.1	9.063632	21390.175	-129430	10
2	71.745953	-3168.0	6534.6	-17.9482	-51320.7	357230	0.57
3	-46.83552	1884.2	-3288.7	11.34027	37064.54	-315530	-6.7
4	-2.467982	-0.82376	-2.7171	20.52142	1103.742	1390.2	-8
5	-0.50272	-3.1935	2.0883	-56.6377	-3264.61	-4518.2	...
6	8.0956883	3.7090	0	40.53683	2556.181	4241.6	...

Table 2: $\phi_{i,n}$ coefficients

3.3.1 Differential terms

Differentials of K^{HS}:

$$\frac{\partial K^{\mathrm{HS}}}{\partial \eta} = \frac{4\left(\eta^2 - 5\eta - 2\right)(1-\eta)^3}{\left(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4\right)^2}, \tag{88}$$

$$\frac{\partial^2 K^{\mathrm{HS}}}{\partial \eta^2} = \frac{4\left(3\eta^6 - 30\eta^5 + 77\eta^4 - 80\eta^3 + 39\eta^2 + 82\eta + 17\right)(1-\eta)^2}{\left(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4\right)^3}, \tag{89}$$

$$\frac{\partial^3 K^{\mathrm{HS}}}{\partial \eta^3} = \frac{48\left(\eta^{10} - 15\eta^9 + 77\eta^8 - 210\eta^7 + 372\eta^6 - 352\eta^5 + 238\eta^3 - 109\eta^2 - 97\eta - 13\right)(1-\eta)}{\left(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4\right)^4}. \tag{90}$$

Differentials of χ:

$$\frac{\partial \chi}{\partial \bar{\zeta}_x} = f_1(\alpha) + 5 f_2(\alpha)\bar{\zeta}_x^4 + 8 f_3(\alpha)\bar{\zeta}_x^7, \tag{91}$$

$$\frac{\partial^2 \chi}{\partial \bar{\zeta}_x^2} = 20 f_2(\alpha)\bar{\zeta}_x^3 + 56 f_3(\alpha)\bar{\zeta}_x^6, \tag{92}$$

$$\frac{\partial^3 \chi}{\partial \bar{\zeta}_x^3} = 60 f_2(\alpha)\bar{\zeta}_x^2 + 336 f_3(\alpha)\bar{\zeta}_x^5. \tag{93}$$

The $\bar{\zeta}_x$ differentials become,

$$\frac{\partial \bar{\zeta}_x}{\partial V} = -\frac{\bar{\zeta}_x}{V}, \tag{94}$$

$$\frac{\partial^2 \bar{\zeta}_x}{\partial V^2} = \frac{2\bar{\zeta}_x}{V^2}, \tag{95}$$

$$\frac{\partial^3 \bar{\zeta}_x}{\partial V^3} = -\frac{6\bar{\zeta}_x}{V^3}. \tag{96}$$

a_2 is split before differentiating, as the second and third order differentials will become ugly. Since χ is a function of $\bar{\zeta}_x$, and not η and x_0, it will is best to separate the differentials from

χ and the rest of the terms.

$$a_2 = a_{2,1} a_{2,2}, \tag{97}$$

$$a_{2,1} = \frac{1}{2} K^{\mathrm{HS}} \left(1 + \chi\right) \epsilon \mathcal{C}^2, \tag{98}$$

$$a_{2,2} = x_0^{2\lambda_\mathrm{a}} \left(a^{\mathrm{S}}_{1(2\lambda_\mathrm{a})} + B_{(2\lambda_\mathrm{a})} \right) - 2 x_0^{\lambda_\mathrm{a}+\lambda_\mathrm{r}} \left(a^{\mathrm{S}}_{1(\lambda_\mathrm{a}+\lambda_\mathrm{r})} + B_{(\lambda_\mathrm{a}+\lambda_\mathrm{r})} \right) + x_0^{2\lambda_\mathrm{r}} \left(a^{\mathrm{S}}_{1(2\lambda_\mathrm{r})} + B_{(2\lambda_\mathrm{r})} \right), \tag{99}$$

$$\bar{a}_{2,1} = \frac{a_{2,1}}{1 + \chi}, \tag{100}$$

$$a_{2,\chi} = \bar{a}_{2,1} a_{2,2}. \tag{101}$$

(102)

The differentials of $\bar{a}_{2,1}$ simply becomes:

$$\frac{\partial \bar{a}_{2,1}}{\partial \eta} = \frac{\epsilon \mathcal{C}^2}{2} \frac{\partial K^{\mathrm{HS}}}{\partial \eta}, \tag{103}$$

$$\frac{\partial^2 \bar{a}_{2,1}}{\partial \eta^2} = \frac{\epsilon \mathcal{C}^2}{2} \frac{\partial^2 K^{\mathrm{HS}}}{\partial \eta^2}, \tag{104}$$

$$\frac{\partial^3 \bar{a}_{2,1}}{\partial \eta^3} = \frac{\epsilon \mathcal{C}^2}{2} \frac{\partial^3 K^{\mathrm{HS}}}{\partial \eta^3}. \tag{105}$$

Differentials of $a_{2,2}$ then becomes:

$$\begin{aligned}\frac{\partial a_{2,2}}{\partial x_0} =& 2\lambda_a x_0^{(2\lambda_a-1)}\left(a^S_{1(2\lambda_a)} + B_{(2\lambda_a)}\right) - 2\left(\lambda_a+\lambda_r\right)x_0^{(\lambda_a+\lambda_r-1)}\left(a^S_{1(\lambda_a+\lambda_r)} + B_{(\lambda_a+\lambda_r)}\right)\\ &+ 2\lambda_r x_0^{(2\lambda_r-1)}\left(a^S_{1(2\lambda_r)} + B_{(2\lambda_r)}\right)\\ &+ x_0^{2\lambda_a}\frac{\partial B_{(2\lambda_a)}}{\partial x_0} - 2x_0^{\lambda_a+\lambda_r}\frac{\partial B_{(\lambda_a+\lambda_r)}}{\partial x_0} + x_0^{2\lambda_r}\frac{\partial B_{(2\lambda_r)}}{\partial x_0},\end{aligned} \tag{106}$$

$$\begin{aligned}\frac{\partial^2 a_{2,2}}{\partial {x_0}^2} =& 2\lambda_a\left(2\lambda_a-1\right)x_0^{(2\lambda_a-2)}\left(a^S_{1(2\lambda_a)} + B_{(2\lambda_a)}\right)\\ &- 2\left(\lambda_a+\lambda_r\right)\left(\lambda_a+\lambda_r-1\right)x_0^{(\lambda_a+\lambda_r-2)}\left(a^S_{1(\lambda_a+\lambda_r)} + B_{(\lambda_a+\lambda_r)}\right)\\ &+ 2\lambda_r\left(2\lambda_r-1\right)x_0^{(2\lambda_r-2)}\left(a^S_{1(2\lambda_r)} + B_{(2\lambda_r)}\right)\\ &+ x_0^{2\lambda_a}\frac{\partial^2 B_{(2\lambda_a)}}{\partial {x_0}^2} - 2x_0^{\lambda_a+\lambda_r}\frac{\partial^2 B_{(\lambda_a+\lambda_r)}}{\partial {x_0}^2} + x_0^{2\lambda_r}\frac{\partial^2 B_{(2\lambda_r)}}{\partial {x_0}^2}\\ &+ 4\lambda_a x_0^{(2\lambda_a-1)}\frac{\partial B_{(2\lambda_a)}}{\partial x_0} - 4\left(\lambda_a+\lambda_r\right)x_0^{(\lambda_a+\lambda_r-1)}\frac{\partial B_{(\lambda_a+\lambda_r)}}{\partial x_0} + 4\lambda_r x_0^{(2\lambda_r-1)}\frac{\partial B_{(2\lambda_r)}}{\partial x_0}\end{aligned} \tag{107}$$

$$\begin{aligned}\frac{\partial a_{2,2}}{\partial \eta} =& x_0^{2\lambda_a}\left(\frac{\partial a^S_{1(2\lambda_a)}}{\partial \eta} + \frac{\partial B_{(2\lambda_a)}}{\partial \eta}\right) - 2x_0^{\lambda_a+\lambda_r}\left(\frac{\partial a^S_{1(\lambda_a+\lambda_r)}}{\partial \eta} + \frac{\partial B_{(\lambda_a+\lambda_r)}}{\partial \eta}\right)\\ &+ x_0^{2\lambda_r}\left(\frac{\partial a^S_{1(2\lambda_r)}}{\partial \eta} + \frac{\partial B_{(2\lambda_r)}}{\partial \eta}\right),\end{aligned} \tag{108}$$

$$\begin{aligned}\frac{\partial^2 a_{2,2}}{\partial \eta^2} =& x_0^{2\lambda_a}\left(\frac{\partial^2 a^S_{1(2\lambda_a)}}{\partial \eta^2} + \frac{\partial^2 B_{(2\lambda_a)}}{\partial \eta^2}\right) - 2x_0^{\lambda_a+\lambda_r}\left(\frac{\partial^2 a^S_{1(\lambda_a+\lambda_r)}}{\partial \eta^2} + \frac{\partial^2 B_{(\lambda_a+\lambda_r)}}{\partial \eta^2}\right)\\ &+ x_0^{2\lambda_r}\left(\frac{\partial^2 a^S_{1(2\lambda_r)}}{\partial \eta^2} + \frac{\partial^2 B_{(2\lambda_r)}}{\partial \eta^2}\right),\end{aligned} \tag{109}$$

$$\begin{aligned}\frac{\partial^3 a_{2,2}}{\partial \eta^3} =& x_0^{2\lambda_a}\left(\frac{\partial^3 a^S_{1(2\lambda_a)}}{\partial \eta^3} + \frac{\partial^3 B_{(2\lambda_a)}}{\partial \eta^3}\right) - 2x_0^{\lambda_a+\lambda_r}\left(\frac{\partial^3 a^S_{1(\lambda_a+\lambda_r)}}{\partial \eta^3} + \frac{\partial^3 B_{(\lambda_a+\lambda_r)}}{\partial \eta^3}\right)\\ &+ x_0^{2\lambda_r}\left(\frac{\partial^3 a^S_{1(2\lambda_r)}}{\partial \eta^3} + \frac{\partial^3 B_{(2\lambda_r)}}{\partial \eta^3}\right),\end{aligned} \tag{110}$$

$$\begin{aligned}\frac{\partial^2 a_{2,2}}{\partial \eta \partial x_0} =& 2\lambda_a x_0^{(2\lambda_a-1)}\left(\frac{\partial a^S_{1(2\lambda_a)}}{\partial \eta} + \frac{\partial B_{(2\lambda_a)}}{\partial \eta}\right) - 2\left(\lambda_a+\lambda_r\right)x_0^{(\lambda_a+\lambda_r-1)}\left(\frac{\partial a^S_{1(\lambda_a+\lambda_r)}}{\partial \eta} + \frac{\partial B_{(\lambda_a+\lambda_r)}}{\partial \eta}\right)\\ &+ 2\lambda_r x_0^{(2\lambda_r-1)}\left(\frac{\partial a^S_{1(2\lambda_r)}}{\partial \eta} + \frac{\partial B_{(2\lambda_r)}}{\partial \eta}\right)\\ &+ x_0^{2\lambda_a}\frac{\partial^2 B_{(2\lambda_a)}}{\partial x_0 \partial \eta} - 2x_0^{\lambda_a+\lambda_r}\frac{\partial^2 B_{(\lambda_a+\lambda_r)}}{\partial x_0 \partial \eta} + x_0^{2\lambda_r}\frac{\partial^2 B_{(2\lambda_r)}}{\partial x_0 \partial \eta},\end{aligned} \tag{111}$$

$$\frac{\partial^3 a_{2,2}}{\partial\eta^2\partial x_0} = 2\lambda_{\mathrm{a}} x_0^{(2\lambda_{\mathrm{a}}-1)}\left(\frac{\partial^2 a^{\mathrm{S}}_{1(2\lambda_{\mathrm{a}})}}{\partial\eta^2}+\frac{\partial^2 B_{(2\lambda_{\mathrm{a}})}}{\partial\eta^2}\right) - 2\left(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}\right) x_0^{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}-1)}\left(\frac{\partial^2 a^{\mathrm{S}}_{1(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial\eta^2}+\frac{\partial^2 B_{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial\eta^2}\right)$$
$$+ 2\lambda_{\mathrm{r}} x_0^{(2\lambda_{\mathrm{r}}-1)}\left(\frac{\partial^2 a^{\mathrm{S}}_{1(2\lambda_{\mathrm{r}})}}{\partial\eta^2}+\frac{\partial^2 B_{(2\lambda_{\mathrm{r}})}}{\partial\eta^2}\right)$$
$$+ x_0^{2\lambda_{\mathrm{a}}}\frac{\partial^3 B_{(2\lambda_{\mathrm{a}})}}{\partial\eta^2\partial x_0} - 2x_0^{\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}}\frac{\partial^3 B_{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial\eta^2\partial x_0} + x_0^{2\lambda_{\mathrm{r}}}\frac{\partial^3 B_{(2\lambda_{\mathrm{r}})}}{\partial\eta^2\partial x_0}, \tag{112}$$

$$\frac{\partial^3 a_{2,2}}{\partial {x_0}^2\partial\eta} = 2\lambda_{\mathrm{a}}\left(2\lambda_{\mathrm{a}}-1\right) x_0^{(2\lambda_{\mathrm{a}}-2)}\left(\frac{\partial a^{\mathrm{S}}_{1(2\lambda_{\mathrm{a}})}}{\partial\eta}+\frac{\partial B_{(2\lambda_{\mathrm{a}})}}{\partial\eta}\right)$$
$$- 2\left(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}\right)\left(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}-1\right) x_0^{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}-2)}\left(\frac{\partial a^{\mathrm{S}}_{1(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial\eta}+\frac{\partial B_{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial\eta}\right)$$
$$+ 2\lambda_{\mathrm{r}}\left(2\lambda_{\mathrm{r}}-1\right) x_0^{(2\lambda_{\mathrm{r}}-2)}\left(\frac{\partial a^{\mathrm{S}}_{1(2\lambda_{\mathrm{r}})}}{\partial\eta}+\frac{\partial B_{(2\lambda_{\mathrm{r}})}}{\partial\eta}\right)$$
$$+ 4\lambda_{\mathrm{a}} x_0^{(2\lambda_{\mathrm{a}}-1)}\frac{\partial^2 B_{(2\lambda_{\mathrm{a}})}}{\partial x_0\partial\eta} - 4\left(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}\right) x_0^{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}-1)}\frac{\partial^2 B_{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial x_0\partial\eta} + 4\lambda_{\mathrm{r}} x_0^{(2\lambda_{\mathrm{r}}-1)}\frac{\partial^2 B_{(2\lambda_{\mathrm{r}})}}{\partial x_0\partial\eta}$$
$$+ x_0^{2\lambda_{\mathrm{a}}}\frac{\partial^3 B_{(2\lambda_{\mathrm{a}})}}{\partial {x_0}^2\partial\eta} - 2x_0^{\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}}}\frac{\partial^3 B_{(\lambda_{\mathrm{a}}+\lambda_{\mathrm{r}})}}{\partial {x_0}^2\partial\eta} + x_0^{2\lambda_{\mathrm{r}}}\frac{\partial^3 B_{(2\lambda_{\mathrm{r}})}}{\partial {x_0}^2\partial\eta}. \tag{113}$$

Combining $\bar{a}_{2,1}$ and $a_{2,2}$, using $a_{2,\chi} = \bar{a}_{2,1}a_{2,2}$,

$$\frac{\partial a_{2,\chi}}{\partial x_0} = \bar{a}_{2,1}\frac{\partial a_{2,2}}{\partial x_0}, \tag{114}$$
$$\frac{\partial^2 a_{2,\chi}}{\partial {x_0}^2} = \bar{a}_{2,1}\frac{\partial^2 a_{2,2}}{\partial {x_0}^2}, \tag{115}$$
$$\frac{\partial a_{2,\chi}}{\partial\eta} = \bar{a}_{2,1}\frac{\partial a_{2,2}}{\partial\eta} + a_{2,2}\frac{\partial\bar{a}_{2,1}}{\partial\eta}, \tag{116}$$
$$\frac{\partial^2 a_{2,\chi}}{\partial\eta^2} = \bar{a}_{2,1}\frac{\partial^2 a_{2,2}}{\partial\eta^2} + 2\frac{\partial\bar{a}_{2,1}}{\partial\eta}\frac{\partial a_{2,2}}{\partial\eta} + a_{2,2}\frac{\partial^2\bar{a}_{2,1}}{\partial\eta^2}, \tag{117}$$
$$\frac{\partial^3 a_{2,\chi}}{\partial\eta^3} = \bar{a}_{2,1}\frac{\partial^3 a_{2,2}}{\partial\eta^3} + 3\frac{\partial^2\bar{a}_{2,1}}{\partial\eta^2}\frac{\partial a_{2,2}}{\partial\eta} + 3\frac{\partial\bar{a}_{2,1}}{\partial\eta}\frac{\partial^2 a_{2,2}}{\partial\eta^2} + a_{2,2}\frac{\partial^3\bar{a}_{2,1}}{\partial\eta^3}, \tag{118}$$
$$\frac{\partial^2 a_{2,\chi}}{\partial\eta\partial x_0} = \frac{\partial\bar{a}_{2,1}}{\partial\eta}\frac{\partial a_{2,2}}{\partial x_0} + \bar{a}_{2,1}\frac{\partial^2 a_{2,2}}{\partial x_0\partial\eta}, \tag{119}$$
$$\frac{\partial^3 a_{2,\chi}}{\partial\eta^2\partial x_0} = \bar{a}_{2,1}\frac{\partial^3 a_{2,2}}{\partial\eta^2\partial x_0} + 2\frac{\partial\bar{a}_{2,1}}{\partial\eta}\frac{\partial^2 a_{2,2}}{\partial\eta\partial x_0} + a_{2,2}\frac{\partial^3\bar{a}_{2,1}}{\partial\eta^2\partial x_0}. \tag{120}$$

(121)

The a_2 differentials become,

$$\frac{\partial a_2}{\partial T} = (1+\chi)\frac{\partial a_{2,\chi}}{\partial T}, \tag{122}$$

$$\frac{\partial^2 a_2}{\partial T^2} = (1+\chi)\frac{\partial^2 a_{2,\chi}}{\partial T^2}, \tag{123}$$

$$\frac{\partial a_2}{\partial V} = (1+\chi)\frac{\partial a_{2,\chi}}{\partial V} + a_{2,\chi}\frac{\partial \chi}{\partial V}, \tag{124}$$

$$\frac{\partial^2 a_2}{\partial V^2} = (1+\chi)\frac{\partial^2 a_{2,\chi}}{\partial V^2} + 2\frac{\partial a_{2,\chi}}{\partial V}\frac{\partial \chi}{\partial V} + a_{2,\chi}\frac{\partial^2 \chi}{\partial V^2}, \tag{125}$$

$$\frac{\partial^3 a_2}{\partial V^3} = (1+\chi)\frac{\partial^3 a_{2,\chi}}{\partial V^3} + 3\frac{\partial^2 a_{2,\chi}}{\partial V^2}\frac{\partial \chi}{\partial V} + 3\frac{\partial a_{2,\chi}}{\partial V}\frac{\partial^2 \chi}{\partial V^2} + a_{2,\chi}\frac{\partial^3 \chi}{\partial V^3}, \tag{126}$$

$$\frac{\partial^2 a_2}{\partial T \partial V} = (1+\chi)\frac{\partial^2 a_{2,\chi}}{\partial T \partial V} + \frac{\partial \chi}{\partial V}\frac{\partial a_{2,\chi}}{\partial T}, \tag{127}$$

$$\frac{\partial^3 a_2}{\partial V^2 \partial T} = (1+\chi)\frac{\partial^3 a_{2,\chi}}{\partial V^2 \partial T} + 2\frac{\partial^2 a_{2,\chi}}{\partial V \partial T}\frac{\partial \chi}{\partial V} + \frac{\partial a_{2,\chi}}{\partial T}\frac{\partial^2 \chi}{\partial V^2}. \tag{128}$$

