An open-source thermodynamic software library

Ritschel, Tobias Kasper Skovborg; Gaspar, Jozsef; Capolei, Andrea; Jørgensen, John Bagterp

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

An open-source thermodynamic software library*

DTU Compute Technical Report-2016-12

Tobias K. S. Ritschel, Jozsef Gaspar, Andrea Capolei, John Bagterp Jørgensen

Department of Applied Mathematics and Computer Science & Center for Energy Resources Engineering (CERE), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Abstract

This is a technical report which accompanies the article "An open-source thermodynamic software library" which describes an efficient Matlab and C implementation for evaluation of thermodynamic properties. In this technical report we present the model equations, that are also presented in the paper, together with a full set of first and second order derivatives with respect to temperature and pressure, and in cases where applicable, also with respect to mole numbers. The library is based on parameters and correlations from the DIPPR database and the Peng-Robinson and the Soave-Redlich-Kwong equations of state.

Keywords: Thermodynamic functions, Software, Phase equilibrium

1. Introduction

The purpose of this technical report is to document the equations describing vapor-liquid enthalpy, entropy and volume of real and ideal mixtures and pure components, together with their first and second order derivatives with respect to temperature and pressure, and for mixture properties, also with respect to mole numbers. For completeness, this technical report also describes logarithmic fugacity coefficients together with first and second order derivatives. The fugacity coefficients are defined by means of residual properties that are also described in this report. However, their second order derivatives require third order derivatives of the residual properties, which are not described in this report[2].

Section 2 presents DIPPR correlations together with derived expressions that are necessary in the ideal gas and liquid models. Section 3 presents ideal gas properties and Section 4 presents ideal liquid properties. Section 5 presents real mixture properties based on the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK) equations of state.

2. DIPPR correlations for pure components

This section describes the DIPPR correlations (Thomson, 1996) for ideal gas heat capacity, vapor pressure and liquid volume together with necessary integrals and temperature derivatives.

*This project is funded partly by Innovation Fund Denmark in the CITIES project (1305-00027B) and in the OPTION project (63-2013-3), and partly by the interreg project Smart Cities Accelerator (10606 SCA).

[2]The main motivation for including second order derivatives of fugacity coefficients is that they are necessary for formulating second order algorithms for dynamic optimization of flash processes.

Furthermore, we present all derivatives of these correlations and derived properties, that are necessary for the first and second order derivatives in the ideal gas and liquid models.

2.1. Ideal gas heat capacity

The ideal gas heat capacity of the i'th component, $c_{P,i}^{ig} = c_{P,i}^{ig}(T)$, is

$$c_{P,i}^{ig} = A_i + B_i \left(\frac{\frac{C_i}{T}}{\sinh\left(\frac{C_i}{T}\right)} \right)^2 + D_i \left(\frac{\frac{E_i}{T}}{\cosh\left(\frac{E_i}{T}\right)} \right)^2 \tag{1}$$

The parameters $(A_i, B_i, C_i, D_i, E_i)$ are specific to each substance and also to the ideal gas heat capacity correlation. They are provided by the DIPPR database. The unit for the molar ideal gas heat capacity is J/(kmoles K) and the temperature must be in K. The integral of the ideal gas heat capacity is used in computation of ideal gas enthalpy and is expressed using the auxiliary function $\Gamma_i = \Gamma_i(T)$

$$\int_{T_0}^{T_1} c_{P,i}^{ig} dT = \Gamma_i(T_1) - \Gamma_i(T_0) \tag{2a}$$

$$\Gamma_i(T) = A_i T + B_i C_i \coth\left(\frac{C_i}{T}\right) - D_i E_i \tanh\left(\frac{E_i}{T}\right) \tag{2b}$$