3.4 Third order monomer perturbation

The second order monomer perturbation is given as,

$$a_3 = -\epsilon^3 f_4(\alpha)\,\bar{\zeta}_x \exp\left(f_5(\alpha)\,\bar{\zeta}_x + f_6(\alpha)\,\bar{\zeta}_x^2\right). \tag{129}$$

3.4.1 Differential terms

Differentials of a_3 then becomes:

$$\frac{\partial a_3}{\partial \bar{\zeta}_x} = a_3\left[\frac{1}{\bar{\zeta}_x} + f_5 + 2 f_6 \bar{\zeta}_x\right], \tag{130}$$

$$\frac{\partial^2 a_3}{\partial \bar{\zeta}_x^2} = a_3\left[\frac{2 f_5}{\bar{\zeta}_x} + 6 f_6 + \left(f_5 + 2 f_6 \bar{\zeta}_x\right)^2\right]. \tag{131}$$

3.5 Chains of monomer Mie segments

The Mie segments are assumed to be tangentially bounded at $r = \sigma$ from m_s segments. The reduced Helmholtz contribution for the chain formation is given by the Wertheim TPT1 from,

$$a^{\mathrm{chain}} = -\left(m_\mathrm{s} - 1\right) \ln\left(g^{\mathrm{Mie}}(\sigma)\right), \tag{132}$$

where g^{Mie} is the RDF at contact,

$$g^{\mathrm{Mie}}(\sigma) = g_d^{\mathrm{HS}}(\sigma) \exp\left[\frac{\beta\epsilon g_1(\sigma) + (\beta\epsilon)^2 g_2(\sigma)}{g_d^{\mathrm{HS}}(\sigma)}\right]. \tag{133}$$

Here,

$$g_d^{\mathrm{HS}}(\sigma) = \exp\left(k_0 + k_1 x_0 + k_2 x_0^2 + k_3 x_0^3\right), \tag{134}$$

with

$$k_0 = -\ln(1-\eta) + \frac{42\eta - 39\eta^2 + 9\eta^3 - 2\eta^4}{6(1-\eta)^3}, \tag{135}$$

$$k_1 = \frac{\eta^4 + 6\eta^2 - 12\eta}{2(1-\eta)^3}, \tag{136}$$

$$k_2 = \frac{-3\eta^2}{8(1-\eta)^2}, \tag{137}$$

$$k_3 = \frac{-\eta^4 + 3\eta^2 + \ 3\eta}{6(1-\eta)^3}. \tag{138}$$

For g_1 we have,

$$\begin{aligned} g_1(\sigma) =& \frac{1}{2\pi\epsilon d^3}\left[3\frac{\partial a_1}{\partial \rho_\mathrm{s}} - \mathcal{C}\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}} \frac{a_1^\mathrm{S}(\eta;\lambda_\mathrm{a}) + B(\eta;\lambda_\mathrm{a})}{\rho_\mathrm{s}} + \mathcal{C}\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}} \frac{a_1^\mathrm{S}(\eta;\lambda_\mathrm{r}) + B(\eta;\lambda_\mathrm{r})}{\rho_\mathrm{s}}\right], \\ =& \frac{1}{12\epsilon}\left[3\frac{\partial a_1}{\partial \rho_\mathrm{s}}\frac{\rho_\mathrm{s}}{\eta} - \mathcal{C}\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}} \frac{a_1^\mathrm{S}(\eta;\lambda_\mathrm{a}) + B(\eta;\lambda_\mathrm{a})}{\eta} + \mathcal{C}\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}} \frac{a_1^\mathrm{S}(\eta;\lambda_\mathrm{r}) + B(\eta;\lambda_\mathrm{r})}{\eta}\right], \\ =& \frac{1}{12\epsilon}\left[-3\frac{\partial a_1}{\partial V}\frac{V}{\eta} - \mathcal{C}\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\tilde{a}_1^\mathrm{S}(\eta;\lambda_\mathrm{a}) + \tilde{B}(\eta;\lambda_\mathrm{a})\right) + \mathcal{C}\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\tilde{a}_1^\mathrm{S}(\eta;\lambda_\mathrm{r}) + \tilde{B}(\eta;\lambda_\mathrm{r})\right)\right]. \end{aligned} \tag{139}$$

For g_2 we have,

$$g_2(\sigma) = (1+\gamma_\mathrm{C})\, g_2^\mathrm{MCA}(\sigma), \tag{140}$$

were

$$\begin{aligned} g_2^\mathrm{MCA}(\sigma) =& \frac{1}{2\pi\epsilon^2 d^3}\left[3\frac{\partial\left(\frac{a_2}{1+\chi}\right)}{\partial\rho_\mathrm{s}} + \epsilon K^\mathrm{HS}\mathcal{C}^2(\lambda_\mathrm{r}+\lambda_\mathrm{a})\, x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\frac{a_1^\mathrm{S}(\eta;\lambda_\mathrm{r}+\lambda_\mathrm{a}) + B(\eta;\lambda_\mathrm{r}+\lambda_\mathrm{a})}{\rho_\mathrm{s}}\right. \\ & - \epsilon K^\mathrm{HS}\mathcal{C}^2\lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\frac{a_1^\mathrm{S}(\eta;2\lambda_\mathrm{a}) + B(\eta;2\lambda_\mathrm{a})}{\rho_\mathrm{s}} \\ & \left. -\epsilon K^\mathrm{HS}\mathcal{C}^2\lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\frac{a_1^\mathrm{S}(\eta;2\lambda_\mathrm{r}) + B(\eta;2\lambda_\mathrm{r})}{\rho_\mathrm{s}}\right], \end{aligned} \tag{141}$$

$$\begin{aligned} =& \frac{1}{12\epsilon^2}\left[-3\frac{\partial a_{2,\chi}}{\partial V}\frac{V}{\eta} + \epsilon K^\mathrm{HS}\mathcal{C}^2(\lambda_\mathrm{r}+\lambda_\mathrm{a})\, x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\left(\tilde{a}_1^\mathrm{S}(\eta;\lambda_\mathrm{r}+\lambda_\mathrm{a}) + \tilde{B}(\eta;\lambda_\mathrm{r}+\lambda_\mathrm{a})\right)\right. \\ & - \epsilon K^\mathrm{HS}\mathcal{C}^2\lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\left(\tilde{a}_1^\mathrm{S}(\eta;2\lambda_\mathrm{a}) + \tilde{B}(\eta;2\lambda_\mathrm{a})\right) \\ & \left. -\epsilon K^\mathrm{HS}\mathcal{C}^2\lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\left(\tilde{a}_1^\mathrm{S}(\eta;2\lambda_\mathrm{r}) + \tilde{B}(\eta;2\lambda_\mathrm{r})\right)\right] \end{aligned} \tag{142}$$

and,

$$\gamma_\mathrm{C} = \phi_{7,0}\left(1 - \tanh\left(\phi_{7,1}\left(\phi_{7,2} - \alpha\right)\right)\right)\bar{\zeta}_x\theta\exp\left(\phi_{7,3}\bar{\zeta}_x + \phi_{7,4}\bar{\zeta}_x^2\right). \tag{143}$$

θ is given as

$$\theta = \exp(\beta\epsilon) - 1. \tag{144}$$

3.5.1 Differentials

Before differentiating g_1 and g_2^{MCA} is split as follows,

$$g_1 = g_{1,1} + g_{1,2}, \tag{145}$$
$$g_{1,1} = -\frac{V}{4\epsilon\eta}\frac{\partial a_1}{\partial V}, \tag{146}$$
$$g_{1,2} = \frac{\mathcal{C}}{12\epsilon}\left[-\lambda_{\mathrm{a}} x_0^{\lambda_{\mathrm{a}}}\left(\tilde{a}_1^{\mathrm{S}}(\eta;\lambda_{\mathrm{a}}) + \tilde{B}(\eta;\lambda_{\mathrm{a}})\right) + \lambda_{\mathrm{r}} x_0^{\lambda_{\mathrm{r}}}\left(\tilde{a}_1^{\mathrm{S}}(\eta;\lambda_{\mathrm{r}}) + \tilde{B}(\eta;\lambda_{\mathrm{r}})\right)\right]. \tag{147}$$

$$g_2^{\mathrm{MCA}} = g_{2,1}^{\mathrm{MCA}} + K^{\mathrm{HS}} g_{2,2}^{\mathrm{MCA}}, \tag{148}$$
$$g_{2,1}^{\mathrm{MCA}} = -\frac{V}{4\epsilon^2\eta}\frac{\partial a_{2,\chi}}{\partial V}, \tag{149}$$
$$\begin{aligned} g_{2,2}^{\mathrm{MCA}} = \frac{\mathcal{C}^2}{12\epsilon}\Bigg[& -\lambda_{\mathrm{r}} x_0^{2\lambda_{\mathrm{r}}}\left(\tilde{a}_1^{\mathrm{S}}(\eta;2\lambda_{\mathrm{r}}) + \tilde{B}(\eta;2\lambda_{\mathrm{r}})\right) \\ & + (\lambda_{\mathrm{r}}+\lambda_{\mathrm{a}})\, x_0^{(\lambda_{\mathrm{r}}+\lambda_{\mathrm{a}})}\left(\tilde{a}_1^{\mathrm{S}}(\eta;\lambda_{\mathrm{r}}+\lambda_{\mathrm{a}}) + \tilde{B}(\eta;\lambda_{\mathrm{r}}+\lambda_{\mathrm{a}})\right) \\ & -\lambda_{\mathrm{a}} x_0^{2\lambda_{\mathrm{a}}}\left(\tilde{a}_1^{\mathrm{S}}(\eta;2\lambda_{\mathrm{a}}) + \tilde{B}(\eta;2\lambda_{\mathrm{a}})\right)\Bigg]. \end{aligned} \tag{150}$$

Differentials for k_i,

$$\frac{\partial k_0}{\partial \eta} = \frac{\eta^4 - 7\eta^3 + 3\eta^2 - 6\eta + 24}{3(1-\eta)^4}, \tag{151}$$
$$\frac{\partial^2 k_0}{\partial \eta^2} = -\frac{\eta^3 + 5\eta^2 + 4\eta - 30}{(1-\eta)^5}, \tag{152}$$
$$\frac{\partial k_1}{\partial \eta} = \frac{-12 - 12\eta + 6\eta^2 + 4\eta^3 - \eta^4}{2(1-\eta)^4}, \tag{153}$$
$$\frac{\partial^2 k_1}{\partial \eta^2} = \frac{(-6\left(5 + 2\eta - 2\eta^2\right)}{(1-\eta)^5}, \tag{154}$$
$$\frac{\partial k_2}{\partial \eta} = \frac{-3\eta}{4(1-\eta)^3}, \tag{155}$$
$$\frac{\partial^2 k_2}{\partial \eta^2} = -\frac{3(2\eta+1)}{4(1-\eta)^4}, \tag{156}$$
$$\frac{\partial k_3}{\partial \eta} = \frac{3 + 12\eta + 3\eta^2 - 4\eta^3 + \eta^4}{6(1-\eta)^4}, \tag{157}$$
$$\frac{\partial^2 k_3}{\partial \eta^2} = -\frac{-4 - 7\eta + \eta^2}{(1-\eta)^5}. \tag{158}$$

The differentials for g_d^{HS} becomes,

$$\frac{\partial g_d^{\text{HS}}}{\partial \eta} = g_d^{\text{HS}} \left(\frac{\partial k_0}{\partial \eta} + \frac{\partial k_1}{\partial \eta} x_0 + \frac{\partial k_2}{\partial \eta} x_0^2 + \frac{\partial k_3}{\partial \eta} x_0^3 \right), \tag{159}$$

$$\frac{\partial^2 g_d^{\text{HS}}}{\partial \eta^2} = g_d^{\text{HS}} \left[\left(\frac{\partial k_0}{\partial \eta} + \frac{\partial k_1}{\partial \eta} x_0 + \frac{\partial k_2}{\partial \eta} x_0^2 + \frac{\partial k_3}{\partial \eta} x_0^3 \right)^2 + \left(\frac{\partial^2 k_0}{\partial \eta^2} + \frac{\partial^2 k_1}{\partial \eta^2} x_0 + \frac{\partial^2 k_2}{\partial \eta^2} x_0^2 + \frac{\partial^2 k_3}{\partial \eta^2} x_0^3 \right) \right], \tag{160}$$

$$\frac{\partial g_d^{\text{HS}}}{\partial x_0} = g_d^{\text{HS}} \left(k_1 + 2k_2 x_0 + 3k_3 x_0^2 \right), \tag{161}$$

$$\frac{\partial g_d^{\text{HS}}}{\partial x_0} = g_d^{\text{HS}} \left[\left(k_1 + 2k_2 x_0 + 3k_3 x_0^2 \right)^2 + \left(2k_2 + 6k_3 x_0 \right) \right], \tag{162}$$

$$\frac{\partial^2 g_d^{\text{HS}}}{\partial x_0 \partial \eta} = g_d^{\text{HS}} \left[\left(\frac{\partial k_0}{\partial \eta} + \frac{\partial k_1}{\partial \eta} x_0 + \frac{\partial k_2}{\partial \eta} x_0^2 + \frac{\partial k_3}{\partial \eta} x_0^3 \right) \left(k_1 + 2k_2 x_0 + 3k_3 x_0^2 \right) + \left(\frac{\partial k_1}{\partial \eta} + 2\frac{\partial k_2}{\partial \eta} x_0 + 3\frac{\partial k_3}{\partial \eta} x_0^2 \right) \right]. \tag{163}$$

Differentiating $g_{1,1}$,

$$\frac{\partial g_{1,1}}{\partial V} = -\frac{3V^2}{2\epsilon\pi N_{\text{s}} d^3} \left(\frac{2}{V} \frac{\partial a_1}{\partial V} + \frac{\partial^2 a_1}{\partial V^2} \right), \tag{164}$$

$$\frac{\partial^2 g_{1,1}}{\partial V^2} = -\frac{3V^2}{2\epsilon\pi N_{\text{s}} d^3} \left(\frac{2}{V^2} \frac{\partial a_1}{\partial V} + \frac{4}{V} \frac{\partial^2 a_1}{\partial V^2} + \frac{\partial^3 a_1}{\partial V^3} \right), \tag{165}$$

$$\frac{\partial g_{1,1}}{\partial T} = -\frac{3V^2}{2\epsilon\pi N_{\text{s}} d^3} \frac{\partial^2 a_1}{\partial V \partial T} - \frac{3g_{1,1}}{d} \frac{\partial d}{\partial T}, \tag{166}$$

$$\frac{\partial^2 g_{1,1}}{\partial T^2} = -\frac{3V^2}{2\epsilon\pi N_{\text{s}} d^3} \frac{\partial^3 a_1}{\partial T^2 \partial V} - \frac{6g_{1,1}}{d^2} \left(\frac{\partial d}{\partial T} \right)^2 - \frac{3g_{1,1}}{d} \frac{\partial^2 d}{\partial T^2} - \frac{6}{d} \frac{\partial d}{\partial T} \frac{\partial g_{1,1}}{\partial T}, \tag{167}$$

$$\frac{\partial^2 g_{1,1}}{\partial T \partial V} = -\frac{3V^2}{2\epsilon\pi N_{\text{s}} d^3} \left(\frac{2}{V} \frac{\partial^2 a_1}{\partial V \partial T} + \frac{\partial^3 a_1}{\partial V^2 \partial T} \right) + \frac{3}{d} \frac{\partial d}{\partial T} \frac{\partial g_{1,1}}{\partial V}. \tag{168}$$

Differentiating $g_{1,2}$,

$$\frac{\partial g_{1,2}}{\partial \eta} = \frac{\mathcal{C}}{12\epsilon}\left[-\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta}+\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right)+\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta}+\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right)\right], \tag{169}$$

$$\frac{\partial^2 g_{1,2}}{\partial \eta^2} = \frac{\mathcal{C}}{12\epsilon}\left[-\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta^2}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta^2}\right)+\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta^2}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta^2}\right)\right], \tag{170}$$

$$\begin{aligned}\frac{\partial g_{1,2}}{\partial x_0} = &\frac{\mathcal{C}}{12\epsilon}\left[-\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial x_0}+\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0}\right)+\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial x_0}+\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0}\right)\right.\\ &\left.-{\lambda_\mathrm{a}}^2 x_0^{(\lambda_\mathrm{a}-1)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}+\tilde{B}_{\lambda_\mathrm{a}}\right)+{\lambda_\mathrm{r}}^2 x_0^{(\lambda_\mathrm{r}-1)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}+\tilde{B}_{\lambda_\mathrm{r}}\right)\right],\end{aligned} \tag{171}$$

$$\begin{aligned}\frac{\partial^2 g_{1,2}}{\partial {x_0}^2} = &\frac{\mathcal{C}}{12\epsilon}\left[-\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial {x_0}^2}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial {x_0}^2}\right)+\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial {x_0}^2}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial {x_0}^2}\right)\right.\\ &-{\lambda_\mathrm{a}}^2\left(\lambda_\mathrm{a}-1\right) x_0^{(\lambda_\mathrm{a}-2)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}+\tilde{B}_{\lambda_\mathrm{a}}\right)+{\lambda_\mathrm{r}}^2\left(\lambda_\mathrm{r}-1\right) x_0^{(\lambda_\mathrm{r}-2)}\left(\tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}+\tilde{B}_{\lambda_\mathrm{r}}\right)\\ &\left.-2{\lambda_\mathrm{a}}^2 x_0^{(\lambda_\mathrm{a}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial x_0}+\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial x_0}\right)+2{\lambda_\mathrm{r}}^2 x_0^{(\lambda_\mathrm{r}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial x_0}+\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial x_0}\right)\right],\end{aligned} \tag{172}$$

$$\begin{aligned}\frac{\partial^2 g_{1,2}}{\partial \eta \partial x_0} = &\frac{\mathcal{C}}{12\epsilon}\left[-{\lambda_\mathrm{a}}^2 x_0^{(\lambda_\mathrm{a}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta}+\frac{\partial \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta}\right)+{\lambda_\mathrm{r}}^2 x_0^{(\lambda_\mathrm{r}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta}+\frac{\partial \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta}\right)\right.\\ &\left.-\lambda_\mathrm{a} x_0^{\lambda_\mathrm{a}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{a}}}{\partial \eta \partial x_0}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{a}}}{\partial \eta \partial x_0}\right)+\lambda_\mathrm{r} x_0^{\lambda_\mathrm{r}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1\lambda_\mathrm{r}}}{\partial \eta \partial x_0}+\frac{\partial^2 \tilde{B}_{\lambda_\mathrm{r}}}{\partial \eta \partial x_0}\right)\right].\end{aligned} \tag{173}$$

The differentials for $g_{2,1}^{\mathrm{MCA}}$ is given from equations 164 to 168, simply by replacing a_1 with $a_{2,\chi}$, and dividing with ϵ.

Differentiating $g_{2,2}^{\mathrm{MCA}}$,

$$\begin{aligned}\frac{\partial g_{2,2}^{\mathrm{MCA}}}{\partial \eta} = &\frac{\mathcal{C}^2}{12\epsilon}\left[-\lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{r})}}{\partial \eta}+\frac{\partial \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial \eta}\right)\right.\\ &+\left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta}+\frac{\partial \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta}\right)\\ &\left.-\lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{a})}}{\partial \eta}+\frac{\partial \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial \eta}\right)\right],\end{aligned} \tag{174}$$

$$\begin{aligned}\frac{\partial^2 g_{2,2}^{\mathrm{MCA}}}{\partial \eta^2} = &\frac{\mathcal{C}^2}{12\epsilon}\left[-\lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{r})}}{\partial \eta^2}+\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial \eta^2}\right)\right.\\ &+\left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta^2}+\frac{\partial^2 \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta^2}\right)\\ &\left.-\lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\left(\frac{\partial^2 \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{a})}}{\partial \eta^2}+\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial \eta^2}\right)\right],\end{aligned} \tag{175}$$

$$\frac{\partial g_{2,2}^{\mathrm{MCA}}}{\partial x_0} = \frac{\mathcal{C}^2}{12\epsilon}\Bigg[-2{\lambda_\mathrm{r}}^2 x_0^{2\lambda_\mathrm{r}-1}\left(\tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{r})}+\tilde{B}_{(2\lambda_\mathrm{r})}\right) + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right)^2 x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a}-1)}\left(\tilde{a}^\mathrm{S}_{1(\lambda_\mathrm{r}+\lambda_\mathrm{a})}+\tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\right) - 2{\lambda_\mathrm{a}}^2 x_0^{2\lambda_\mathrm{a}-1}\left(\tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{a})}+\tilde{B}_{(2\lambda_\mathrm{a})}\right) - \lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\frac{\partial \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial x_0} + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\frac{\partial \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial x_0} - \lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\frac{\partial \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial x_0}\Bigg], \tag{176}$$

$$\frac{\partial^2 g_{2,2}^{\mathrm{MCA}}}{\partial {x_0}^2} = \frac{\mathcal{C}^2}{12\epsilon}\Bigg[-2{\lambda_\mathrm{r}}^2\left(2\lambda_\mathrm{r}-1\right) x_0^{2\lambda_\mathrm{r}-2}\left(\tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{r})}+\tilde{B}_{(2\lambda_\mathrm{r})}\right) + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right)^2\left(\lambda_\mathrm{r}+\lambda_\mathrm{a}-1\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a}-2)}\left(\tilde{a}^\mathrm{S}_{1(\lambda_\mathrm{r}+\lambda_\mathrm{a})}+\tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\right) - 2{\lambda_\mathrm{a}}^2\left(2\lambda_\mathrm{a}-1\right) x_0^{2\lambda_\mathrm{a}-2}\left(\tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{a})}+\tilde{B}_{(2\lambda_\mathrm{a})}\right) - 2{\lambda_\mathrm{r}}^2 x_0^{2\lambda_\mathrm{r}-1}\frac{\partial \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial x_0} + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right)^2 x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a}-1)}\frac{\partial \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial x_0} - 2{\lambda_\mathrm{a}}^2 x_0^{2\lambda_\mathrm{a}-1}\frac{\partial \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial x_0} - \lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial {x_0}^2} + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\frac{\partial^2 \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial {x_0}^2} - \lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial {x_0}^2}\Bigg], \tag{177}$$

$$\frac{\partial^2 g_{2,2}^{\mathrm{MCA}}}{\partial x_0 \partial \eta} = \frac{\mathcal{C}^2}{12\epsilon}\Bigg[-2{\lambda_\mathrm{r}}^2 x_0^{2\lambda_\mathrm{r}-1}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{r})}}{\partial \eta}+\frac{\partial \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial \eta}\right) + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right)^2 x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a}-1)}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta}+\frac{\partial \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial \eta}\right) - 2{\lambda_\mathrm{a}}^2 x_0^{2\lambda_\mathrm{a}-1}\left(\frac{\partial \tilde{a}^\mathrm{S}_{1(2\lambda_\mathrm{a})}}{\partial \eta}+\frac{\partial \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial \eta}\right) - \lambda_\mathrm{r} x_0^{2\lambda_\mathrm{r}}\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{r})}}{\partial x_0 \partial \eta} + \left(\lambda_\mathrm{r}+\lambda_\mathrm{a}\right) x_0^{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}\frac{\partial^2 \tilde{B}_{(\lambda_\mathrm{r}+\lambda_\mathrm{a})}}{\partial x_0 \partial \eta} - \lambda_\mathrm{a} x_0^{2\lambda_\mathrm{a}}\frac{\partial^2 \tilde{B}_{(2\lambda_\mathrm{a})}}{\partial x_0 \partial \eta}\Bigg]. \tag{178}$$

The differentials of $g_{2,1}$ differe structure only in the pre-factor from the $g_{1,1}$ differentials in Equation 164-168.

Introducing an auxiliary function for γ_C, $f\left(\bar{\zeta}_x\right) = \phi_{7,3}\bar{\zeta}_x + \phi_{7,4}\bar{\zeta}_x^2$, and differentiating $\gamma_\mathrm{C}^\theta = \gamma_\mathrm{C}/\theta$ we get,

$$\frac{\partial \gamma_\mathrm{C}^\theta}{\partial \bar{\zeta}_x} = \gamma_\mathrm{C}^\theta\left[\frac{1}{\bar{\zeta}_x}+\frac{\partial f}{\partial \bar{\zeta}_x}\right], \tag{179}$$

$$\frac{\partial^2 \gamma_\mathrm{C}^\theta}{\partial \bar{\zeta}_x^2} = \gamma_\mathrm{C}^\theta\left[\frac{2}{\bar{\zeta}_x}\frac{\partial f}{\partial \bar{\zeta}_x}+\left(\frac{\partial f}{\partial \bar{\zeta}_x}\right)^2+\frac{\partial^2 f}{\partial \bar{\zeta}_x^2}\right], \tag{180}$$

$$\frac{\partial f}{\partial \bar{\zeta}_x} = \phi_{7,3} + 2\phi_{7,4}\bar{\zeta}_x, \tag{181}$$

$$\frac{\partial^2 f}{\partial \bar{\zeta}_x^2} = 2\phi_{7,4}. \tag{182}$$

Differentiating θ,

$$\frac{\partial \theta}{\partial T} = - \exp\left(\frac{\epsilon}{k_\mathrm{B} T}\right)\frac{\epsilon}{k_\mathrm{B} T^2}, \tag{183}$$

$$\frac{\partial^2 \theta}{\partial T^2} = \exp\left(\frac{\epsilon}{k_\mathrm{B} T}\right)\left[\left(\frac{\epsilon}{k_\mathrm{B} T^2}\right)^2 + \frac{2\epsilon}{k_\mathrm{B} T^3}\right]. \tag{184}$$

Differentiating $\gamma_\mathrm{C}^\theta \theta$,

$$\frac{\partial \gamma_\mathrm{C}}{\partial T} = \gamma_\mathrm{C}^\theta \frac{\partial \theta}{\partial T} + \theta \frac{\partial \gamma_\mathrm{C}^\theta}{\partial T}, \tag{185}$$

$$\frac{\partial^2 \gamma_\mathrm{C}}{\partial T^2} = \gamma_\mathrm{C}^\theta \frac{\partial^2 \theta}{\partial T^2} + 2 \frac{\partial \gamma_\mathrm{C}^\theta}{\partial T}\frac{\partial \theta}{\partial T} + \theta \frac{\partial^2 \gamma_\mathrm{C}^\theta}{\partial T^2}, \tag{186}$$

$$\frac{\partial \gamma_\mathrm{C}}{\partial V} = \theta \frac{\partial \gamma_\mathrm{C}^\theta}{\partial V}, \tag{187}$$

$$\frac{\partial^2 \gamma_\mathrm{C}}{\partial V^2} = \theta \frac{\partial^2 \gamma_\mathrm{C}^\theta}{\partial V^2}, \tag{188}$$

$$\frac{\partial^2 \gamma_\mathrm{C}}{\partial T \partial V} = \frac{\partial \gamma_\mathrm{C}^\theta}{\partial V}\frac{\partial \theta}{\partial T} + \theta \frac{\partial^2 \gamma_\mathrm{C}^\theta}{\partial T \partial V}. \tag{189}$$

For $X \in \{T, V\}$ we have,

$$\frac{\partial a^\mathrm{chain}}{\partial X_i} = - (m_\mathrm{s} - 1) \frac{1}{g^\mathrm{Mie}} \frac{\partial g^\mathrm{Mie}}{\partial X_i}, \tag{190}$$

$$\frac{\partial^2 a^\mathrm{chain}}{\partial X_i \partial X_j} = - (m_\mathrm{s} - 1) \frac{1}{g^\mathrm{Mie}} \left(- \frac{1}{g^\mathrm{Mie}} \frac{\partial g^\mathrm{Mie}}{\partial X_i} \frac{\partial g^\mathrm{Mie}}{\partial X_j} + \frac{\partial^2 g^\mathrm{Mie}}{\partial X_i \partial X_j}\right). \tag{191}$$

(192)

Introduce auxiliary function, w,

$$w = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) g_1 + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 g_2 \right], \tag{193}$$

$$\frac{\partial w}{\partial T} = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) \left(-\frac{g_1}{T} + \frac{\partial g_1}{\partial T}\right) + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 \left(-\frac{2g_2}{T} + \frac{\partial g_2}{\partial T}\right) - w\frac{\partial g_d^{\text{HS}}}{\partial T} \right], \tag{194}$$

$$\frac{\partial^2 w}{\partial T^2} = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) \left(\frac{2g_1}{T^2} - \frac{2}{T}\frac{\partial g_1}{\partial T} + \frac{\partial^2 g_1}{\partial T^2}\right) + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 \left(\frac{6g_2}{T^2} - \frac{4}{T}\frac{\partial g_2}{\partial T} + \frac{\partial^2 g_2}{\partial T^2}\right) \right.$$
$$\left. - 2\frac{\partial g_d^{\text{HS}}}{\partial T}\frac{\partial w}{\partial T} - w\frac{\partial^2 g_d^{\text{HS}}}{\partial T^2} \right], \tag{195}$$

$$\frac{\partial w}{\partial V} = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) \frac{\partial g_1}{\partial V} + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 \frac{\partial g_2}{\partial V} - w\frac{\partial g_d^{\text{HS}}}{\partial V} \right], \tag{196}$$

$$\frac{\partial^2 w}{\partial V^2} = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) \frac{\partial^2 g_1}{\partial V^2} + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 \frac{\partial^2 g_2}{\partial V^2} - 2\frac{\partial w}{\partial V}\frac{\partial g_d^{\text{HS}}}{\partial V} - w\frac{\partial^2 g_d^{\text{HS}}}{\partial V^2} \right], \tag{197}$$

$$\frac{\partial^2 w}{\partial T \partial V} = \frac{1}{g_d^{\text{HS}}} \left[\left(\frac{\epsilon}{k_{\text{B}}T}\right) \left(-\frac{1}{T}\frac{\partial g_1}{\partial V} + \frac{\partial^2 g_1}{\partial T \partial V}\right) + \left(\frac{\epsilon}{k_{\text{B}}T}\right)^2 \left(-\frac{2}{T}\frac{\partial g_2}{\partial V} + \frac{\partial^2 g_2}{\partial T \partial V}\right) \right.$$
$$\left. - \frac{\partial w}{\partial T}\frac{\partial g_d^{\text{HS}}}{\partial V} - \frac{\partial w}{\partial V}\frac{\partial g_d^{\text{HS}}}{\partial T} - w\frac{\partial^2 g_d^{\text{HS}}}{\partial V \partial T} \right]. \tag{198}$$

The g^{Mie} differentials, for $X \in \{T, V\}$, then become as follows,

$$\frac{\partial g^{\text{Mie}}}{\partial X_i} = g^{\text{Mie}} \left[\frac{1}{g_d^{\text{HS}}}\frac{\partial g_d^{\text{HS}}}{\partial X_i} + \frac{\partial w}{\partial X_i} \right], \tag{199}$$

$$\frac{\partial^2 g^{\text{Mie}}}{\partial X_i \partial X_j} = g^{\text{Mie}} \left[\frac{1}{g_d^{\text{HS}}} \left(\frac{\partial^2 g_d^{\text{HS}}}{\partial X_i \partial X_j} + \frac{\partial g_d^{\text{HS}}}{\partial X_i}\frac{\partial w}{\partial X_j} + \frac{\partial g_d^{\text{HS}}}{\partial X_j}\frac{\partial w}{\partial X_i} \right) + \frac{\partial w}{\partial X_i}\frac{\partial w}{\partial X_j} + \frac{\partial^2 w}{\partial X_i \partial X_j} \right]. \tag{200}$$

4 Mixtures

When describing mixing in the SAFT-VR-Mie framework, the following mixing rules are applied for the parameters,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \tag{201}$$

$$d_{ij} = \frac{d_{ii} + d_{jj}}{2}, \tag{202}$$

$$\epsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\epsilon_{ii}\epsilon_{jj}}, \tag{203}$$

$$\lambda_{r,ij} - 3 = (1 - \gamma_{ij}) \sqrt{(\lambda_{r,ii} - 3)(\lambda_{r,jj} - 3)}, \tag{204}$$

$$\alpha_{ij} = \alpha\left(\lambda_{\text{a}ij}, \lambda_{\text{r}ij}\right) \tag{205}$$

Here k_{ij} and γ_{ij} are tunable interaction parameters.

4.1 Mixture hard-sphere term

For mixtures, the term

$$\alpha^{hs} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right], \tag{206}$$

is used for the hard spheres. Here,

$$\zeta_l = \frac{\pi}{6}\rho_{\mathrm{s}}\sum_i x_{\mathrm{s},i} d_{ii}^l, \qquad l = 0, 1, 2, 3. \tag{207}$$

The mole fraction of segments of component i, $x_{\mathrm{s},i}$, is given as,

$$x_{\mathrm{s},i} = \frac{m_{\mathrm{s},i}x_i}{\sum_{k=1}^{\mathrm{N}} m_{\mathrm{s},k}x_k}. \tag{208}$$

The overall density is related to the segment density by $\rho_{\mathrm{s}} = \rho\sum_{k=1}^{\mathrm{N}} m_{\mathrm{s},k}x_k$. Using this, and $\rho V = \mathrm{N_A} n$, we get,

$$\zeta_l = \frac{\pi \mathrm{N_A}}{6V}\sum_i m_{\mathrm{s},i} n_i d_{ii}^l, \qquad l = 0, 1, 2, 3, \tag{209}$$

That can be differentiated directly in n_i, V and T.

4.1.1 Differentials

The ζ_l differentials applies for $l = 0, 1, 2, 3$ if nothing else is specified,

$$\frac{\partial \zeta_l}{\partial V} = -\frac{\zeta_l}{V}, \tag{210}$$

$$\frac{\partial^2 \zeta_l}{\partial V^2} = \frac{2\zeta_l}{V^2}, \tag{211}$$

$$\frac{\partial \zeta_l}{\partial n_i} = \frac{\pi \mathrm{N_A} m_{\mathrm{s},i} d_{ii}^l}{6V}, \tag{212}$$

$$\frac{\partial^2 \zeta_l}{\partial n_i \partial n_j} = 0, \tag{213}$$

$$\frac{\partial \zeta_l}{\partial T} = \begin{cases} 0, & l = 0 \\ \frac{l\pi \mathrm{N_A}}{6V} \sum_i m_{\mathrm{s},i} n_i d_{ii}^{l-1} \frac{\partial d_{ii}}{\partial T}, & l = 1, 2, 3 \end{cases} \tag{214}$$

$$\frac{\partial^2 \zeta_l}{\partial T^2} = \begin{cases} 0, & l = 0 \\ \frac{l\pi \mathrm{N_A}}{6V} \sum_i m_{\mathrm{s},i} n_i d_{ii}^{l-1} \frac{\partial^2 d_{ii}}{\partial T^2}, & l = 1 \\ \frac{l\pi \mathrm{N_A}}{6V} \sum_i m_{\mathrm{s},i} n_i d_{ii}^{l-1} \frac{\partial^2 d_{ii}}{\partial T^2} + \frac{l(l-1)\pi \mathrm{N_A}}{6V} \sum_i m_{\mathrm{s},i} n_i d_{ii}^{l-2} \left(\frac{\partial d_{ii}}{\partial T}\right)^2, & l = 2, 3 \end{cases} \tag{215}$$

$$\frac{\partial^2 \zeta_l}{\partial V \partial n_i} = -\frac{\pi \mathrm{N_A} m_{\mathrm{s},i} d_{ii}^l}{6V^2}, \tag{216}$$

$$\frac{\partial^2 \zeta_l}{\partial V \partial T} = \begin{cases} 0, & l = 0 \\ -\frac{l\pi \mathrm{N_A}}{6V^2} \sum_i m_{\mathrm{s},i} n_i d_{ii}^{l-1} \frac{\partial d_{ii}}{\partial T}, & l = 1, 2, 3 \end{cases} \tag{217}$$

$$\frac{\partial^2 \zeta_l}{\partial n_k \partial T} = \begin{cases} 0, & l = 0 \\ \frac{l\pi \mathrm{N_A} m_{\mathrm{s},k} d_{kk}^{l-1}}{6V} \frac{\partial d_{kk}}{\partial T}, & l = 1, 2, 3 \end{cases} \tag{218}$$

$$\tag{219}$$

The differentials for the mixture hard-sphere term with respect to ζ_l becomes

$$\frac{\partial \alpha^{hs}}{\partial \zeta_0} = -\frac{\alpha^{hs} + \ln(1-\zeta_3)}{\zeta_0}, \tag{220}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial {\zeta_0}^2} = \frac{2\alpha^{hs} + 2\ln(1-\zeta_3)}{\zeta_0^2}, \tag{221}$$

$$\frac{\partial \alpha^{hs}}{\partial \zeta_1} = \frac{3\zeta_2}{(1-\zeta_3)\,\zeta_0}, \tag{222}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial {\zeta_1}^2} = 0, \tag{223}$$

$$\frac{\partial \alpha^{hs}}{\partial \zeta_2} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1}{1-\zeta_3} + \frac{3\zeta_2^2}{\zeta_3(1-\zeta_3)^2} + \frac{3\zeta_2^2}{\zeta_3^2}\ln(1-\zeta_3)\right], \tag{224}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial {\zeta_2}^2} = \frac{6\zeta_2}{\zeta_0\zeta_3}\left[\frac{1}{(1-\zeta_3)^2} + \frac{1}{\zeta_3}\ln(1-\zeta_3)\right], \tag{225}$$

$$\frac{\partial \alpha^{hs}}{\partial \zeta_3} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{\zeta_2^3\,(3\zeta_3-1)}{\zeta_3^2(1-\zeta_3)^3} - \frac{2\zeta_2^3}{\zeta_3^3}\ln(1-\zeta_3) - \frac{\zeta_2^3-\zeta_0}{\zeta_3^2\,(1-\zeta_3)}\right], \tag{226}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial {\zeta_3}^2} = \frac{1}{\zeta_0}\left[\frac{6\zeta_1\zeta_2}{(1-\zeta_3)^3} + \frac{2\zeta_2^3\left(1-4\zeta_3+6\zeta_3^2\right)}{\zeta_3^3(1-\zeta_3)^4} + \frac{6\zeta_2^3}{\zeta_3^4}\ln(1-\zeta_3) + \frac{4\zeta_2^3}{\zeta_3^3\,(1-\zeta_3)} + \frac{\zeta_2^3-\zeta_0\zeta_3^2}{\zeta_3^2\,(1-\zeta_3)^2}\right], \tag{227}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial \zeta_0 \partial \zeta_1} = -\frac{1}{\zeta_0}\frac{\partial \alpha^{hs}}{\partial \zeta_1}, \tag{228}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial \zeta_0 \partial \zeta_2} = -\frac{1}{\zeta_0}\frac{\partial \alpha^{hs}}{\partial \zeta_2}, \tag{229}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial \zeta_0 \partial \zeta_3} = -\frac{1}{\zeta_0}\frac{\partial \alpha^{hs}}{\partial \zeta_3} + \frac{1}{\zeta_0\,(1-\zeta_3)}, \tag{230}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial \zeta_1 \partial \zeta_2} = \frac{3}{\zeta_0\,(1-\zeta_3)}, \tag{231}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial \zeta_2 \partial \zeta_3} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1}{(1-\zeta_3)^2} + \frac{3\zeta_2^2\,(3\zeta_3-1)}{\zeta_3^2(1-\zeta_3)^3} - \frac{6\zeta_2^2}{\zeta_3^3}\ln(1-\zeta_3) - \frac{3\zeta_2^2}{\zeta_3^2\,(1-\zeta_3)}\right]. \tag{232}$$

The differentials of the hard-sphere term with respect to $X \in \{T, V, n_1 \ldots, n_\mathrm{N}\}$ take the form,

$$\frac{\partial \alpha^{hs}}{\partial X_i} = \sum_{l=0}^{3} \frac{\partial \alpha^{hs}}{\partial \zeta_l}\frac{\partial \zeta_l}{\partial X_i}, \tag{233}$$

$$\frac{\partial^2 \alpha^{hs}}{\partial X_i \partial X_j} = \sum_{l=0}^{3}\sum_{k=0}^{3} \frac{\partial^2 \alpha^{hs}}{\partial \zeta_l \partial \zeta_k}\frac{\partial \zeta_l}{\partial X_i}\frac{\partial \zeta_k}{\partial X_j} + \sum_{l=0}^{3} \frac{\partial \alpha^{hs}}{\partial \zeta_l}\frac{\partial^2 \zeta_l}{\partial X_i \partial X_j}. \tag{234}$$

4.2 First order term

The first order term is described as,

$$a_1 = \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} x_{\mathrm{s},i} x_{\mathrm{s},j} a_{1,ij} \tag{235}$$

For mixtures, a mixture property is used instead of is used instead of η,

$$\zeta_x = \frac{\pi \rho_{\mathrm{s}}}{6} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} x_{\mathrm{s},i} x_{\mathrm{s},j} d_{ij}^3, \tag{236}$$

$$= \frac{\pi \mathrm{N_A}}{6 V n_{\mathrm{s}}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j d_{ij}^3, \tag{237}$$

where $n_{\mathrm{s}} = \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i$.