The integral of the ideal gas heat capacity divided by temperature is used for the ideal gas entropy and is expressed using the auxiliary function $\Pi_i = \Pi_i(T)$

$$\int_{T_0}^{T_1} \frac{c_{P,i}^{ig}}{T} dT = \Pi_i(T_1) - \Pi_i(T_0) \tag{3a}$$

$$\begin{aligned} \Pi_i(T) = {} & A_i \ln(T) + B_i \left(\frac{C_i}{T} \coth\left(\frac{C_i}{T}\right) - \ln \sinh\left(\frac{C_i}{T}\right) \right) \\ & - D_i \left(\frac{E_i}{T} \tanh\left(\frac{E_i}{T}\right) - \ln \cosh\left(\frac{E_i}{T}\right) \right) \end{aligned} \tag{3b}$$

The only necessary derivative of the ideal gas heat capacity is the first order temperature derivative

$$\frac{\partial c_{P,i}^{ig}}{\partial T} = \frac{2}{T^2} \left[\left(A_i - c_{P,i}^{ig}\right) T + \frac{B_i C_i}{\tanh\left(\frac{C_i}{T}\right)} \left(\frac{\frac{C_i}{T}}{\sinh\left(\frac{C_i}{T}\right)} \right)^2 + D_i E_i \tanh\left(\frac{E_i}{T}\right) \left(\frac{\frac{E_i}{T}}{\cosh\left(\frac{E_i}{T}\right)} \right)^2 \right] \tag{4}$$

2.2. Vapor pressure

The vapor pressure or saturation pressure of the i'th component, $P_i^{sat} = P_i^{sat}(T)$, is

$$P_i^{sat} = \exp\left(\ln P_i^{sat}\right) \tag{5a}$$

$$\ln P_i^{sat} = A_i + \frac{B_i}{T} + C_i \ln(T) + D_i T^{E_i} \tag{5b}$$

The substance specific correlation parameters $(A_i, B_i, C_i, D_i, E_i)$ are provided by the DIPPR database and are specific to the vapor pressure correlation. Because both the vapor pressure and its first order temperature derivative appear in the ideal liquid model, we present first, second and third

order derivatives of the above correlation. The derivatives of the vapor pressure are expressed through the derivatives of the logarithmic vapor pressure

$$\frac{\partial P_i^{sat}}{\partial T} = P_i^{sat} \frac{\partial \ln P_i^{sat}}{\partial T} \tag{6a}$$

$$\frac{\partial^2 P_i^{sat}}{\partial T^2} = P_i^{sat} \left(\left(\frac{\partial \ln P_i^{sat}}{\partial T} \right)^2 + \frac{\partial^2 \ln P_i^{sat}}{\partial T^2} \right) \tag{6b}$$

$$\frac{\partial^3 P_i^{sat}}{\partial T^3} = P_i^{sat} \left(\frac{\partial^3 \ln P_i^{sat}}{\partial T^3} + 3 \frac{\partial^2 \ln P_i^{sat}}{\partial T^2} \frac{\partial \ln P_i^{sat}}{\partial T} + \left(\frac{\partial \ln P_i^{sat}}{\partial T} \right)^3 \right) \tag{6c}$$

The derivatives of the logarithmic vapor pressure correlation are

$$\frac{\partial \ln P_i^{sat}}{\partial T} = \frac{1}{T} \left(C_i - \frac{B_i}{T} + D_i E_i T^{E_i} \right) \tag{7a}$$

$$\frac{\partial^2 \ln P_i^{sat}}{\partial T^2} = \frac{1}{T^2} \left(2\frac{B_i}{T} - C_i + D_i E_i (E_i - 1) T^{E_i} \right) \tag{7b}$$

$$\frac{\partial^3 \ln P_i^{sat}}{\partial T^3} = \frac{1}{T^3} \left(-6\frac{B_i}{T} + 2C_i + D_i E_i (E_i - 1)(E_i - 2) T^{E_i} \right) \tag{7c}$$