The $a_{1,ij}$ is given as for pure fluids, Equation 33, evaluated using mixture parameters. The only difference is in the treatment of a_1^{S} and B, where the integrals are evaluated as both a function of η and ζ_x. Dividing through with η give functions of ζ_x only. For mixtures, $\tilde{a}_{1,ij}^{\mathrm{S}}$, take the form,

$$\tilde{a}_{1,ij}^{\mathrm{S}} = \frac{a_{1,ij}^{\mathrm{S}}\left(\eta_{ij}, \zeta_x; \lambda_{ij}\right)}{\eta_{ij}} = -12\epsilon_{ij} \left(\frac{1}{\lambda_{ij} - 3}\right) \frac{1 - \eta_{\mathrm{eff}}\left(\zeta_x; \lambda_{ij}\right)/2}{\left(1 - \eta_{\mathrm{eff}}\left(\zeta_x; \lambda_{ij}\right)\right)^3}, \tag{238}$$

and $\tilde{B}_{ij}$ take the following form,

$$\tilde{B}_{ij} = \frac{B_{ij}\left(\eta_{ij}, \zeta_x; \lambda_{ij}\right)}{\eta_{ij}} = 12\epsilon_{ij} \left(\frac{1 - \zeta_x/2}{\left(1 - \zeta_x\right)^3} I_{\lambda_{ij}} - \frac{9\zeta_x\left(1 + \zeta_x\right)}{2\left(1 - \zeta_x\right)^3} J_{\lambda_{ij}}\right). \tag{239}$$

4.2.1 Differentials

The volume and temperature differentials of Equation 240 is straight forward. The mol number differentials become, after multiplying twice with n_{s},

$$n_{\mathrm{s}}^2 a_1 = \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j a_{1,ij} \tag{240}$$

$$2 m_{\mathrm{s},k} n_{\mathrm{s}} a_1 + n_{\mathrm{s}}^2 \frac{\partial a_1}{\partial n_k} = m_{\mathrm{s},k} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j a_{1,kj} + m_{\mathrm{s},k} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i a_{1,ik} + \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j \frac{\partial a_{1,ij}}{\partial n_k} \tag{241}$$

$$\begin{aligned} 2 m_{\mathrm{s},k} m_{\mathrm{s},l} a_1 + 2 m_{\mathrm{s},k} n_{\mathrm{s}} \frac{\partial a_1}{\partial n_l} + 2 m_{\mathrm{s},l} n_{\mathrm{s}} \frac{\partial a_1}{\partial n_k} + n_{\mathrm{s}}^2 \frac{\partial^2 a_1}{\partial n_k \partial n_l} = \\ m_{\mathrm{s},k} m_{\mathrm{s},l} a_{1,kl} + m_{\mathrm{s},k} m_{\mathrm{s},l} a_{1,lk} + m_{\mathrm{s},k} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j \frac{\partial a_{1,kj}}{\partial n_l} + m_{\mathrm{s},k} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i \frac{\partial a_{1,ik}}{\partial n_l} + \\ m_{\mathrm{s},l} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j \frac{\partial a_{1,lj}}{\partial n_k} + m_{\mathrm{s},l} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i \frac{\partial a_{1,il}}{\partial n_k} + \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j \frac{\partial^2 a_{1,ij}}{\partial n_k \partial n_l} \end{aligned} \tag{242}$$

$$\frac{\partial a_1}{\partial n_k} = \frac{1}{n_s^2}\left[m_{s,k}\sum_{j=1}^{N} m_{s,j}n_j a_{1,kj} + m_{s,k}\sum_{i=1}^{N} m_{s,i}n_i a_{1,ik} + \sum_{i=1}^{N}\sum_{j=1}^{N} m_{s,i}n_i m_{s,j}n_j \frac{\partial a_{1,ij}}{\partial n_k} - 2m_{s,k}n_s a_1\right] \tag{243}$$

$$\frac{\partial^2 a_1}{\partial n_k \partial n_l} = \frac{1}{n_s^2}\left[m_{s,k}m_{s,l}a_{1,kl} + m_{s,k}m_{s,l}a_{1,lk} + m_{s,k}\sum_{j=1}^{N} m_{s,j}n_j \frac{\partial a_{1,kj}}{\partial n_l} + m_{s,k}\sum_{i=1}^{N} m_{s,i}n_i \frac{\partial a_{1,ik}}{\partial n_l} + m_{s,l}\sum_{j=1}^{N} m_{s,j}n_j \frac{\partial a_{1,lj}}{\partial n_k} + m_{s,l}\sum_{i=1}^{N} m_{s,i}n_i \frac{\partial a_{1,il}}{\partial n_k} + \sum_{i=1}^{N}\sum_{j=1}^{N} m_{s,i}n_i m_{s,j}n_j \frac{\partial^2 a_{1,ij}}{\partial n_k \partial n_l} - 2m_{s,k}m_{s,l}a_1 - 2m_{s,k}n_s \frac{\partial a_1}{\partial n_l} - 2m_{s,l}n_s \frac{\partial a_1}{\partial n_k}\right] \tag{244}$$

Differentiating Equation 236,

$$\frac{\partial \zeta_x}{\partial V} = -\frac{\zeta_x}{V} \tag{245}$$

$$\frac{\partial^2 \zeta_x}{\partial V^2} = \frac{2\zeta_x}{V^2} \tag{246}$$

$$\frac{\partial^3 \zeta_x}{\partial V^3} = -\frac{6\zeta_x}{V^2} \tag{247}$$

$$\frac{\partial \zeta_x}{\partial T} = \frac{\pi \mathrm{N_A}}{2V n_\mathrm{s}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j d_{ij}^2 \frac{\partial d_{ij}}{\partial T} \tag{248}$$

$$\frac{\partial^2 \zeta_x}{\partial T^2} = \frac{\pi \mathrm{N_A}}{V n_\mathrm{s}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j d_{ij} \left(\frac{\partial d_{ij}}{\partial T}\right)^2 + \frac{\pi \mathrm{N_A}}{2V n_\mathrm{s}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j d_{ij}^2 \frac{\partial^2 d_{ij}}{\partial T^2} \tag{249}$$

$$\frac{\partial \zeta_x}{\partial n_k} = \frac{\pi \mathrm{N_A}}{6V n_\mathrm{s}} \left(m_{\mathrm{s},k} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j d_{kj}^3 + m_{\mathrm{s},k} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i d_{ik}^3 \right) - \frac{m_{\mathrm{s},k}}{n_\mathrm{s}} \zeta_x, \tag{250}$$

$$\frac{\partial^2 \zeta_x}{\partial n_k \partial n_l} = \frac{\pi \mathrm{N_A}}{6V n_\mathrm{s}} \left(m_{\mathrm{s},k} m_{\mathrm{s},l} d_{lj}^3 + m_{\mathrm{s},k} m_{\mathrm{s},l} d_{lk}^3 \right) - \frac{m_{\mathrm{s},k}}{n_\mathrm{s}} \frac{\partial \zeta_x}{\partial n_l} - \frac{m_{\mathrm{s},l}}{n_\mathrm{s}} \frac{\partial \zeta_x}{\partial n_k}, \tag{251}$$

$$\frac{\partial^2 \zeta_x}{\partial n_k \partial V} = -\frac{1}{V} \frac{\partial \zeta_x}{\partial n_k}, \tag{252}$$

$$\frac{\partial^2 \zeta_x}{\partial n_k \partial T} = \frac{\pi \mathrm{N_A}}{2V n_\mathrm{s}} \left(m_{\mathrm{s},k} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j d_{kj}^2 \frac{\partial d_{kj}}{\partial T} + m_{\mathrm{s},k} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i d_{ik}^2 \frac{\partial d_{ik}}{\partial T} \right) - \frac{m_{\mathrm{s},k}}{n_\mathrm{s}} \frac{\partial \zeta_x}{\partial T}, \tag{253}$$

$$\frac{\partial^3 \zeta_x}{\partial V^2 \partial n_k} = \frac{2}{V^2} \frac{\partial \zeta_x}{\partial n_k}, \tag{254}$$

$$\frac{\partial^2 \zeta_x}{\partial V \partial T} = -\frac{1}{V} \frac{\partial \zeta_x}{\partial T}, \tag{255}$$

$$\frac{\partial^3 \zeta_x}{\partial V \partial T \partial n_k} = -\frac{1}{V} \frac{\partial^2 \zeta_x}{\partial T \partial n_k}, \tag{256}$$

$$\frac{\partial^3 \zeta_x}{\partial V \partial n_k \partial n_l} = -\frac{1}{V} \frac{\partial^2 \zeta_x}{\partial n_k \partial n_l}, \tag{257}$$

$$\frac{\partial^3 \zeta_x}{\partial V^2 \partial T} = \frac{2}{V^2} \frac{\partial \zeta_x}{\partial T}, \tag{258}$$

$$\frac{\partial^3 \zeta_x}{\partial T^2 \partial V} = -\frac{1}{V} \frac{\partial^2 \zeta_x}{\partial T^2} \tag{259}$$

The missing mol number differentials needed to convert from η and x_0 differentials to

TVn differentials,

$$\begin{aligned}
a_{n_k} =& a_e e_{n_k}, & (260)\\
a_{n_k n_l} =& a_{ee} e_{n_k} e_{n_l} + a_e e_{n_k n_l}, & (261)\\
a_{V n_k n_l} =& a_{eee} e_V e_{n_k} e_{n_l} + a_{ee} e_{V n_k} e_{n_l} + a_{ee} e_{n_k} e_{V n_l} + a_{ee} e_V e_{n_k n_l} + a_e e_{V n_k n_l}, & (262)\\
a_{T n_k} =& a_{ee} e_T e_{n_k} + a_e e_{T n_k} + a_{ex} x_T e_{n_k}, & (263)\\
a_{V n_k} =& a_{ee} e_V e_{n_k} + a_e e_{V n_k}, & (264)\\
a_{VV n_k} =& a_{eee} e_V^2 e_{n_k} + a_{ee} e_{VV} e_{n_k} + 2 a_{ee} e_V e_{V n_k} + a_e e_{VV n_k}, & (265)\\
a_{VT n_k} =& a_{eee} e_V e_T e_{n_k} + a_{ee} e_{VT} e_{n_k} + a_{ee} e_T e_{V n_k} + a_{ee} e_V e_{T n_k} \\
& + a_e e_{VT n_k} + a_{eex} e_V x_T e_{n_k} + a_{ex} x_T e_{V n_k}. & (266)
\end{aligned}$$

The missing mol number η differentials,

$$\begin{aligned}
\frac{\partial \eta}{\partial n_k} =& \eta \frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}}, & (267)\\
\frac{\partial^2 \eta}{\partial n_k \partial n_l} =& 0, & (268)\\
\frac{\partial^2 \eta}{\partial T \partial n_k} =& \frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}} \frac{\partial \eta}{\partial T}, & (269)\\
\frac{\partial^2 \eta}{\partial V \partial n_k} =& -\frac{1}{V} \frac{\partial \eta}{\partial n_k}, & (270)\\
\frac{\partial^3 \eta}{\partial V^2 \partial n_k} =& -\frac{2}{V} \frac{\partial^2 \eta}{\partial V \partial n_k}, & (271)\\
\frac{\partial^3 \eta}{\partial V \partial n_k \partial n_l} =& 0, & (272)\\
\frac{\partial^3 \eta}{\partial V \partial T \partial n_k} =& -\frac{1}{V} \frac{\partial^2 \eta}{\partial T \partial n_k}. & (273)
\end{aligned}$$

4.3 Second order term

The second order term is for mixtures described as,

$$a_2 = \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} x_{\mathrm{s},i} x_{\mathrm{s},j} a_{2,ij}. \tag{274}$$

For mixtures $\bar{\zeta}_x$ take the following form,

$$\bar{\zeta}_x = \frac{\pi \rho_{\mathrm{s}}}{6} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} x_{\mathrm{s},i} x_{\mathrm{s},j} \sigma_{ij}^3 = \frac{\pi \mathrm{N_A}}{6 V n_{\mathrm{s}}} \sum_{i=1}^{\mathrm{N}} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i m_{\mathrm{s},j} n_j \sigma_{ij}^3. \tag{275}$$

4.3.1 Differentials

Differentials for $\bar{\zeta}_x$,

$$\frac{\partial \bar{\zeta}_x}{\partial V} = -\frac{\bar{\zeta}_x}{V} \tag{276}$$

$$\frac{\partial^2 \bar{\zeta}_x}{\partial V^2} = \frac{2\bar{\zeta}_x}{V^2} \tag{277}$$

$$\frac{\partial^3 \bar{\zeta}_x}{\partial V^3} = -\frac{6\bar{\zeta}_x}{V^3}, \tag{278}$$

$$\frac{\partial \bar{\zeta}_x}{\partial n_k} = \frac{\pi \mathrm{N_A}}{6 V n_\mathrm{s}} \left(m_{\mathrm{s},k} \sum_{j=1}^{\mathrm{N}} m_{\mathrm{s},j} n_j \sigma_{kj}^3 + m_{\mathrm{s},k} \sum_{i=1}^{\mathrm{N}} m_{\mathrm{s},i} n_i \sigma_{ik}^3 \right) - \frac{m_{\mathrm{s},k}}{n_\mathrm{s}} \bar{\zeta}_x, \tag{279}$$

$$\frac{\partial^2 \bar{\zeta}_x}{\partial n_k \partial n_l} = \frac{\pi \mathrm{N_A}}{6 V n_\mathrm{s}} \left(m_{\mathrm{s},k} m_{\mathrm{s},l} \sigma_{lj}^3 + m_{\mathrm{s},k} m_{\mathrm{s},l} \sigma_{lk}^3 \right) - \frac{m_{\mathrm{s},k}}{n_\mathrm{s}} \frac{\partial \bar{\zeta}_x}{\partial n_l} - \frac{m_{\mathrm{s},l}}{n_\mathrm{s}} \frac{\partial \bar{\zeta}_x}{\partial n_k}, \tag{280}$$

$$\frac{\partial^2 \bar{\zeta}_x}{\partial n_k \partial V} = -\frac{1}{V} \frac{\partial \bar{\zeta}_x}{\partial n_k}, \tag{281}$$

$$\frac{\partial^3 \bar{\zeta}_x}{\partial V^2 \partial n_k} = \frac{2}{V^2} \frac{\partial \bar{\zeta}_x}{\partial n_k}, \tag{282}$$

$$\frac{\partial^3 \bar{\zeta}_x}{\partial V \partial n_k \partial n_l} = -\frac{1}{V} \frac{\partial^2 \bar{\zeta}_x}{\partial n_k \partial n_l}. \tag{283}$$

The differentials for a_2 can be calculated from Equation 240, by substituting $a_{1,ij}$ with $a_{2,ij}$.

4.4 Third order term

For mixtures the third order term take the same form as for pure fluids, with $\bar{\zeta}_x$ instead of η.

4.5 Chain contribution

The chain contribution is slightly different, as it is only a single sum,

$$a^{\mathrm{chain}} = -\frac{1}{n} \sum_{i=1}^{\mathrm{N}} n_i \left(m_{\mathrm{s},i} - 1 \right) \ln \left(g_{ii}^{\mathrm{Mie}} \left(\sigma_{ii} \right) \right). \tag{284}$$

g_{ii}^{Mie} is evaluated as Equation 133, using (average) molecular properties,

$$\sigma_{ii} = \sigma_i, \tag{285}$$

$$\epsilon_{ii} = \epsilon_i, \tag{286}$$

$$d_{ii} = d_i, \tag{287}$$

$$\lambda_{ii} = \lambda_i. \tag{288}$$

4.5.1 Differentials

$$\frac{\partial a^{\text{chain}}}{\partial n_k} = -\frac{1}{n}\left[(m_{\text{s},k}-1)\ln\left(g_{kk}^{\text{Mie}}\right) + \sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{g_{ii}^{\text{Mie}}}\frac{\partial g_{ii}^{\text{Mie}}}{\partial n_k} + a^{\text{chain}}\right], \tag{289}$$

$$\begin{aligned}\frac{\partial^2 a^{\text{chain}}}{\partial n_k \partial n_l} =& \frac{1}{n}\left[-\left(m_{\text{s},k}-1\right)\frac{1}{g_{kk}^{\text{Mie}}}\frac{\partial g_{kk}^{\text{Mie}}}{\partial n_l} - \left(m_{\text{s},l}-1\right)\frac{1}{g_{ll}^{\text{Mie}}}\frac{\partial g_{ll}^{\text{Mie}}}{\partial n_k}\right.\\ &+ \sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left(\frac{\partial g_{ii}^{\text{Mie}}}{\partial n_k}\frac{\partial g_{ii}^{\text{Mie}}}{\partial n_l} - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial n_k \partial n_l}\right)\\ &\left.-\frac{\partial a^{\text{chain}}}{\partial n_l} - \frac{\partial a^{\text{chain}}}{\partial n_k}\right],\end{aligned} \tag{290}$$

$$\frac{\partial a^{\text{chain}}}{\partial T} = -\frac{1}{n}\sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{g_{ii}^{\text{Mie}}}\frac{\partial g_{ii}^{\text{Mie}}}{\partial T}, \tag{291}$$

$$\frac{\partial^2 a^{\text{chain}}}{\partial T^2} = \frac{1}{n}\sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left[\left(\frac{\partial g_{ii}^{\text{Mie}}}{\partial T}\right)^2 - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial T^2}\right], \tag{292}$$

$$\frac{\partial a^{\text{chain}}}{\partial V} = -\frac{1}{n}\sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{g_{ii}^{\text{Mie}}}\frac{\partial g_{ii}^{\text{Mie}}}{\partial V}, \tag{293}$$

$$\frac{\partial^2 a^{\text{chain}}}{\partial V^2} = \frac{1}{n}\sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left[\left(\frac{\partial g_{ii}^{\text{Mie}}}{\partial V}\right)^2 - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial V^2}\right], \tag{294}$$

$$\frac{\partial^2 a^{\text{chain}}}{\partial V \partial T} = \frac{1}{n}\sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left[\frac{\partial g_{ii}^{\text{Mie}}}{\partial V}\frac{\partial g_{ii}^{\text{Mie}}}{\partial T} - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial V \partial T}\right], \tag{295}$$

$$\begin{aligned}\frac{\partial^2 a^{\text{chain}}}{\partial n_k \partial T} =& \frac{1}{n}\left[-\left(m_{\text{s},k}-1\right)\frac{1}{g_{kk}^{\text{Mie}}}\frac{\partial g_{kk}^{\text{Mie}}}{\partial T}\right.\\ &\left.+ \sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left(\frac{\partial g_{ii}^{\text{Mie}}}{\partial n_k}\frac{\partial g_{ii}^{\text{Mie}}}{\partial T} - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial n_k \partial T}\right) - \frac{\partial a^{\text{chain}}}{\partial T}\right],\end{aligned} \tag{296}$$

$$\begin{aligned}\frac{\partial^2 a^{\text{chain}}}{\partial n_k \partial V} =& \frac{1}{n}\left[-\left(m_{\text{s},k}-1\right)\frac{1}{g_{kk}^{\text{Mie}}}\frac{\partial g_{kk}^{\text{Mie}}}{\partial V}\right.\\ &\left.+ \sum_{i=1}^{\text{N}} n_i\left(m_{\text{s},i}-1\right)\frac{1}{\left(g_{ii}^{\text{Mie}}\right)^2}\left(\frac{\partial g_{ii}^{\text{Mie}}}{\partial n_k}\frac{\partial g_{ii}^{\text{Mie}}}{\partial V} - g_{ii}^{\text{Mie}}\frac{\partial^2 g_{ii}^{\text{Mie}}}{\partial n_k \partial V}\right) - \frac{\partial a^{\text{chain}}}{\partial V}\right].\end{aligned} \tag{297}$$

To get the g_{ii}^{Mie} mol number differentials, the mole number differentials of Equation 193 is required,

$$\frac{\partial w}{\partial n_k} = \frac{1}{g_d^{\mathrm{HS}}}\left[\left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)\frac{\partial g_1}{\partial n_k} + \left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)^2\frac{\partial g_2}{\partial n_k} - w\frac{\partial g_d^{\mathrm{HS}}}{\partial n_k}\right], \tag{298}$$

$$\frac{\partial^2 w}{\partial n_k \partial n_l} = \frac{1}{g_d^{\mathrm{HS}}}\left[\left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)\frac{\partial^2 g_1}{\partial n_k \partial n_l} + \left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)^2\frac{\partial^2 g_2}{\partial n_k \partial n_l} - \frac{\partial w}{\partial n_k}\frac{\partial g_d^{\mathrm{HS}}}{\partial n_l} - \frac{\partial w}{\partial n_l}\frac{\partial g_d^{\mathrm{HS}}}{\partial n_k} - w\frac{\partial^2 g_d^{\mathrm{HS}}}{\partial n_k \partial n_l}\right], \tag{299}$$

$$\begin{aligned}\frac{\partial^2 w}{\partial T \partial n_k} = \frac{1}{g_d^{\mathrm{HS}}}\Bigg[&\left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)\left(-\frac{1}{T}\frac{\partial g_1}{\partial n_k} + \frac{\partial^2 g_1}{\partial T \partial n_k}\right) + \left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)^2\left(-\frac{2}{T}\frac{\partial g_2}{\partial n_k} + \frac{\partial^2 g_2}{\partial T \partial n_k}\right)\\ &-\frac{\partial w}{\partial T}\frac{\partial g_d^{\mathrm{HS}}}{\partial n_k} - \frac{\partial w}{\partial n_k}\frac{\partial g_d^{\mathrm{HS}}}{\partial T} - w\frac{\partial^2 g_d^{\mathrm{HS}}}{\partial T \partial n_k}\Bigg],\end{aligned} \tag{300}$$

$$\frac{\partial^2 w}{\partial V \partial n_k} = \frac{1}{g_d^{\mathrm{HS}}}\left[\left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)\frac{\partial^2 g_1}{\partial V \partial n_k} + \left(\frac{\epsilon}{k_{\mathrm{B}}T}\right)^2\frac{\partial^2 g_2}{\partial V \partial n_k} - \frac{\partial w}{\partial V}\frac{\partial g_d^{\mathrm{HS}}}{\partial n_k} - \frac{\partial w}{\partial n_k}\frac{\partial g_d^{\mathrm{HS}}}{\partial V} - w\frac{\partial^2 g_d^{\mathrm{HS}}}{\partial V \partial n_k}\right]. \tag{301}$$

Differentiating $g_{1,1}$ with respect to mol numbers,

$$\frac{\partial g_{1,1}}{\partial n_k} = \frac{3V^2}{2\epsilon\pi \mathrm{N_A} n_{\mathrm{s}} d^3}\frac{\partial^2 a_1}{\partial V \partial n_k} - g_{1,1}\frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}}, \tag{302}$$

$$\frac{\partial^2 g_{1,1}}{\partial V \partial n_k} = \frac{3V^2}{2\epsilon\pi \mathrm{N_A} n_{\mathrm{s}} d^3}\left(\frac{2}{V}\frac{\partial^2 a_1}{\partial V \partial n_k} + \frac{\partial^3 a_1}{\partial V^2 \partial n_k}\right) - \frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}}\frac{\partial g_{1,1}}{\partial V}, \tag{303}$$

$$\frac{\partial^2 g_{1,1}}{\partial T \partial n_k} = \frac{3V^2}{2\epsilon\pi \mathrm{N_A} n_{\mathrm{s}} d^3}\frac{\partial^3 a_1}{\partial V \partial T \partial n_k} - \frac{3}{d}\frac{\partial g_{1,1}}{\partial n_k}\frac{\partial d}{\partial T} - \frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}}\frac{\partial g_{1,1}}{\partial T} - g_{1,1}\frac{3}{d}\frac{m_{\mathrm{s},k}}{n_{\mathrm{s}}}\frac{\partial d}{\partial T}, \tag{304}$$

$$\frac{\partial^2 g_{1,1}}{\partial n_k \partial n_l} = \frac{3V^2}{2\epsilon\pi \mathrm{N_A} n_{\mathrm{s}} d^3}\frac{\partial^3 a_1}{\partial V \partial n_k \partial n_l} - \frac{m_{\mathrm{s},l}}{n_{\mathrm{s}}}\frac{\partial g_{1,1}}{\partial n_l} - \frac{m_{\mathrm{s},l}}{n_{\mathrm{s}}}\frac{\partial g_{1,1}}{\partial n_k}. \tag{305}$$

5 Temperature dependency in σ

If a temperature dependent σ is introduced in the SAFT-VR Mie framework, basically three parts of the model changes. The temperature dependency of x_0 changes, and, α and $\bar{\zeta}_x$ becomes temperature dependent.

5.1 Differentiasl with temperature dependency in σ

The new differentials for x_0 becomes,

$$\frac{\partial x_0}{\partial T} = \frac{1}{d}\frac{\partial \sigma}{\partial T} - \frac{x_0}{d}\frac{\partial d}{\partial T}, \tag{306}$$

$$\frac{\partial^2 x_0}{\partial T^2} = \frac{1}{d}\frac{\partial^2 \sigma}{\partial T^2} - \frac{2}{d}\frac{\partial x_0}{\partial T}\frac{\partial d}{\partial T} - \frac{x_0}{d}\frac{\partial^2 d}{\partial T^2}. \tag{307}$$

When the dimesionless van der Waals energy, α, become temperature dependent, the function $f(\alpha)$ must be differentiated. Using $f = m/p$, we get,

$$m = \sum_{n=0}^{n=3} \phi_{i,n}\alpha^{n}, \tag{308}$$

$$m_{\alpha} = \sum_{n=1}^{n=3} n\phi_{i,n}\alpha^{n-1}, \tag{309}$$

$$m_{\alpha\alpha} = \sum_{n=2}^{n=3} n(n-1)\phi_{i,n}\alpha^{n-2}, \tag{310}$$

$$p = 1 + \sum_{n=4}^{n=6} \phi_{i,n}\alpha^{n-3}, \tag{311}$$

$$p_{\alpha} = \sum_{n=4}^{n=6} (n-3)\phi_{i,n}\alpha^{n-4}, \tag{312}$$

$$p_{\alpha\alpha} = \sum_{n=5}^{n=6} (n-3)(n-4)\phi_{i,n}\alpha^{n-5}, \tag{313}$$

$$f_{\alpha} = \frac{1}{p}\left[m_{\alpha} - f p_{\alpha}\right], \tag{314}$$

$$f_{\alpha\alpha} = \frac{1}{p}\left[m_{\alpha\alpha} - 2f_{\alpha}p_{\alpha} - f p_{\alpha\alpha}\right]. \tag{315}$$

The quantum corrected Mie potential take the following form, if corrected to second order,

$$\begin{aligned} u^{Q,\mathrm{Mie}}(r,T) =& \mathcal{C}\epsilon\left(\left[\frac{\sigma}{r}\right)^{\lambda_\mathrm{r}} - \left(\frac{\sigma}{r}\right)^{\lambda_\mathrm{a}}\right. \\ &+ \frac{D}{r^2}\left(Q_{1,r}\left(\frac{\sigma}{r}\right)^{\lambda_\mathrm{r}} - Q_{1,a}\left(\frac{\sigma}{r}\right)^{\lambda_\mathrm{a}}\right) \\ &\left.+\frac{D^2}{r^4}\left(Q_{2,r}\left(\frac{\sigma}{r}\right)^{\lambda_\mathrm{r}} - Q_{2,a}\left(\frac{\sigma}{r}\right)^{\lambda_\mathrm{a}}\right)\right]. \end{aligned} \tag{316}$$

The dimensionelss van der Waals energy is given as,

$$\alpha = -\frac{1}{\epsilon\sigma_Q^3}\int_{\sigma_Q}^{\infty} u^{Q,\mathrm{Mie}} r^2 dr \tag{317}$$

$$\begin{aligned} =& \mathcal{C}\left[\left(\frac{\sigma}{\sigma_Q}\right)^{\lambda_\mathrm{a}}\frac{1}{\lambda_\mathrm{a}-3} - \left(\frac{\sigma}{\sigma_Q}\right)^{\lambda_\mathrm{r}}\frac{1}{\lambda_\mathrm{r}-3}\right. \\ &+ \frac{D}{\sigma^2}\left(\left(\frac{\sigma}{\sigma_Q}\right)^{2+\lambda_\mathrm{a}}\frac{Q_{1,\mathrm{a}}}{\lambda_\mathrm{a}-1} - \left(\frac{\sigma}{\sigma_Q}\right)^{2+\lambda_\mathrm{r}}\frac{Q_{1,\mathrm{r}}}{\lambda_\mathrm{r}-1}\right) \\ &\left.+\left(\frac{D}{\sigma^2}\right)^2\left(\left(\frac{\sigma}{\sigma_Q}\right)^{4+\lambda_\mathrm{a}}\frac{Q_{2,\mathrm{a}}}{\lambda_\mathrm{a}+1} - \left(\frac{\sigma}{\sigma_Q}\right)^{4+\lambda_\mathrm{r}}\frac{Q_{2,\mathrm{r}}}{\lambda_\mathrm{r}+1}\right)\right]. \end{aligned} \tag{318}$$

Introdusing new variables and a constant $\tilde{D}$,

$$\tilde{D} = \frac{DT}{\sigma^2}, \tag{319}$$

$$\tilde{Q}_{1,\mathrm{a}} = \left(\frac{\sigma}{\sigma_Q}\right)^{2+\lambda_\mathrm{a}} \frac{Q_{1,a}}{\lambda_\mathrm{a} - 1}, \tag{320}$$

$$\tilde{Q}_{1,\mathrm{r}} = \left(\frac{\sigma}{\sigma_Q}\right)^{2+\lambda_\mathrm{r}} \frac{Q_{1,r}}{\lambda_\mathrm{r} - 1}, \tag{321}$$

$$\tilde{Q}_{2,\mathrm{a}} = \left(\frac{\sigma}{\sigma_Q}\right)^{4+\lambda_\mathrm{a}} \frac{Q_{2,a}}{\lambda_\mathrm{a} + 1}, \tag{322}$$

$$\tilde{Q}_{2,\mathrm{r}} = \left(\frac{\sigma}{\sigma_Q}\right)^{4+\lambda_\mathrm{r}} \frac{Q_{2,r}}{\lambda_\mathrm{r} + 1}, \tag{323}$$

$$M_\mathrm{a} = \left(\frac{\sigma}{\sigma_Q}\right)^{\lambda_\mathrm{a}} \frac{1}{\lambda_\mathrm{a} - 3}, \tag{324}$$

$$M_\mathrm{r} = \left(\frac{\sigma}{\sigma_Q}\right)^{\lambda_\mathrm{r}} \frac{1}{\lambda_\mathrm{r} - 3}, \tag{325}$$

α becomes,

$$\alpha = \mathcal{C}\left[M_\mathrm{a} - M_\mathrm{r} + \frac{\tilde{D}}{T}\left(\tilde{Q}_{1,\mathrm{a}} - \tilde{Q}_{1,\mathrm{r}}\right) + \left(\frac{\tilde{D}}{T}\right)^2 \left(\tilde{Q}_{2,\mathrm{a}} - \tilde{Q}_{2,\mathrm{r}}\right)\right]. \tag{326}$$

Differentiating α, using the above,

$$\begin{aligned}\alpha_T =& -\frac{\mathcal{C}}{\sigma_Q}\left[M_{\mathrm{a}}\lambda_{\mathrm{a}} - M_{\mathrm{r}}\lambda_{\mathrm{r}} + \frac{D}{T}\left(\left(2+\lambda_{\mathrm{a}}\right)\tilde{Q}_{1,\mathrm{a}} - \left(2+\lambda_{\mathrm{r}}\right)\tilde{Q}_{1,\mathrm{r}}\right)\right.\\ &\left.+\left(\frac{D}{T}\right)^2\left(\left(4+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{a}} - \left(4+\lambda_{\mathrm{r}}\right)\tilde{Q}_{2,\mathrm{r}}\right)\right]\frac{\partial \sigma_Q}{\partial T}\\ &-\mathcal{C}\left[\frac{\tilde{D}}{T^2}\left(\tilde{Q}_{1,\mathrm{a}} - \tilde{Q}_{1,\mathrm{r}}\right) + \frac{2\tilde{D}^2}{T^3}\left(\tilde{Q}_{2,\mathrm{a}} - \tilde{Q}_{2,\mathrm{r}}\right)\right],\end{aligned} \tag{327}$$

$$\begin{aligned}\alpha_{TT} =& \frac{\mathcal{C}}{\sigma_Q^2}\left[M_{\mathrm{a}}\lambda_{\mathrm{a}}\left(\lambda_{\mathrm{a}}+1\right) - M_{\mathrm{r}}\lambda_{\mathrm{r}}\left(\lambda_{\mathrm{r}}+1\right)\right.\\ &+\frac{D}{T}\left(\left(2+\lambda_{\mathrm{a}}\right)\left(3+\lambda_{\mathrm{a}}\right)\tilde{Q}_{1,\mathrm{a}} - \left(2+\lambda_{\mathrm{r}}\right)\left(3+\lambda_{\mathrm{r}}\right)\tilde{Q}_{1,\mathrm{r}}\right)\\ &\left.+\left(\frac{D}{T}\right)^2\left(\left(4+\lambda_{\mathrm{a}}\right)\left(5+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{a}} - \left(4+\lambda_{\mathrm{r}}\right)\left(5+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{r}}\right)\right]\left(\frac{\partial \sigma_Q}{\partial T}\right)^2\\ &-\frac{\mathcal{C}}{\sigma_Q}\left[M_{\mathrm{a}}\lambda_{\mathrm{a}} - M_{\mathrm{r}}\lambda_{\mathrm{r}} + \frac{D}{T}\left(\left(2+\lambda_{\mathrm{a}}\right)\tilde{Q}_{1,\mathrm{a}} - \left(2+\lambda_{\mathrm{r}}\right)\tilde{Q}_{1,\mathrm{r}}\right)\right.\\ &\left.+\left(\frac{D}{T}\right)^2\left(\left(4+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{a}} - \left(4+\lambda_{\mathrm{r}}\right)\tilde{Q}_{2,\mathrm{r}}\right)\right]\frac{\partial^2 \sigma_Q}{\partial T^2}\\ &+\frac{2\mathcal{C}}{\sigma_Q}\left[\frac{\tilde{D}}{T^2}\left(\left(2+\lambda_{\mathrm{a}}\right)\tilde{Q}_{1,\mathrm{a}} - \left(2+\lambda_{\mathrm{r}}\right)\tilde{Q}_{1,\mathrm{r}}\right)\right.\\ &\left.+\frac{2\tilde{D}^2}{T^3}\left(\left(4+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{a}} - \left(4+\lambda_{\mathrm{a}}\right)\tilde{Q}_{2,\mathrm{r}}\right)\right]\frac{\partial \sigma_Q}{\partial T}\\ &+\mathcal{C}\left[\frac{2\tilde{D}}{T^3}\left(\tilde{Q}_{1,\mathrm{a}} - \tilde{Q}_{1,\mathrm{r}}\right) + \frac{6\tilde{D}^2}{T^4}\left(\tilde{Q}_{2,\mathrm{a}} - \tilde{Q}_{2,\mathrm{r}}\right)\right].\end{aligned} \tag{328}$$

The differentials of $\bar{\zeta}_x$ with respect to temperature will take the same form as the ζ_x differentials.

6 The non-additive hard sphere model

The model by Santos et al. [12] is derived for an arbitarry dimension, d, in the following we will only consider $d = 3$. The model is also extended to account for the monomer segments of each molecule. This gives tha same packing fraction as used by [8] in the original SAFT-VR Mie modell.

The prefactor, v_{d}, becomes for 3 dimensions,

$$v_{\mathrm{d}=3} = \left(\frac{\pi}{4}\right)^{\left(\frac{3}{2}\right)}\frac{1}{\Gamma\left(1+\frac{3}{2}\right)} = \frac{\pi}{6}. \tag{329}$$

$$\langle d_{\mathrm{HS}}^3\rangle = \sum m_{\mathrm{s},i}x_i\left(d_i^{\mathrm{HS}}\right)^3 = \frac{\sum m_{\mathrm{s},i}n_i\left(d_i^{\mathrm{HS}}\right)^3}{\sum n_i}. \tag{330}$$

The packing fraction, becomes,

$$\eta = v_{\mathrm{d}=3}\rho_{\mathrm{s}}\langle d_{\mathrm{HS}}^3\rangle = \frac{\rho_{\mathrm{s}}\pi\sum m_{\mathrm{s},i}x_i\left(d_i^{\mathrm{HS}}\right)^3}{6} = \frac{\pi \mathrm{N_A}\sum m_{\mathrm{s},i}n_i\left(d_i^{\mathrm{HS}}\right)^3}{6V}. \tag{331}$$

The resudial compressibillity factor is defined as,

$$Z_{\mathrm{SYH}}^{\mathrm{R}} = \frac{\eta}{1-\eta}\frac{b_3\langle d_{\mathrm{HS}}^3\rangle\overline{B_2} - b_2\overline{B_3}}{\left(b_3-b_2\right)\langle d_{\mathrm{HS}}^3\rangle^2} + Z_{\mathrm{pure}}^{\mathrm{R}}\left(\eta\right)\frac{\overline{B_3} - \langle d_{\mathrm{HS}}^3\rangle\overline{B_2}}{\left(b_3-b_2\right)\langle d_{\mathrm{HS}}^3\rangle^2}, \tag{332}$$

$$= \frac{\eta}{1-\eta}A_1\left(T,\mathbf{n}\right) + Z_{\mathrm{pure}}^{\mathrm{R}}A_2\left(T,\mathbf{n}\right). \tag{333}$$

Here,

$$\overline{B_2} = \frac{4}{v_3}\sum_i\sum_j x_{\mathrm{s},i}x_{\mathrm{s},j}d_{i,j}^3 = \frac{24}{\pi}\frac{\sum_i\sum_j m_{\mathrm{s},i}n_i m_{\mathrm{s},j}n_j d_{i,j}^3}{\left(\sum_i m_{\mathrm{s},i}n_i\right)^2} = \frac{\overline{B_2}^*}{\left(\sum_i m_{\mathrm{s},i}n_i\right)^2}, \tag{334}$$

$$\overline{B_3} = \frac{1}{v_3^2}\sum_k\sum_i\sum_j x_{\mathrm{s},k}x_{\mathrm{s},i}x_{\mathrm{s},j}\overline{B}_{i,j,k}^3 = \frac{36}{\pi^2}\frac{\sum_i\sum_j\sum_k m_{\mathrm{s},i}n_i m_{\mathrm{s},j}n_j m_{\mathrm{s},k}n_k\overline{B}_{i,j,k}^3}{\left(\sum_i m_{\mathrm{s},i}n_i\right)^3}$$

$$= \frac{\overline{B_3}^*}{\left(\sum_i m_{\mathrm{s},i}n_i\right)^3}. \tag{335}$$

For $\overline{B}_{i,j,k}$ we have,

$$\overline{B}_{i,j,k} = \frac{4}{3}\left(c_{k;ij}d_{ij}^3 + c_{j;ik}d_{ik}^3 + c_{i;jk}d_{jk}^3\right), \tag{336}$$

$$c_{k;ij} = d_{k;ij}^3 + \frac{3}{2}\frac{d_{k;ij}^2}{d_{ij}}d_{i;jk}d_{j;ik}, \tag{337}$$

$$d_{k;ij} = \max\left(d_{ik} + d_{jk} - d_{ij}, 0\right). \tag{338}$$

The residual reduced Helmholtz energy per segment, then becomes,

$$F_{\mathrm{SYH}} = \frac{a_{\mathrm{SYH}}^{\mathrm{R}}}{\mathrm{N_A}k_{\mathrm{B}}T} = \left(\sum_i m_{\mathrm{s},i}n_i\right)\int_V^\infty \frac{Z_{\mathrm{SYH}}^{\mathrm{R}}}{V}dV$$

$$= n_{\mathrm{s}}\left(-\ln\left(1-\eta\right)A_1\left(T,\mathbf{n}\right) + \frac{F_{\mathrm{pure}}}{n}A_2\left(T,\mathbf{n}\right)\right). \tag{339}$$