2.3. Liquid volume

The liquid volume of the i'th component, $v_i^l = v_i^l(T)$, is

$$v_i^l = \frac{B_i^{1+\left(1-\frac{T}{C_i}\right)^{D_i}}}{A_i} \tag{8}$$

The substance specific correlation parameters (A_i, B_i, C_i, D_i) are provided by the DIPPR database and are specific to this correlation. Because both the liquid volume and its first order derivative appear in the ideal liquid model, we present first, second and third order temperature derivatives of the liquid volume correlation. The derivatives are

$$\frac{\partial v_i^l}{\partial T} = -\ln B_i \frac{D_i}{C_i} \left(1 - \frac{T}{C_i} \right)^{D_i - 1} v_i^l \tag{9a}$$

$$\frac{\partial^2 v_i^l}{\partial T^2} = -\left(\ln B_i \frac{D_i}{C_i} \left(1 - \frac{T}{C_i} \right)^{D_i - 1} + \frac{D_i - 1}{C_i \left(1 - \frac{T}{C_i} \right)} \right) \frac{\partial v_i^l}{\partial T} \tag{9b}$$

$$\frac{\partial^3 v_i^l}{\partial T^3} = -\left(\ln B_i \frac{D_i}{C_i} + \frac{D_i - 1}{C_i \left(1 - \frac{T}{C_i} \right)} \right) \frac{\partial^2 v_i^l}{\partial T^2} - \frac{D_i - 1}{C_i \left(1 - \frac{T}{C_i} \right)} \left(\ln B_i \frac{D_i}{C_i} + \frac{1}{C_i \left(1 - \frac{T}{C_i} \right)} \right) \frac{\partial v_i^l}{\partial T} \tag{9c}$$

3. Thermodynamic functions for ideal gases

This section presents enthalpy, entropy and volume of ideal gas mixtures and pure components. These equations are based on the reference enthalpy and entropy of formation provided by the DIPPR database, together with the correlation for the ideal gas heat capacity and the ideal gas law.

3.1. Pure component properties

We describe the computation of enthalpy, entropy and volume of a pure component i

3.1.1. Enthalpy

The molar ideal gas enthalpy, $h_i^{ig} = h_i^{ig}(T)$, is a function of temperature only

$$h_i^{ig} = \underbrace{h_i^{ig}(T_0, P_0) - \Gamma_i(T_0)}_{\hat{h}_{f,i}^{ig}} + \Gamma_i(T) \tag{10}$$

It is more efficient to store $\hat{h}_{f,i}^{ig} = h_i^{ig}(T_0, P_0) - \Gamma_i(T_0)$ rather than storing $h_i^{ig}(T_0, P_0)$ and recomputing $\Gamma_i(T_0)$ at every evaluation of h_i^{ig}. The derivatives of the molar enthalpy are

$$\frac{\partial h_i^{ig}}{\partial T} = c_{P,i}^{ig} \tag{11a}$$

$$\frac{\partial^2 h_i^{ig}}{\partial T^2} = \frac{\partial c_{P,i}^{ig}}{\partial T} \tag{11b}$$

where the ideal gas heat capacity and its temperature derivative are given by (1) and (4).

3.1.2. Entropy

The molar ideal gas entropy, $s_i^{ig} = s_i^{ig}(T, P)$, is a function of temperature and pressure

$$\begin{aligned} s_i^{ig} &= \Pi_i(T) - R\ln(P) \\ &\quad + \underbrace{s_i^{ig}(T_0, P_0) - \Pi_i(T_0) + R\ln(P_0)}_{\hat{s}_{f,i}^{ig}} \end{aligned} \tag{12}$$

It is more efficient to store $\hat{s}_{f,i}^{ig} = s_i^{ig}(T_0, P_0) - \Pi_i(T_0) + R\ln(P_0)$ than recomputing $\Pi_i(T_0)$ at every evaluation of s_i^{ig}. The first order temperature and pressure derivatives of the molar ideal gas entropy are

$$\frac{\partial s_i^{ig}}{\partial T} = \frac{c_{P,i}^{ig}}{T} \tag{13a}$$

$$\frac{\partial s_i^{ig}}{\partial P} = -\frac{R}{P} \tag{13b}$$

The second order derivatives of the molar ideal gas entropy are

$$\frac{\partial^2 s_i^{ig}}{\partial T^2} = \frac{1}{T}\frac{dc_{P,i}^{ig}}{dT} - \frac{1}{T^2}c_{P,i}^{ig} \tag{14a}$$

$$\frac{\partial^2 s_i^{ig}}{\partial P^2} = \frac{R}{P^2} \tag{14b}$$

$$\frac{\partial^2 s_i^{ig}}{\partial T \partial P} = 0 \tag{14c}$$

where again, the ideal gas heat capacity and its temperature derivative are given by (1) and (4).