6.1 Pure fluid hard-spere model

The pure fluid hard-sphere compressibillity is given by the Carnahan-Starling-Kolafa [7] EOS,

$$Z_{\mathrm{pure}}^{\mathrm{CSK}}\left(\eta\right) = \frac{1+\eta+\eta^2-2\eta^3\left(1+\eta\right)/3}{\left(1-\eta\right)^3}. \tag{340}$$

The residual reduced Helmholtz energy per segment, then becomes,

$$F_{\mathrm{CSK,pure}} = \frac{a_{\mathrm{CSK,pure}}^{\mathrm{R}}}{\mathrm{N_A}k_{\mathrm{B}}T} = n_{\mathrm{s}}\int_V^\infty \frac{Z_{\mathrm{CSK}}-1}{V}dV = n_{\mathrm{s}}\int_0^\eta \frac{Z_{\mathrm{CSK}}-1}{\eta}d\eta$$

$$= \frac{n_{\mathrm{s}}}{3}\left(\frac{5}{2(1-\eta)^2} + \frac{10}{1-\eta} + 2\eta + 5\ln\left(1-\eta\right)\right). \tag{341}$$

$$\frac{\partial\left(\frac{F_{\mathrm{CSK,pure}}}{n_{\mathrm{s}}}\right)}{\partial\eta} = \frac{12-6\eta+\eta^2-2\eta^3}{3\left(1-\eta\right)^3}, \tag{342}$$

$$\frac{\partial^2\left(\frac{F_{\mathrm{CSK,pure}}}{n_{\mathrm{s}}}\right)}{\partial\eta^2} = \frac{-5\left(-6+2\eta+\eta^2\right)}{3\left(1-\eta\right)^4}. \tag{343}$$

Alternatively the simpler Carnahan-Starling [5] EOS can be used.

$$Z^{\mathrm{CS}}_{\mathrm{pure}}\left(\eta\right) = \frac{1+\eta+\eta^2-\eta^3}{\left(1-\eta\right)^3}. \tag{344}$$

$$\frac{a^{\mathrm{R}}_{\mathrm{CS,pure}}}{\mathrm{N_A}k_{\mathrm{B}}T} = n_{\mathrm{s}}\int_V^{\infty}\frac{Z_{\mathrm{CS}}-1}{V}dV = n_{\mathrm{s}}\int_0^{\eta}\frac{Z_{\mathrm{CS}}-1}{\eta}d\eta = n_{\mathrm{s}}\frac{3-2\eta}{\left(1-\eta\right)^2}. \tag{345}$$

The excess configurational energy is given from,

$$a^{\mathrm{ex}}_{\mathrm{CS,pure}} = \frac{4\eta-3\eta^2}{\left(1-\eta\right)^2} = a^{\mathrm{R}}_{\mathrm{CS,pure}}-3. \tag{346}$$

Differentials of the hard-sphere term:

$$\frac{\partial a^{\mathrm{R}}_{\mathrm{CS,pure}}}{\partial\eta} = -\frac{2\left(\left(\eta-2\right)\right.}{\left(1-\eta\right)^3}, \tag{347}$$

$$\frac{\partial^2 a^{\mathrm{R}}_{\mathrm{CS,pure}}}{\partial\eta^2} = \frac{10-4\eta}{\left(1-\eta\right)^4}. \tag{348}$$

6.2 Model differentials

Before differentiating, it will help to split the expressions in sub contributions tho the Helmholtz energy. In the follwing, segments will be ignored, impying $m_{\mathrm{s}} = 1$. The HS superscript on the hard sphere diameter will also be dropped.

Grouping of termes,

$$\begin{aligned} F_{\mathrm{SYH}} &= \left[-\ln\left(1-\eta\right)\right]\left[nA_1\right] + \left[\frac{F_{\mathrm{pure}}}{n}\right]\left[nA_2\right], \\ &= F_{11}F_{12} + F_{21}F_{22}. \end{aligned} \tag{349}$$

$$\begin{aligned} F_{12} = nA_1\left(T,\mathbf{n}\right) &= n\frac{b_3\left(\frac{\sum n_i d_i^3}{n}\right)\frac{\overline{B_2}^*}{n^2} - b_2\frac{\overline{B_3}^*}{n^3}}{\left(b_3-b_2\right)\left(\frac{\sum n_i d_i^3}{n}\right)^2} \\ &= \frac{b_3\left(\sum n_i d_i^3\right)\overline{B_2}^* - b_2\overline{B_3}^*}{\left(b_3-b_2\right)\left(\sum n_i d_i^3\right)^2} \end{aligned} \tag{350}$$

$$F_{22} = nA_2(T, \mathbf{n}) = n\frac{\frac{\overline{B_3}^*}{n^3} - \left(\frac{\sum n_i d_i^3}{n}\right)\frac{\overline{B_2}^*}{n^2}}{(b_3 - b_2)\left(\frac{\sum n_i d_i^3}{n}\right)^2}$$
$$= \frac{\overline{B_3}^* - \left(\sum n_i d_i^3\right)\overline{B_2}^*}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2} \tag{351}$$

Differentials for F_{12}:

$$F_{12,i} = \frac{b_3 d_i^3 \overline{B_2}^* + b_3\left(\sum n_i d_i^3\right)\overline{B_{2i}}^* - b_2\overline{B_{3i}}^* - 2(b_3 - b_2)\left(\sum n_i d_i^3\right) d_i^3 F_{12}}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2}, \tag{352}$$

$$F_{12,ij} = \frac{1}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2}\left[b_3 d_i^3 \overline{B_{2j}}^* + b_3 d_j^3 \overline{B_{2i}}^* + b_3\left(\sum n_i d_i^3\right)\overline{B_{2ij}}^* - b_2\overline{B_{3ij}}^*\right.$$
$$- 2(b_3 - b_2) d_j^3 d_i^3 F_{12} - 2(b_3 - b_2)\left(\sum n_i d_i^3\right) d_i^3 F_{12,j}$$
$$\left. -2(b_3 - b_2)\left(\sum n_i d_i^3\right) d_j^3 F_{12,i}\right], \tag{353}$$

$$F_{12,T} = \frac{1}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2}\left[b_3\left(\sum n_i d_i^3\right)_T \overline{B_2}^* + b_3\left(\sum n_i d_i^3\right)\overline{B_{2T}}^* - b_2\overline{B_{3T}}^*\right.$$
$$\left. -2(b_3 - b_2)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{12}\right], \tag{354}$$

$$F_{12,TT} = \frac{1}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2}\left[b_3\left(\sum n_i d_i^3\right)_{TT}\overline{B_2}^* + 2b_3\left(\sum n_i d_i^3\right)_T\overline{B_{2T}}^*\right.$$
$$+ b_3\left(\sum n_i d_i^3\right)\overline{B_{2TT}}^* - b_2\overline{B_{3TT}}^* - 2(b_3 - b_2)\left(\left(\sum n_i d_i^3\right)_T\right)^2 F_{12}$$
$$\left. -2(b_3 - b_2)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_{TT} F_{12} - 4(b_3 - b_2)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{12,T}\right], \tag{355}$$

$$F_{12,iT} = \frac{1}{(b_3 - b_2)\left(\sum n_i d_i^3\right)^2}\left[3b_3 d_i^2 d_{iT}\overline{B_2}^* + b_3 d_i^3\overline{B_{2T}}^* + b_3\left(\sum n_i d_i^3\right)_T\overline{B_{2i}}^*\right.$$
$$+ b_3\left(\sum n_i d_i^3\right)\overline{B_{2iT}}^* - b_2\overline{B_{3iT}}^* - 2(b_3 - b_2)\left(\sum n_i d_i^3\right)_T d_i^3 F_{12}$$
$$- 6(b_3 - b_2)\left(\sum n_i d_i^3\right) d_i^2 d_{iT} F_{12}$$
$$\left. -2(b_3 - b_2)\left(\sum n_i d_i^3\right) d_i^3 F_{12,T} - 2(b_3 - b_2)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{12,i}\right] \tag{356}$$

Here we have used,

$$\left(\sum n_i d_i^3\right)_T = 3\sum n_i d_i^2 d_{iT}, \tag{357}$$
$$\left(\sum n_i d_i^3\right)_{TT} = 6\sum n_i d_i d_{iT}^2 + 3\sum n_i d_i^2 d_{iTT}. \tag{358}$$

Differentials for F_{12}:

$$F_{22,i} = \frac{\overline{B_{3}}^{*}_{i} - d_i^3 \overline{B_2}^{*} - \left(\sum n_i d_i^3\right) \overline{B_2}^{*}_{i} - 2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right) d_i^3 F_{22}}{\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)^2}, \tag{359}$$

$$\begin{aligned} F_{22,ij} = & \frac{1}{\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)^2}\left[\overline{B_3}^{*}_{ij} - d_i^3 \overline{B_2}^{*}_{j} - d_j^3 \overline{B_2}^{*}_{i} - \left(\sum n_i d_i^3\right) \overline{B_2}^{*}_{ij} \right. \\ & - 2\left(b_3 - b_2\right) d_j^3 d_i^3 F_{22} - 2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right) d_i^3 F_{22,j} \\ & \left. -2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right) d_j^3 F_{22,i}\right], \end{aligned} \tag{360}$$

$$\begin{aligned} F_{22,T} = & \frac{1}{\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)^2}\left[\overline{B_3}^{*}_{T} - \left(\sum n_i d_i^3\right)_T \overline{B_2}^{*} - \left(\sum n_i d_i^3\right) \overline{B_2}^{*}_{T} \right. \\ & \left. -2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{22}\right], \end{aligned} \tag{361}$$

$$\begin{aligned} F_{22,TT} = & -\frac{1}{\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)^2}\left[\overline{B_3}^{*}_{TT} - \left(\sum n_i d_i^3\right)_{TT} \overline{B_2}^{*} - 2\left(\sum n_i d_i^3\right)_T \overline{B_2}^{*}_{T} \right. \\ & - \left(\sum n_i d_i^3\right) \overline{B_2}^{*}_{TT} - 2\left(b_3 - b_2\right)\left(\left(\sum n_i d_i^3\right)_T\right)^2 F_{22} \\ & \left. -2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_{TT} F_{22} - 4\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{22,T}\right], \end{aligned} \tag{362}$$

$$\begin{aligned} F_{22,iT} = & \frac{1}{\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)^2}\left[\overline{B_3}^{*}_{iT} - 3 d_i^2 d_{iT} \overline{B_2}^{*} - d_i^3 \overline{B_2}^{*}_{T} - \left(\sum n_i d_i^3\right)_T \overline{B_2}^{*}_{i} \right. \\ & - \left(\sum n_i d_i^3\right) \overline{B_2}^{*}_{iT} - 2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)_T d_i^3 F_{22} \\ & - 6\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right) d_i^2 d_{iT} F_{22} \\ & \left. -2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right) d_i^3 F_{22,T} - 2\left(b_3 - b_2\right)\left(\sum n_i d_i^3\right)\left(\sum n_i d_i^3\right)_T F_{22,i}\right] \end{aligned} \tag{363}$$

The packing fraction differentials, becomes,

$$\eta_V = -\frac{\eta}{V} \tag{364}$$
$$\eta_{VV} = 2\frac{\eta}{V^2} \tag{365}$$
$$\eta_i = \frac{\pi \mathrm{N_A} d_i^3}{6V}, \tag{366}$$
$$\eta_{ij} = 0, \tag{367}$$
$$\eta_{iT} = \frac{\pi \mathrm{N_A} d_i^2 d_{iT}}{2V}, \tag{368}$$
$$\eta_{iV} = -\frac{\eta_i}{V}, \tag{369}$$
$$\eta_T = \frac{\pi \mathrm{N_A} \sum n_i d_i^2 d_{iT}}{2V}, \tag{370}$$
$$\eta_{TV} = -\frac{\eta_T}{V}, \tag{371}$$
$$\eta_{TT} = \frac{\pi \mathrm{N_A} \left(2 \sum n_i d_i d_{iT}^2 + \sum n_i d_i^2 d_{iTT}\right)}{2V}, \tag{372}$$
$$\tag{373}$$

Differentials for F_{11}:

$$F_{11,\eta} = \frac{1}{1-\eta} \tag{374}$$
$$F_{11,\eta\eta} = \frac{1}{(1-\eta)^2} \tag{375}$$
$$\tag{376}$$

The differentials of F_{21} is given in Equation 342.
The differentials of $\overline{B_2}^*$ becomes,

$$\overline{B_2}^* = 4 \sum_i \sum_j n_i n_j d_{i,j}^3 \tag{377}$$
$$\overline{B_{2T}}^* = 12 \sum_i \sum_j n_i n_j d_{i,j}^2 d_{i,j,T} \tag{378}$$
$$\overline{B_{2TT}}^* = 12 \sum_i \sum_j n_i n_j \left(2 d_{i,j} d_{i,j,T}^2 + d_{i,j}^2 d_{i,j,TT}\right) \tag{379}$$
$$\overline{B_{2Tk}}^* = 24 \sum_j n_j d_{k,j}^2 d_{k,j,T} \tag{380}$$
$$\overline{B_{2k}}^* = 8 \sum_j n_j d_{k,j}^3 \tag{381}$$
$$\overline{B_{2kl}}^* = 8 d_{k,l}^3 \tag{382}$$

The differentials of $\overline{B_3}^*$ becomes,

$$\overline{B_3}^* = \sum_i \sum_j \sum_k n_i n_j n_k \overline{B}_{i,j,k} \tag{383}$$

$$\overline{B_3}^*_T = \sum_i \sum_j \sum_k n_i n_j n_k \overline{B}_{i,j,k,T} \tag{384}$$

$$\overline{B_3}^*_{TT} = \sum_i \sum_j \sum_k n_i n_j n_k \overline{B}_{i,j,k,TT} \tag{385}$$

$$\overline{B_3}^*_{Tl} = \sum_j \sum_k n_j n_k \overline{B}_{l,j,k,T} + \sum_i \sum_k n_i n_k \overline{B}_{i,l,k,T} + \sum_i \sum_j n_i n_j \overline{B}_{i,j,l,T} \tag{386}$$

$$\overline{B_3}^*_{l} = \sum_j \sum_k n_j n_k \overline{B}^3_{l,j,k} + \sum_i \sum_k n_i n_k \overline{B}^3_{i,l,k} + \sum_i \sum_j n_i n_j \overline{B}^3_{i,j,l} \tag{387}$$

$$\overline{B_3}^*_{lm} = \sum_k n_k \overline{B}^3_{l,m,k} + \sum_k n_k \overline{B}^3_{m,l,k} + \sum_j n_j \overline{B}^3_{m,j,l} + \sum_j n_j \overline{B}^3_{l,j,m} + \sum_i n_i \overline{B}^3_{i,l,m} + \sum_i n_i \overline{B}^3_{i,m,l} \tag{388}$$

(389)

7 Pure fluid hard-spere reference

According to Leonard et al. [9], using a pure fluid reference, the Barker-Henderson diameter is described as,

$$d_{\text{pure}} = \sum_j \sum_i x_i x_j d_{ij}. \tag{390}$$

The packing fraction used with the pure fluid hard-sphere EOS then becomes,

$$\eta^{\text{pure}} = \frac{\pi \mathrm{N_A} n d_{\text{pure}}^3}{6V} = \frac{\pi \mathrm{N_A} \left(\sum_j \sum_i n_i n_j d_{ij} \right)^3}{6V n^5}. \tag{391}$$

Before differentiating, we introduce,

$$\hat{d} = \sum_j \sum_i n_i n_j d_{ij}. \tag{392}$$

The packing fraction differentials, becomes,

$$\eta_V^{\text{pure}} = -\frac{\eta^{\text{pure}}}{V} \tag{393}$$

$$\eta_{VV}^{\text{pure}} = 2\frac{\eta^{\text{pure}}}{V^2} \tag{394}$$

$$\eta_k^{\text{pure}} = \frac{1}{n^5}\left(\frac{\pi \mathrm{N_A}\hat{d}^2\hat{d}_k}{2V} - 5n^4\eta^{\text{pure}}\right), \tag{395}$$

$$\eta_{kl}^{\text{pure}} = \frac{1}{n^5}\left(\frac{\pi \mathrm{N_A}\hat{d}\left(2\hat{d}_l\hat{d}_k + \hat{d}\hat{d}_{kl}\right)}{2V} - 5n^4\eta_k^{\text{pure}} - 5n^4\eta_l^{\text{pure}} - 20n^3\eta^{\text{pure}}\right), \tag{396}$$

$$\eta_{kT}^{\text{pure}} = \frac{1}{n^5}\left(\frac{\pi \mathrm{N_A}\hat{d}\left(2\hat{d}_T\hat{d}_k + \hat{d}\hat{d}_{kT}\right)}{2V} - 5n^4\eta_T^{\text{pure}}\right), \tag{397}$$

$$\eta_{kV}^{\text{pure}} = -\frac{\eta_k^{\text{pure}}}{V}, \tag{398}$$

$$\eta_T^{\text{pure}} = \frac{\pi \mathrm{N_A}\hat{d}^2\hat{d}_T}{2Vn^5}, \tag{399}$$

$$\eta_{TV}^{\text{pure}} = -\frac{\eta_T^{\text{pure}}}{V}, \tag{400}$$

$$\eta_{TT}^{\text{pure}} = \frac{\pi \mathrm{N_A}\hat{d}\left(2\hat{d}_T^2 + \hat{d}\hat{d}_{TT}\right)}{2Vn^5}. \tag{401}$$

7.1 Segments for the pure fluid hard-spere reference

In order to account for segments, the $x_{\mathrm{s},i}$ is interchanged with x_i etc.

$$d_{\text{pure}} = \sum_j \sum_i x_{\mathrm{s},i} x_{\mathrm{s},i} d_{ij}. \tag{402}$$

The packing fraction used with the pure fluid hard-sphere EOS including segments then becomes,

$$\eta^{\text{pure}} = \frac{\pi \mathrm{N_A} n_{\mathrm{s}} d_{\text{pure}}^3}{6V} = \frac{\pi \mathrm{N_A}\left(\sum_j \sum_i n_{\mathrm{s},i} n_{\mathrm{s},i} d_{ij}\right)^3}{6Vn_{\mathrm{s}}^5}. \tag{403}$$

Before differentiating, we again introduce,

$$\hat{d} = \sum_j \sum_i n_{\mathrm{s},i} n_{\mathrm{s},j} d_{ij}. \tag{404}$$

The packing fraction differentials, becomes,

$$\eta_V^{\text{pure}} = -\frac{\eta^{\text{pure}}}{V} \tag{405}$$

$$\eta_{VV}^{\text{pure}} = 2\frac{\eta^{\text{pure}}}{V^2} \tag{406}$$

$$\eta_k^{\text{pure}} = \frac{1}{n_{\text{s}}^5}\left(\frac{\pi \mathrm{N_A} \hat{d}^2 \hat{d}_k}{2V} - 5m_{\text{s},k} n_{\text{s}}^4 \eta^{\text{pure}}\right), \tag{407}$$

$$\begin{aligned}\eta_{kl}^{\text{pure}} =& \frac{1}{n_{\text{s}}^5}\left(\frac{\pi \mathrm{N_A} \hat{d}\left(2\hat{d}_l \hat{d}_k + \hat{d}\hat{d}_{kl}\right)}{2V} - 5m_{\text{s},l} n_{\text{s}}^4 \eta_k^{\text{pure}}\right.\\ &\left. - 5m_{\text{s},k} n_{\text{s}}^4 \eta_l^{\text{pure}} - 20 m_{\text{s},k} m_{\text{s},l} n_{\text{s}}^3 \eta^{\text{pure}}\right),\end{aligned} \tag{408}$$

$$\eta_{kT}^{\text{pure}} = \frac{1}{n_{\text{s}}^5}\left(\frac{\pi \mathrm{N_A} \hat{d}\left(2\hat{d}_T \hat{d}_k + \hat{d}\hat{d}_{kT}\right)}{2V} - 5m_{\text{s},k} n_{\text{s}}^4 \eta_T^{\text{pure}}\right), \tag{409}$$

$$\eta_{kV}^{\text{pure}} = -\frac{\eta_k^{\text{pure}}}{V}, \tag{410}$$

$$\eta_T^{\text{pure}} = \frac{\pi \mathrm{N_A} \hat{d}^2 \hat{d}_T}{2V n_{\text{s}}^5}, \tag{411}$$

$$\eta_{TV}^{\text{pure}} = -\frac{\eta_T^{\text{pure}}}{V}, \tag{412}$$

$$\eta_{TT}^{\text{pure}} = \frac{\pi \mathrm{N_A} \hat{d}\left(2\hat{d}_T^2 + \hat{d}\hat{d}_{TT}\right)}{2V n_{\text{s}}^5}. \tag{413}$$