3.1.3. Volume

The molar ideal gas volume, $v_i^{ig} = v_i^{ig}(T, P)$, is

$$v_i^{ig} = \frac{RT}{P} \tag{15}$$

The first order derivatives of the ideal gas molar volume are

$$\frac{\partial v_i^{ig}}{\partial T} = \frac{R}{P} \tag{16a}$$

$$\frac{\partial v_i^{ig}}{\partial P} = -\frac{RT}{P^2} \tag{16b}$$

The second order derivatives are

$$\frac{\partial^2 v_i^{ig}}{\partial T^2} = 0 \tag{17a}$$

$$\frac{\partial^2 v_i^{ig}}{\partial P^2} = 2\frac{RT}{P^3} \tag{17b}$$

$$\frac{\partial^2 v_i^{ig}}{\partial T \partial P} = -\frac{R}{P^2} \tag{17c}$$

3.2. Mixture properties

We describe the computation of volume, enthalpy and entropy of an ideal gas mixture of N_C components using the molar properties of each component and the composition of the gas mixture. The mixture contains $n = \{n_i\}_{i=1}^{N_C}$ moles of each component.

3.2.1. Enthalpy

The ideal gas mixture enthalpy, $H^{ig} = H^{ig}(T, n)$, is

$$H^{ig} = \sum_{i=1}^{N_C} n_i h_i^{ig} \tag{18}$$

The first order derivatives are

$$\frac{\partial H^{ig}}{\partial T} = \sum_{i=1}^{N_C} n_i c_{P,i}^{ig} \tag{19a}$$

$$\frac{\partial H^{ig}}{\partial n_k} = h_k^{ig} \tag{19b}$$

The second order derivatives are

$$\frac{\partial^2 H^{ig}}{\partial T^2} = \sum_{i=1}^{N_C} n_i \frac{\partial^2 h_i^{ig}}{\partial T^2} \tag{20a}$$

$$\frac{\partial^2 H^{ig}}{\partial T \partial n_k} = c_{P,k}^{ig} \tag{20b}$$

$$\frac{\partial^2 H^{ig}}{\partial n_l \partial n_k} = 0 \tag{20c}$$

3.2.2. Entropy

The ideal gas mixture enthalpy, $S^{ig} = S^{ig}(T, P, n)$, is

$$S^{ig} = \sum_{i=1}^{N_C} n_i s_i^{ig} - R \sum_{i=1}^{N_C} n_i \ln(y_i) \tag{21}$$

where the total amount of moles, N, and the vapor mole fraction, y_i, are

$$y_i = \frac{n_i}{N} \tag{22a}$$

$$N = \sum_{i=1}^{N_C} n_i \tag{22b}$$

The derivatives of the mixture entropy are

$$\frac{\partial S^{ig}}{\partial T} = \frac{1}{T} \sum_{i=1}^{N_C} n_i c_{P,i}^{ig} \tag{23a}$$

$$\frac{\partial S^{ig}}{\partial P} = -\frac{NR}{P} \tag{23b}$$

$$\frac{\partial S^{ig}}{\partial n_k} = s_k^{ig} - R \ln(y_k) \tag{23c}$$

The second order derivatives are

$$\frac{\partial^2 S^{ig}}{\partial T^2} = \frac{1}{T} \sum_{i=1}^{N_C} n_i \left(\frac{\partial c_{P,i}^{ig}}{\partial T} - \frac{1}{T} c_{P,i}^{ig} \right) \tag{24a}$$