7.2 Compositional dependence in hard-sphere diameter d

Need to handle situation where $d > \sigma$. Since $g = 0$ for $r < d$, the integral for $\sigma \to \infty$ simplifies to an integral from $d \to \infty$.

$$d^{\text{pure}}(\mathbf{n}, T) = \frac{1}{n_{\text{s}}^2}\sum_j \sum_i n_{\text{s},i} n_{\text{s},j} d_{ij}(T). \tag{414}$$

The differentials then become, when assuming $d_{ij} = d_{ji}$,

$$d_T^{\text{pure}} = \frac{1}{n_{\text{s}}^2} \sum_j \sum_i n_{\text{s},i} n_{\text{s},j} d_{ij,T} \tag{415}$$

$$d_{TT}^{\text{pure}} = \frac{1}{n_{\text{s}}^2} \sum_j \sum_i n_{\text{s},i} n_{\text{s},j} d_{ij,TT} \tag{416}$$

$$d_k^{\text{pure}} = \frac{2 m_{\text{s},k}}{n_{\text{s}}^2} \left(\sum_i n_{\text{s},j} d_{ik} - n_{\text{s}} d^{\text{pure}} \right) \tag{417}$$

$$d_{kl}^{\text{pure}} = \frac{2}{n_{\text{s}}^2} \left(m_{\text{s},k} m_{\text{s},l} d_{lk} - m_{\text{s},k} m_{\text{s},l} d^{\text{pure}} - m_{\text{s},k} n_{\text{s}} d_l^{\text{pure}} - m_{\text{s},l} n_{\text{s}} d_k^{\text{pure}} \right) \tag{418}$$

$$d_{Tk}^{\text{pure}} = \frac{2 m_{\text{s},k}}{n_{\text{s}}^2} \left(\sum_i n_{\text{s},j} d_{ik,T} - n_{\text{s}} d_T^{\text{pure}} \right) \tag{419}$$

8 New term in the perturbation of mixtures

9 New term

In the excellent paper entitled "Perturbation theory and Liquid Mixtures", Leonard et al. (a student of Barker and Henderson) derives a perturbation theory for mixtures. Three references are considered:

- Single-component hard-sphere reference fluid
- Additive mixture of hard-spheres as reference
- Non-additive mixture of hard-spheres as reference

In the current treatment of SAFT-VR-Mie, the pair-correlation of the single-component hard-sphere fluid is used, hence, in a consistent treatment, the Carnahan-Starling EoS for a single-component fluid of diameter:

$$d = \sum_{i,j} x_i x_j \delta_{ij}, \tag{420}$$

should be used, where:

$$\delta_{ij} = \int_0^{\sigma_{ij}} \left[1 - \exp\left(-\beta u_{ij}(z) \right) \right] dz. \tag{421}$$

The best mixture to use as a reference, which is closest to the fluid mixture to be described is a non-additive mixture where ($d_{ij} \neq 0.5(d_{ii} + d_{jj})$. However, this also implies that the pair-correlation function for a non-additive mixture should be used when computing a_1, a_2, etc, and this pair-correlation function is in general unknown. The pair-correlation of an additive mixture of hard-spheres is more well understood even tough exact models for this fluid is also not known. If the additive mixture of hard-spheres is used as a reference, there is a missing terms (superscript M) that should be added to the perturbation expansion:

$$A^{\text{M}} \beta = \alpha^{\text{M}} = -\frac{2\pi}{V} \sum_{ij} n_i n_j d_{ij}^2 g_{0,c}^{ij} \left[d_{ij} - \delta_{ij} \right] \tag{422}$$

we keep in mind that $\delta_{ij} = d_{ij}$. The first order derivatives are:

$$\frac{\partial \alpha^{\mathrm{M}}}{\partial T} = -\frac{2\pi}{V}\sum_{ij} n_i n_j \left(2d_{ij}\frac{\partial d_{ij}}{\partial T} g_{0,c}^{ij}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2 \frac{\partial g_{0,c}^{ij}}{\partial T}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2 g_{0,c}^{ij}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right]\right) \tag{423}$$

$$\frac{\partial \alpha^{\mathrm{M}}}{\partial V} = \frac{-\alpha^{\mathrm{M}}}{V} - \frac{2\pi}{V}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial g_{0,c}^{ij}}{\partial V}\left[d_{ij}-\delta_{ij}\right] \tag{424}$$

$$\frac{\partial \alpha^{\mathrm{M}}}{\partial n_k} = -\frac{4\pi}{V}\sum_{i} n_i d_{ik}^2 \left[d_{ik}-\delta_{ik}\right] g_{0,c}^{ik} - \frac{2\pi}{V}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial g_{0,c}^{ij}}{\partial n_k}\left[d_{ij}-\delta_{ij}\right] \tag{425}$$

where we have used that $a_{ij} = a_{ji}$ for all variables. We proceed to the second order derivatives:

$$\begin{aligned}\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial T^2} = -\frac{2\pi}{V}\sum_{ij} n_i n_j \Bigg(& 2\left(\frac{\partial d_{ij}}{\partial T}\right)^2 g_{0,c}^{ij}\left[d_{ij}-\delta_{ij}\right] + 2d_{ij}\frac{\partial^2 d_{ij}}{\partial T^2} g_{0,c}^{ij}\left[d_{ij}-\delta_{ij}\right] + \\ & 2d_{ij}\frac{\partial d_{ij}}{\partial T}\frac{\partial g_{0,c}^{ij}}{\partial T}\left[d_{ij}-\delta_{ij}\right] + 2d_{ij}\frac{\partial d_{ij}}{\partial T} g_{0,c}^{ij}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + \\ & 2d_{ij}\frac{\partial d_{ij}}{\partial T}\frac{\partial g_{0,c}^{ij}}{\partial T}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial^2 g_{0,c}^{ij}}{\partial T^2}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial g_{0,c}^{ij}}{\partial T}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + \\ & 2d_{ij}\frac{\partial d_{ij}}{\partial T} g_{0,c}^{ij}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + d_{ij}^2\frac{\partial g_{0,c}^{ij}}{\partial T}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + d_{ij}^2 g_{0,c}^{ij}\left[\frac{\partial^2 d_{ij}}{\partial T^2}-\frac{\partial^2 \delta_{ij}}{\partial T^2}\right]\Bigg)\end{aligned} \tag{426}$$

Which can be simplified to:

$$\begin{aligned}\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial T^2} = -\frac{2\pi}{V}\sum_{ij} n_i n_j \Bigg(& 2\left(\frac{\partial d_{ij}}{\partial T}\right)^2 g_{0,c}^{ij}\left[d_{ij}-\delta_{ij}\right] + 2d_{ij}\frac{\partial^2 d_{ij}}{\partial T^2} g_{0,c}^{ij}\left[d_{ij}-\delta_{ij}\right] + \\ & 4d_{ij}\frac{\partial d_{ij}}{\partial T}\frac{\partial g_{0,c}^{ij}}{\partial T}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial^2 g_{0,c}^{ij}}{\partial T^2}\left[d_{ij}-\delta_{ij}\right] + \\ & 4d_{ij}\frac{\partial d_{ij}}{\partial T} g_{0,c}^{ij}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + 2d_{ij}^2\frac{\partial g_{0,c}^{ij}}{\partial T}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right] + d_{ij}^2 g_{0,c}^{ij}\left[\frac{\partial^2 d_{ij}}{\partial T^2}-\frac{\partial^2 \delta_{ij}}{\partial T^2}\right]\Bigg)\end{aligned} \tag{427}$$

$$\begin{aligned}\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial V \partial T} = & \frac{-1}{V}\frac{\partial \alpha^{\mathrm{M}}}{\partial T} - \frac{2\pi}{V}\sum_{ij} n_i n_j \Bigg(2d_{ij}\frac{\partial d_{ij}}{\partial T}\frac{\partial g_{0,c}^{ij}}{\partial V}\left[d_{ij}-\delta_{ij}\right] \\ & d_{ij}^2\frac{\partial^2 g_{0,c}^{ij}}{\partial V \partial T}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial g_{0,c}^{ij}}{\partial V}\left[\frac{\partial d_{ij}}{\partial T}-\frac{\partial \delta_{ij}}{\partial T}\right]\Bigg)\end{aligned} \tag{428}$$

$$\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial n_k \partial T} = -\frac{4\pi}{V}\sum_i n_i \left(2 d_{ik}\frac{\partial d_{ik}}{\partial T}\left[d_{ik}-\delta_{ik}\right] g_{0,c}^{ik} + \right.$$
$$\left. d_{ik}^2\left[\frac{\partial d_{ik}}{\partial T} - \frac{\partial \delta_{ik}}{\partial T}\right] g_{0,c}^{ik} + d_{ik}^2\left[d_{ik}-\delta_{ik}\right]\left(\frac{\partial g_{0,c}^{ik}}{\partial T}\right)\right) +$$
$$-\frac{2\pi}{V}\sum_{ij} n_i n_j \left(2 d_{ij}\frac{\partial d_{ij}}{\partial T}\frac{\partial g_{0,c}^{ij}}{\partial n_k}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial^2 g_{0,c}^{ij}}{\partial T \partial n_k}\left[d_{ij}-\delta_{ij}\right] + d_{ij}^2\frac{\partial g_{0,c}^{ij}}{\partial n_k}\left[\frac{\partial d_{ij}}{\partial T} - \frac{\partial \delta_{ij}}{\partial T}\right]\right) \tag{429}$$

$$\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial V^2} = \frac{\alpha^{\mathrm{M}}}{V^2} - \frac{1}{V}\frac{\partial \alpha^{\mathrm{M}}}{\partial V} + \frac{2\pi}{V^2}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial g_{0,c}^{ij}}{\partial V}\left[d_{ij}-\delta_{ij}\right] - \frac{2\pi}{V}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial^2 g_{0,c}^{ij}}{\partial V^2}\left[d_{ij}-\delta_{ij}\right] \tag{430}$$

$$\frac{\partial^2 \alpha^{\mathrm{M}}}{\partial n_k \partial V} = -\frac{1}{V}\frac{\partial \alpha^{\mathrm{M}}}{\partial n_k} - \frac{4\pi}{V}\sum_i n_i d_{ik}^2\left[d_{ik}-\delta_{ik}\right]\frac{\partial g_{0,c}^{ik}}{\partial V} - \frac{2\pi}{V}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial^2 g_{0,c}^{ij}}{\partial n_k \partial V}\left[d_{ij}-\delta_{ij}\right] \tag{431}$$

$$\begin{aligned} \frac{\partial^2 \alpha^{\mathrm{M}}}{\partial n_k \partial n_l} = &- \frac{4\pi}{V}\left(d_{lk}^2\left[d_{lk}-\delta_{lk}\right] g_{0,c}^{lk} + \sum_i n_i d_{ik}^2\left[d_{ik}-\delta_{ik}\right]\frac{\partial g_{0,c}^{ik}}{\partial n_l}\right) \\ &- \frac{4\pi}{V}\sum_i n_i d_{il}^2 \frac{\partial g_{0,c}^{il}}{\partial n_k}\left[d_{il}-\delta_{il}\right] - \frac{2\pi}{V}\sum_{ij} n_i n_j d_{ij}^2 \frac{\partial^2 g_{0,c}^{ij}}{\partial n_k \partial n_l}\left[d_{ij}-\delta_{ij}\right] \end{aligned} \tag{432}$$

9.1 The pair correlation function at contact

We shall use the Boublik expression for the radial distribution function (at contact), which includes an additional term in comparison to the paper by Leonard et al.:

$$g_{0,c}(d_{ij}) = \frac{1}{1-\zeta_3} + \frac{3\zeta_2}{(1-\zeta_3)^2}\mu_{ij} + \frac{2\zeta_2^2}{(1-\zeta_3)^3}\mu_{ij}^2 \tag{433}$$

where:

$$\mu_{ij} = \frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}} \tag{434}$$

which depends only on the temperature, with the following derivatives:

$$\frac{\partial \mu_{ij}}{\partial T} = \frac{d_{ii}^2 d_{jj,T} + d_{jj}^2 d_{ii,T}}{(d_{ii}+d_{jj})^2} \tag{435}$$

$$\frac{\partial^2 \mu_{ij}}{\partial T^2} = \frac{2(d_{ii}+d_{jj}) d_{ii,T} d_{jj,T} + d_{jj}^2 d_{ii,TT} + d_{ii}^2 d_{jj,TT}}{(d_{ii}+d_{jj})^2} - 2\frac{\left(d_{ii}^2 d_{jj,T} + d_{jj}^2 d_{ii,T}\right)(d_{ii,T}+d_{jj,T})}{(d_{ii}+d_{jj})^3} \tag{436}$$

The first order derivatives of the pair-correlation function at contact are:

$$\frac{\partial g_{0,c}^{ij}}{\partial \mu_{ij}} = \frac{3\zeta_2}{(1-\zeta_3)^2} + \frac{4\zeta_2^2}{(1-\zeta_3)^3}\mu_{ij} \tag{437}$$

$$\frac{\partial g_{0,c}^{ij}}{\partial \zeta_2} = \frac{3}{(1-\zeta_3)^2}\mu_{ij} + \frac{4\zeta_2}{(1-\zeta_3)^3}\mu_{ij}^2 \tag{438}$$

$$\frac{\partial g_{0,c}^{ij}}{\partial \zeta_3} = \frac{1}{(1-\zeta_3)^2} + \frac{6\zeta_2}{(1-\zeta_3)^3}\mu_{ij} + \frac{6\zeta_2^2}{(1-\zeta_3)^4}\mu_{ij}^2 \tag{439}$$

and the second order derivatives:

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}^2} = \frac{4\zeta_2^2}{(1-\zeta_3)^3} \tag{440}$$

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}\partial \zeta_2} = \frac{3}{(1-\zeta_3)^2} + \frac{8\zeta_2}{(1-\zeta_3)^3}\mu_{ij} \tag{441}$$

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}\partial \zeta_3} = \frac{6\zeta_2}{(1-\zeta_3)^3} + \frac{12\zeta_2^2}{(1-\zeta_3)^4}\mu_{ij} \tag{442}$$

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2} = \frac{4}{(1-\zeta_3)^3}\mu_{ij}^2 \tag{443}$$

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2} = \frac{2}{(1-\zeta_3)^3} + \frac{18\zeta_2}{(1-\zeta_3)^4}\mu_{ij} + \frac{24\zeta_2^2}{(1-\zeta_3)^5}\mu_{ij}^2 \tag{444}$$

$$\frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2\partial \zeta_3} = \frac{6}{(1-\zeta_3)^3}\mu_{ij} + \frac{12\zeta_2}{(1-\zeta_3)^4}\mu_{ij}^2 \tag{445}$$

and the following derivatives of the pair-correlation function:

$$\frac{\partial g_{0,c}^{ij}}{\partial T} = \frac{\partial g_{0,c}^{ij}}{\partial \mu_{ij}}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial \zeta_2}{\partial T} + \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial \zeta_3}{\partial T} \tag{446}$$

$$\frac{\partial g_{0,c}^{ij}}{\partial V} = \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial \zeta_2}{\partial V} + \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial \zeta_3}{\partial V} \tag{447}$$

$$\frac{\partial g_{0,c}^{ij}}{\partial n_i} = \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial \zeta_2}{\partial n_i} + \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial \zeta_3}{\partial n_i} \tag{448}$$

and then the second order derivatives:

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial T^2} =& \frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}}\frac{\partial^2 \mu_{ij}}{\partial T^2} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}^2}\left(\frac{\partial \mu_{ij}}{\partial T}\right)^2 + \frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}\partial \zeta_2}\frac{\partial \mu_{ij}}{\partial T}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \mu_{ij}\partial \zeta_3}\frac{\partial \mu_{ij}}{\partial T}\frac{\partial \mu_{ij}}{\partial \zeta_3} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial T^2} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2\partial \mu_{ij}}\frac{\partial \zeta_2}{\partial T}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\left(\frac{\partial \zeta_2}{\partial T}\right)^2 + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2\partial \zeta_3}\frac{\partial \zeta_2}{\partial T}\frac{\partial \zeta_3}{\partial T} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial T^2} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3\partial \mu_{ij}}\frac{\partial \zeta_3}{\partial T}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3\partial \zeta_2}\frac{\partial \zeta_3}{\partial T}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\left(\frac{\partial \zeta_3}{\partial T}\right)^2\end{aligned} \tag{449}$$

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial V \partial T} =& \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial V \partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \mu_{ij}}\frac{\partial \zeta_2}{\partial V}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\frac{\partial \zeta_2}{\partial V}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \zeta_3}\frac{\partial \zeta_2}{\partial V}\frac{\partial \zeta_3}{\partial T} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial V \partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \mu_{ij}}\frac{\partial \zeta_3}{\partial V}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \zeta_2}\frac{\partial \zeta_3}{\partial V}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\frac{\partial \zeta_3}{\partial V}\frac{\partial \zeta_3}{\partial T}\end{aligned} \tag{450}$$

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial n_i \partial T} =& \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial n_i \partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \mu_{ij}}\frac{\partial \zeta_2}{\partial n_i}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\frac{\partial \zeta_2}{\partial n_i}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \zeta_3}\frac{\partial \zeta_2}{\partial n_i}\frac{\partial \zeta_3}{\partial T} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial n_i \partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \mu_{ij}}\frac{\partial \zeta_3}{\partial n_i}\frac{\partial \mu_{ij}}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \zeta_2}\frac{\partial \zeta_3}{\partial n_i}\frac{\partial \zeta_2}{\partial T} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\frac{\partial \zeta_3}{\partial n_i}\frac{\partial \zeta_3}{\partial T}\end{aligned} \tag{451}$$

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial V^2} =& \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial V^2} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\left(\frac{\partial \zeta_2}{\partial V}\right)^2 + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \zeta_3}\frac{\partial \zeta_2}{\partial V}\frac{\partial \zeta_3}{\partial V} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial V^2} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \zeta_2}\frac{\partial \zeta_3}{\partial V}\frac{\partial \zeta_2}{\partial V} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\left(\frac{\partial \zeta_3}{\partial V}\right)^2\end{aligned} \tag{452}$$

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial V \partial n_i} =& \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial V \partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\frac{\partial \zeta_2}{\partial V}\frac{\partial \zeta_2}{\partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \zeta_3}\frac{\partial \zeta_2}{\partial V}\frac{\partial \zeta_3}{\partial n_i} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial V \partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \zeta_2}\frac{\partial \zeta_3}{\partial V}\frac{\partial \zeta_2}{\partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\frac{\partial \zeta_3}{\partial V}\frac{\partial \zeta_3}{\partial n_i}\end{aligned} \tag{453}$$

$$\begin{aligned}\frac{\partial^2 g_{0,c}^{ij}}{\partial n_j \partial n_i} =& \frac{\partial g_{0,c}^{ij}}{\partial \zeta_2}\frac{\partial^2 \zeta_2}{\partial n_j \partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2^2}\frac{\partial \zeta_2}{\partial n_j}\frac{\partial \zeta_2}{\partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_2 \partial \zeta_3}\frac{\partial \zeta_2}{\partial n_j}\frac{\partial \zeta_3}{\partial n_i} \\ & \frac{\partial g_{0,c}^{ij}}{\partial \zeta_3}\frac{\partial^2 \zeta_3}{\partial n_j \partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3 \partial \zeta_2}\frac{\partial \zeta_3}{\partial n_j}\frac{\partial \zeta_2}{\partial n_i} + \frac{\partial^2 g_{0,c}^{ij}}{\partial \zeta_3^2}\frac{\partial \zeta_3}{\partial n_j}\frac{\partial \zeta_3}{\partial n_i}\end{aligned} \tag{454}$$

9.2 The reduced isothermal compressibillity of the mixture hard-sphere model

For the Boublik and Mansoori et al. hard-spere mixture model we have,

$$Z_{\text{mix}}^{\text{HS}} = \frac{P^{\text{HS}}}{k_{\text{B}} T \rho_{\text{s}}} = \frac{1}{\zeta_0}\left[\frac{\zeta_0}{(1-\zeta_3)} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{(3-\zeta_3)\,\zeta_2^3}{(1-\zeta_3)^3}\right]. \tag{455}$$

Here,

$$\zeta_l = \frac{\pi}{6}\rho_{\text{s}} \sum_i x_{\text{s},i} d_{ii}^l, \qquad l = 0,1,2,3. \tag{456}$$

To simplify we introduce, M_l,

$$M_l = \sum_i x_{\text{s},i} d_{ii}^l, \qquad l = 1,2,3. \tag{457}$$

If we also use that $\eta = \zeta_3$, we get,

$$Z_{\text{mix}}^{\text{HS}} = \frac{1}{(1-\eta)} + \frac{M_1 M_2}{M_3}\frac{3\eta}{(1-\eta)^2} + \frac{M_2^3}{M_3^2}\frac{(3-\eta)\,\eta^3}{(1-\eta)^3}. \tag{458}$$

$$K_{\text{mix}}^{\text{HS}} = \frac{\beta_T}{\beta_T^{\text{id}}} = \frac{\frac{1}{\rho_{\text{s}}}\frac{\partial \rho_{\text{s}}}{\partial P^{\text{HS}}}\Big|_T}{\frac{1}{k_{\text{B}}T\rho_{\text{s}}}} = k_{\text{B}}T\frac{\partial \rho_{\text{s}}}{\partial P^{\text{HS}}}\Big|_T = \frac{\partial \rho_{\text{s}}}{\partial\left(\rho_{\text{s}} Z^{\text{HS}}\right)}\Big|_T \tag{459}$$

Differentiating $\rho_{\text{s}} Z^{\text{HS}}$, at constant temperature and setting $K = M_1 M_2/M_3$ and $L = M_2^3/M_3^2$, we get,

$$\begin{aligned}\frac{\partial\left(\rho_{\text{s}} Z^{\text{HS}}\right)}{\partial \rho_{\text{s}}} &= Z^{\text{HS}} + \eta\frac{\partial\left(Z^{\text{HS}}\right)}{\partial \eta} \\ &= \frac{L\eta^4 - 4L\eta^3 + (9L - 6K + 1)\,\eta^2 + (6K-2)\,\eta + 1}{(1-\eta)^4}\end{aligned} \tag{460}$$

We have used,

$$\frac{\partial\left(Z^{\text{HS}}\right)}{\partial \eta} = \frac{-3K(\eta^2-1) + \eta\,(6L + \eta - 2) + 1}{(1-\eta)^4}. \tag{461}$$

This gives the reduced isothermal compressibillity for additive hard-sphere mixtures,

$$K_{\text{mix}}^{\text{HS}} = \frac{(1-\eta)^4}{L\eta^4 - 4L\eta^3 + (9L - 6K + 1)\,\eta^2 + (6K-2)\,\eta + 1}. \tag{462}$$

Setting $L = K = 1$, we see that $K_{\text{mix}}^{\text{HS}}$ reduces to K^{HS}.

9.2.1 Analytical differentials

Differentials are needed down to second order in temperature, mol numbers and volume, additional differentials are required for the chain model. A new symbol, D, is introduced for the denominator, and N is introduced by the nominator,

$$D = L\eta^4 - 4L\eta^3 + (9L - 6K + 1)\,\eta^2 + (6K-2)\,\eta + 1, \tag{463}$$

$$N = (1-\eta)^4\,. \tag{464}$$

$$D_K = -6\eta^2 + 6\eta, \tag{465}$$

$$D_{K\eta} = -12\eta + 6. \tag{466}$$

$$D_L = \eta^4 - 4\eta^3 + 9\eta^2, \tag{467}$$

$$D_{L\eta} = 4\eta^3 - 12\eta^2 + 18\eta, \tag{468}$$

Using $\bar{\beta} = K_{\text{mix}}^{\text{HS}}$,

$$\bar{\beta}_K = -\frac{ND_K}{D^2}, \tag{469}$$

$$\bar{\beta}_{KK} = \frac{2ND_K^2}{D^3}, \tag{470}$$

$$\bar{\beta}_{KL} = \frac{2ND_K D_L}{D^3}, \tag{471}$$

$$\bar{\beta}_{K\eta} = \frac{-N_\eta DD_K - NDD_{K\eta} + 2ND_K D_\eta}{D^3}. \tag{472}$$

The $\bar{\beta}_L$ follow the same pattern.

$$D_\eta = 4L\eta^3 - 12L\eta^2 + 2\left(9L - 6K + 1\right)\eta + 6K - 2, \tag{473}$$
$$D_{\eta\eta} = 12L\eta^2 - 24L\eta + 18L - 12K + 2, \tag{474}$$
$$N_\eta = -4\left(1-\eta\right)^3, \tag{475}$$
$$N_{\eta\eta} = 12\left(1-\eta\right)^2. \tag{476}$$

$$\bar{\beta}_\eta = \frac{DN_\eta - ND_\eta}{D^2}, \tag{477}$$
$$\bar{\beta}_{\eta\eta} = \frac{D^2 N_{\eta\eta} - NDD_{\eta\eta} - 2DN_\eta D_\eta + 2ND_\eta^2}{D^3}. \tag{478}$$

$$\bar{\beta}_T = \bar{\beta}_K K_T + \bar{\beta}_L L_T + \bar{\beta}_\eta \eta_T, \tag{479}$$
$$\bar{\beta}_{TT} = \bar{\beta}_{KK} K_T^2 + \bar{\beta}_{LL} L_T^2 + \bar{\beta}_{\eta\eta}\eta_T^2 + 2\bar{\beta}_{KL} L_T K_T + 2\bar{\beta}_{K\eta} K_T \eta_T + 2\bar{\beta}_{L\eta} L_T \eta_T + \\ + \bar{\beta}_K K_{TT} + \bar{\beta}_L L_{TT} + \bar{\beta}_\eta \eta_{TT}, \tag{480}$$
$$\bar{\beta}_{TV} = \left(\bar{\beta}_{K\eta} K_T + \bar{\beta}_{L\eta} L_T + \bar{\beta}_{\eta\eta}\eta_T\right)\eta_V + \bar{\beta}_\eta \eta_{TV}, \tag{481}$$
$$\bar{\beta}_V = \bar{\beta}_\eta \eta_V, \tag{482}$$
$$\bar{\beta}_{VV} = \bar{\beta}_{\eta\eta}\eta_V^2 + \bar{\beta}_\eta \eta_{VV}, \tag{483}$$
$$\bar{\beta}_i = \bar{\beta}_K K_i + \bar{\beta}_L L_i + \bar{\beta}_\eta \eta_i, \tag{484}$$
$$\bar{\beta}_{ij} = \left(\bar{\beta}_{KK} K_j + \bar{\beta}_{KL} L_j + \bar{\beta}_{K\eta}\eta_j\right) K_i \\ + \left(\bar{\beta}_{KL} K_j + \bar{\beta}_{LL} L_j + \bar{\beta}_{L\eta}\eta_j\right) L_i \\ + \left(\bar{\beta}_{K\eta} K_j + \bar{\beta}_{L\eta} L_j + \bar{\beta}_{\eta\eta}\eta_j\right)\eta_i \\ + \bar{\beta}_K K_{ij} + \bar{\beta}_L L_{ij} + \bar{\beta}_\eta \eta_{ij}, \tag{485}$$
$$\bar{\beta}_{Ti} = \left(\bar{\beta}_{KK} K_i + \bar{\beta}_{KL} L_i + \bar{\beta}_{K\eta}\eta_i\right) K_T \\ + \left(\bar{\beta}_{KL} K_i + \bar{\beta}_{LL} L_i + \bar{\beta}_{L\eta}\eta_i\right) L_T \\ + \left(\bar{\beta}_{K\eta} K_i + \bar{\beta}_{L\eta} L_i + \bar{\beta}_{\eta\eta}\eta_i\right)\eta_T \\ + \bar{\beta}_K K_{Ti} + \bar{\beta}_L L_{Ti} + \bar{\beta}_\eta \eta_{Ti} \tag{486}$$
$$\bar{\beta}_{Vi} = \left(\bar{\beta}_{K\eta} K_i + \bar{\beta}_{L\eta} L_i + \bar{\beta}_{\eta\eta}\eta_i\right)\eta_V + \bar{\beta}_\eta \eta_{Vi}. \tag{487}$$

We introduce $\bar{M}_l = M_l \sum_i m_{\mathrm{s},i} n_i$ and differentiate,

$$\bar{M}_{l,T} = \sum_i m_{\mathrm{s},i} n_i l d_{ii}^{l-1} d_{ii,T} \qquad l \in 1,2,3, \tag{488}$$
$$\bar{M}_{l,TT} = \begin{cases} \sum_i m_{\mathrm{s},i} n_i d_{ii,TT} & l \in 1, \\ \sum_i m_{\mathrm{s},i} n_i l d_{ii}^{l-2}\left(\left(l-1\right) d_{ii,T}^2 + d_{ii} d_{ii,TT}\right) & l \in 2,3, \end{cases} \tag{489}$$
$$\bar{M}_{l,n_i} = m_{\mathrm{s},i} d_{ii}^l \qquad l \in 1,2,3, \tag{490}$$
$$\bar{M}_{l,nn} = 0 \qquad l \in 1,2,3, \tag{491}$$
$$\bar{M}_{l,Tn_i} = m_{\mathrm{s},i} l d_{ii}^{l-1} d_{ii,T} \qquad l \in 1,2,3. \tag{492}$$

Using $\bar{M}_l$ and $n_\mathrm{s} = \sum_i m_{\mathrm{s},i} n_i$, we get $K = \bar{M}_1 \bar{M}_2 / \left(n_\mathrm{s} \bar{M}_3\right)$ and $L = \bar{M}_2^3 / \left(n_\mathrm{s} \bar{M}_3^2\right)$.

$$n_\mathrm{s}\bar{M}_3 K = \bar{M}_1\bar{M}_2, \tag{493}$$

$$n_\mathrm{s}\bar{M}_{3,T} K + n_\mathrm{s}\bar{M}_3 K_T = \bar{M}_{1,T}\bar{M}_2 + \bar{M}_1\bar{M}_{2,T}, \tag{494}$$

$$n_\mathrm{s}\bar{M}_{3,TT} K + 2n_\mathrm{s}\bar{M}_{3,T} K_T + n_\mathrm{s}\bar{M}_3 K_{TT} = \bar{M}_{1,TT}\bar{M}_2 + 2\bar{M}_{1,T}\bar{M}_{2,T} + \bar{M}_1\bar{M}_{2,TT}, \tag{495}$$

$$m_{\mathrm{s},i}\bar{M}_3 K + n_\mathrm{s}\bar{M}_{3,i} K + n_\mathrm{s}\bar{M}_3 K_i = \bar{M}_{1,i}\bar{M}_2 + \bar{M}_1\bar{M}_{2,i}, \tag{496}$$

$$\begin{aligned} m_{\mathrm{s},i}\bar{M}_{3,j} K + m_{\mathrm{s},i}\bar{M}_3 K_j + m_{\mathrm{s},j}\bar{M}_{3,i} K + n_\mathrm{s}\bar{M}_{3,i} K_j + m_{\mathrm{s},j}\bar{M}_3 K_i + n_\mathrm{s}\bar{M}_{3,j} K_i \\ + n_\mathrm{s}\bar{M}_3 K_{ij} = \bar{M}_{1,i}\bar{M}_{2,j} + \bar{M}_{1,j}\bar{M}_{2,i}, \end{aligned} \tag{497}$$

$$\begin{aligned} m_{\mathrm{s}.i}\bar{M}_{3,T} K + n_\mathrm{s}\bar{M}_{3,Ti} K + n_\mathrm{s}\bar{M}_{3,T} K_i + m_{\mathrm{s},i}\bar{M}_3 K_T + n_\mathrm{s}\bar{M}_{3,i} K_T + n_\mathrm{s}\bar{M}_3 K_{Ti} = \\ \bar{M}_{1,Ti}\bar{M}_2 + \bar{M}_{1,T}\bar{M}_{2,i} + \bar{M}_{1,i}\bar{M}_{2,T} + \bar{M}_1\bar{M}_{2,Ti}. \end{aligned} \tag{498}$$

$$K_T = \frac{\bar{M}_{1,T}\bar{M}_2 + \bar{M}_1\bar{M}_{2,T} - n_\mathrm{s}\bar{M}_{3,T} K}{n_\mathrm{s}\bar{M}_3}, \tag{499}$$

$$K_{TT} = \frac{\bar{M}_{1,TT}\bar{M}_2 + 2\bar{M}_{1,T}\bar{M}_{2,T} + \bar{M}_1\bar{M}_{2,TT} - n_\mathrm{s}\bar{M}_{3,TT} K - 2n_\mathrm{s}\bar{M}_{3,T} K_T}{n_\mathrm{s}\bar{M}_3}, \tag{500}$$

$$K_i = \frac{\bar{M}_{1,i}\bar{M}_2 + \bar{M}_1\bar{M}_{2,i} - m_{\mathrm{s},i}\bar{M}_3 K - n_\mathrm{s}\bar{M}_{3,i} K}{n_\mathrm{s}\bar{M}_3}, \tag{501}$$

$$\begin{aligned} K_{ij} =& \frac{\bar{M}_{1,i}\bar{M}_{2,j} + \bar{M}_{1,j}\bar{M}_{2,i} - m_{\mathrm{s},i}\bar{M}_{3,j} K - m_{\mathrm{s},i}\bar{M}_3 K_j - m_{\mathrm{s},j}\bar{M}_{3,i} K}{n_\mathrm{s}\bar{M}_3} \\ &+ \frac{-n_\mathrm{s}\bar{M}_{3,i} K_j - m_{\mathrm{s},j}\bar{M}_3 K_i - n_\mathrm{s}\bar{M}_{3,j} K_i}{n_\mathrm{s}\bar{M}_3}, \end{aligned} \tag{502}$$

$$\begin{aligned} K_{Ti} =& \frac{\bar{M}_{1,Ti}\bar{M}_2 + \bar{M}_{1,T}\bar{M}_{2,i} + \bar{M}_{1,i}\bar{M}_{2,T} + \bar{M}_1\bar{M}_{2,Ti} - m_{\mathrm{s}.i}\bar{M}_{3,T} K - n_\mathrm{s}\bar{M}_{3,Ti} K}{n_\mathrm{s}\bar{M}_3} \\ &+ \frac{-n_\mathrm{s}\bar{M}_{3,T} K_i - m_{\mathrm{s},i}\bar{M}_3 K_T - n_\mathrm{s}\bar{M}_{3,i} K_T}{n_\mathrm{s}\bar{M}_3} \end{aligned} \tag{503}$$

$$n_\mathrm{s}\bar{M}_3^2 L = \bar{M}_2^3 \tag{504}$$

$$2n_\mathrm{s}\bar{M}_3\bar{M}_{3,T} L + n_\mathrm{s}\bar{M}_3^2 L_T = 3\bar{M}_2^2\bar{M}_{2,T} \tag{505}$$

$$2n_\mathrm{s}\bar{M}_{3,T}^2 L + 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,TT} L + 4n_\mathrm{s}\bar{M}_3\bar{M}_{3,T} L_T + n_\mathrm{s}\bar{M}_3^2 L_{TT} = 6\bar{M}_2\bar{M}_{2,T}^2 + 3\bar{M}_2^2\bar{M}_{2,TT} \tag{506}$$

$$\begin{aligned} 2m_{\mathrm{s},i}\bar{M}_3\bar{M}_{3,T} L + 2n_\mathrm{s}\bar{M}_{3,i}\bar{M}_{3,T} L + 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,Ti} L + +2n_\mathrm{s}\bar{M}_3\bar{M}_{3,T} L_i + m_{\mathrm{s},i}\bar{M}_3^2 L_T \\ +2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i} L_T + n_\mathrm{s}\bar{M}_3^2 L_{Ti} = 6\bar{M}_2\bar{M}_{2,i}\bar{M}_{2,T} + 3\bar{M}_2^2\bar{M}_{2,Ti} \end{aligned} \tag{507}$$

$$m_{\mathrm{s},i}\bar{M}_3^2 L + 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i} L + n_\mathrm{s}\bar{M}_3^2 L_i = 3\bar{M}_2^2\bar{M}_{2,i} \tag{508}$$

$$\begin{aligned} 2m_{\mathrm{s},i}\bar{M}_3\bar{M}_{3,j} L + m_{\mathrm{s},i}\bar{M}_3^2 L_j + 2m_{\mathrm{s},j}\bar{M}_3\bar{M}_{3,i} L + 2n_\mathrm{s}\bar{M}_{3,j}\bar{M}_{3,i} L + 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i} L_j \\ +m_{\mathrm{s},j}\bar{M}_3^2 L_i + 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,j} L_i + n_\mathrm{s}\bar{M}_3^2 L_{ij} = 6\bar{M}_2\bar{M}_{2,j}\bar{M}_{2,i} + 3\bar{M}_2^2\bar{M}_{2,ij}. \end{aligned} \tag{509}$$

$$L_T = \frac{3\bar{M}_2^2\bar{M}_{2,T} - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,T}L}{n_\mathrm{s}\bar{M}_3^2} \tag{510}$$

$$L_{TT} = \frac{6\bar{M}_2\bar{M}_{2,T}^2 + 3\bar{M}_2^2\bar{M}_{2,TT} - 2n_\mathrm{s}\bar{M}_{3,T}^2L - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,TT}L - 4n_\mathrm{s}\bar{M}_3\bar{M}_{3,T}L_T}{n_\mathrm{s}\bar{M}_3^2} \tag{511}$$

$$\begin{aligned} L_{Ti} =& \frac{6\bar{M}_2\bar{M}_{2,i}\bar{M}_{2,T} + 3\bar{M}_2^2\bar{M}_{2,Ti} - 2m_{\mathrm{s},i}\bar{M}_3\bar{M}_{3,T}L - 2n_\mathrm{s}\bar{M}_{3,i}\bar{M}_{3,T}L}{n_\mathrm{s}\bar{M}_3^2} \\ &+ \frac{-2n_\mathrm{s}\bar{M}_3\bar{M}_{3,Ti}L - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,T}L_i - m_{\mathrm{s},i}\bar{M}_3^2L_T - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i}L_T}{n_\mathrm{s}\bar{M}_3^2} \end{aligned} \tag{512}$$

$$L_i = \frac{3\bar{M}_2^2\bar{M}_{2,i} - m_{\mathrm{s},i}\bar{M}_3^2L - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i}L}{n_\mathrm{s}\bar{M}_3^2} \tag{513}$$

$$\begin{aligned} L_{ij} =& \frac{6\bar{M}_2\bar{M}_{2,j}\bar{M}_{2,i} + 3\bar{M}_2^2\bar{M}_{2,ij} - 2m_{\mathrm{s},i}\bar{M}_3\bar{M}_{3,j}L - m_{\mathrm{s},i}\bar{M}_3^2L_j - 2m_{\mathrm{s},j}\bar{M}_3\bar{M}_{3,i}L}{n_\mathrm{s}\bar{M}_3^2} \\ &+ \frac{-2n_\mathrm{s}\bar{M}_{3,j}\bar{M}_{3,i}L - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,i}L_j - m_{\mathrm{s},j}\bar{M}_3^2L_i - 2n_\mathrm{s}\bar{M}_3\bar{M}_{3,j}L_i}{n_\mathrm{s}\bar{M}_3^2}. \end{aligned} \tag{514}$$

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