$$\frac{\partial^2 S^{ig}}{\partial P^2} = \frac{NR}{P^2} \tag{24b}$$

$$\frac{\partial^2 S^{ig}}{\partial T \partial P} = 0 \tag{24c}$$

$$\frac{\partial^2 S^{ig}}{\partial T \partial n_k} = \frac{\partial s_k^{ig}}{\partial T} = \frac{c_{P,k}^{ig}}{T} \tag{24d}$$

$$\frac{\partial^2 S^{ig}}{\partial P \partial n_k} = \frac{\partial s_k^{ig}}{\partial P} = -\frac{R}{P} \tag{24e}$$

$$\frac{\partial^2 S^{ig}}{\partial n_l \partial n_k} = -R \left(\frac{\delta_{kl}}{n_l} - \frac{1}{N} \right) \tag{24f}$$

3.2.3. Volume

The ideal gas mixture volume, $V^{ig} = V^{ig}(T, P, n)$, is

$$V^{ig} = \frac{NRT}{P} \tag{25}$$

The first order derivatives of the ideal gas mixture volume are

$$\frac{\partial V^{ig}}{\partial T} = \frac{NR}{P} \tag{26a}$$

$$\frac{\partial V^{ig}}{\partial P} = \frac{NRT}{P^2} \tag{26b}$$

$$\frac{\partial V^{ig}}{\partial n_k} = \frac{RT}{P} \tag{26c}$$

The second order derivatives are

$$\frac{\partial^2 V^{ig}}{\partial T^2} = 0 \tag{27a}$$

$$\frac{\partial^2 V^{ig}}{\partial P^2} = 2\frac{NRT}{P^3} \tag{27b}$$

$$\frac{\partial^2 V^{ig}}{\partial T \partial P} = -\frac{NR}{P^2} \tag{27c}$$

$$\frac{\partial^2 V^{ig}}{\partial T \partial n_k} = \frac{R}{P} \tag{27d}$$

$$\frac{\partial^2 V^{ig}}{\partial P \partial n_k} = -\frac{RT}{P^2} \tag{27e}$$

$$\frac{\partial^2 V^{ig}}{\partial n_l \partial n_k} = 0 \tag{27f}$$

4. Thermodynamic functions for ideal liquids

This section presents enthalpy, entropy and volume of ideal liquid mixtures and pure components. These are based on ideal gas properties, vaporization properties and pressure correcting terms. The latter two are further based on the DIPPR correlations for vapor pressure and liquid volume, together with their first order temperature derivatives.

4.1. Pure component properties

The properties of pure component liquids are based on ideal gas properties at vaporization temperature and pressure, T and $P_i^{sat} = P_i^{sat}(T)$, as well as vaporization properties. The vaporization enthalpy, $\Delta h_i^{vap} = \Delta h_i^{vap}(T)$, entropy, $\Delta s_i^{vap} = \Delta s_i^{vap}(T)$, and volume, $\Delta v_i^{vap} = \Delta v_i^{vap}(T)$, are

$$\Delta v_i^{vap} = \frac{RT}{P_i^{sat}} - v_i^l \tag{28a}$$

$$\Delta s_i^{vap} = \frac{\partial P_i^{sat}}{\partial T} \Delta v_i^{vap} \tag{28b}$$

$$\Delta h_i^{vap} = T \Delta s_i^{vap} \tag{28c}$$

where $P_i^{sat} = P_i^{sat}(T)$ is the vapor pressure (5) and $v_i^l = v_i^l(T)$ is the liquid volume (8). The derivatives of the vaporization volume are

$$\frac{\partial \Delta v_i^{vap}}{\partial T} = \frac{R}{P_i^{sat}}\left(1 - \frac{T}{P_i^{sat}}\frac{\partial P_i^{sat}}{\partial T}\right) - \frac{\partial v_i^l}{\partial T} \tag{29a}$$

$$\frac{\partial^2 \Delta v_i^{vap}}{\partial T^2} = -\frac{R}{\left(P_i^{sat}\right)^2}\left(2\frac{\partial P_i^{sat}}{\partial T}\left(1 - \frac{T}{P_i^{sat}}\frac{\partial P_i^{sat}}{\partial T}\right) + T\frac{\partial^2 P_i^{sat}}{\partial T^2}\right) - \frac{\partial^2 v_i^l}{\partial T^2} \tag{29b}$$

The derivatives of the vaporization enthalpy are

$$\frac{\partial \Delta h_i^{vap}}{\partial T} = \Delta s_i^{vap} + T\frac{\partial \Delta s_i^{vap}}{\partial T} \tag{30a}$$

$$\frac{\partial^2 \Delta h_i^{vap}}{\partial T^2} = 2\frac{\partial \Delta s_i^{vap}}{\partial T} + T\frac{\partial^2 \Delta s_i^{vap}}{\partial T^2} \tag{30b}$$

The derivatives of the vaporization entropy are

$$\frac{\partial \Delta s_i^{vap}}{\partial T} = \frac{\partial^2 P_i^{sat}}{\partial T^2}\Delta v_i^{vap} + \frac{\partial P_i^{sat}}{\partial T}\frac{\partial \Delta v_i^{vap}}{\partial T} \tag{31a}$$

$$\frac{\partial^2 \Delta s_i^{vap}}{\partial T^2} = \frac{\partial^3 P_i^{sat}}{\partial T^3}\Delta v_i^{vap} + 2\frac{\partial^2 P_i^{sat}}{\partial T^2}\frac{\partial \Delta v_i^{vap}}{\partial T} + \frac{\partial P_i^{sat}}{\partial T}\frac{\partial^2 \Delta v_i^{vap}}{\partial T^2} \tag{31b}$$

The molar liquid saturation enthalpy, $h_i^{sat} = h_i^{sat}(T)$, and entropy, $s_i^{sat} = s_i^{sat}(T)$, are

$$h_i^{sat} = h_i^v(T) - \Delta h_i^{vap}(T) \tag{32a}$$

$$s_i^{sat} = s_i^v(T, P_i^{sat}) - \Delta s_i^{vap}(T) \tag{32b}$$

The derivatives of the molar liquid saturation enthalpy are

$$\frac{\partial h_i^{sat}}{\partial T} = c_{P,i}^{ig} - \frac{\partial \Delta h_i^{vap}}{\partial T} \tag{33}$$

$$\frac{\partial^2 h_i^{sat}}{\partial T^2} = \frac{\partial c_{P,i}^{ig}}{\partial T} - \frac{\partial^2 \Delta h_i^{vap}}{\partial T^2} \tag{34}$$

The derivatives of the molar liquid saturation entropy

$$\frac{\partial s_i^{sat}}{\partial T} = \frac{\partial s_i^v}{\partial T}(T, P_i^{sat}) + \frac{\partial s_i^v}{\partial P}(T, P_i^{sat})\frac{\partial P_i^{sat}}{\partial T} - \frac{\partial \Delta s_i^{vap}}{\partial T} \tag{35}$$

$$\frac{\partial^2 s_i^{sat}}{\partial T^2} = \frac{\partial^2 s_i^v}{\partial T^2}(T, P_i^{sat}) + 2\frac{\partial^2 s_i^v}{\partial T \partial P}(T, P_i^{sat})\frac{\partial P_i^{sat}}{\partial T} + \frac{\partial^2 s_i^v}{\partial P^2}(T, P_i^{sat})\left(\frac{\partial P_i^{sat}}{\partial T}\right)^2 - \frac{\partial^2 \Delta s_i^{vap}}{\partial T^2} \tag{36}$$

The molar liquid enthalpy, $h_i^{id} = h_i^{id}(T, P)$, entropy, $s_i^{id} = s_i^{id}(T, P)$, at arbitrary pressure are

$$h_i^{id} = h_i^{sat} + \left(v_i^l - T\frac{\partial v_i^l}{\partial T}\right)\left(P - P_i^{sat}\right) \tag{37a}$$

$$s_i^{id} = s_i^{sat} - \frac{\partial v_i^l}{\partial T}\left(P - P_i^{sat}\right) \tag{37b}$$

The molar ideal liquid volume is given by the DIPPR correlation (8). The first order derivatives of liquid enthalpy are

$$\frac{\partial h_i^{id}}{\partial T} = \frac{\partial h_i^{sat}}{\partial T} - T\frac{\partial^2 v_i^l}{\partial T^2}\left(P - P_i^{sat}\right) - \left(v_i^l - T\frac{\partial v_i^l}{\partial T}\right)\frac{\partial P_i^{sat}}{\partial T} \tag{38a}$$

$$\frac{\partial h_i^{id}}{\partial P} = v_i^l - T\frac{\partial v_i^l}{\partial T} \tag{38b}$$

The second order derivatives are

$$\frac{\partial^2 h_i^{id}}{\partial T^2} = \frac{\partial^2 h_i^{sat}}{\partial T^2} - \left(\frac{\partial^2 v_i^l}{\partial T^2} + T\frac{\partial^3 v_i^l}{\partial T^3}\right)\left(P - P_i^{sat}\right) + 2T\frac{\partial^2 v_i^l}{\partial T^2}\frac{\partial P_i^{sat}}{\partial T} - \left(v_i^l - T\frac{\partial v_i^l}{\partial T}\right)\frac{\partial^2 P_i^{sat}}{\partial T^2} \tag{39a}$$

$$\frac{\partial^2 h_i^{id}}{\partial P^2} = 0 \tag{39b}$$

$$\frac{\partial^2 h_i^{id}}{\partial T \partial P} = -T\frac{\partial^2 v_i^l}{\partial T^2} \tag{39c}$$

The first order derivatives of liquid entropy are

$$\frac{\partial s_i^{id}}{\partial T} = \frac{\partial s_i^{sat}}{\partial T} - \left(\frac{\partial^2 v_i^l}{\partial T^2}\left(P - P_i^{sat}\right) - \frac{\partial v_i^l}{\partial T}\frac{\partial P_i^{sat}}{\partial T}\right) \tag{40a}$$

$$\frac{\partial s_i^{id}}{\partial P} = -\frac{\partial v_i^l}{\partial T} \tag{40b}$$

The second order derivatives are

$$\frac{\partial^2 s_i^{id}}{\partial T^2} = \frac{\partial^2 s_i^{sat}}{\partial T^2} - \left(\frac{\partial^3 v_i^l}{\partial T^3}\left(P - P_i^{sat}\right) - 2\frac{\partial^2 v_i^l}{\partial T^2}\frac{\partial P_i^{sat}}{\partial T} - \frac{\partial v_i^l}{\partial T}\frac{\partial^2 P_i^{sat}}{\partial T^2}\right) \tag{41a}$$

$$\frac{\partial^2 s_i^{id}}{\partial P^2} = 0 \tag{41b}$$

$$\frac{\partial^2 s_i^{id}}{\partial T \partial P} = -\frac{\partial^2 v_i^l}{\partial T^2} \tag{41c}$$

4.2. Mixture properties

We present volume, enthalpy and entropy of an ideal gas mixture of N_C components using the molar properties of each component and the composition of the gas mixture. The mixture contains $n = \{n_i\}_{i=1}^{N_C}$ moles of each component.

4.2.1. Enthalpy

The ideal liquid mixture enthalpy, $H^{id} = H^{id}(T, P, n)$, is

$$H^{id} = \sum_{i=1}^{N_C} n_i h_i^{id} \tag{42}$$

The first order derivatives are

$$\frac{\partial H^{id}}{\partial T} = \sum_{i=1}^{N_C} n_i \frac{\partial h_i^{id}}{\partial T} \tag{43a}$$

$$\frac{\partial H^{id}}{\partial P} = \sum_{i=1}^{N_C} n_i \left(v_i^l - T \frac{\partial v_i^l}{\partial T} \right) \tag{43b}$$

$$\frac{\partial H^{id}}{\partial n_k} = h_k^{id} \tag{43c}$$

The second order derivatives are

$$\frac{\partial^2 H^{id}}{\partial T^2} = \sum_{i=1}^{N_C} n_i \frac{\partial^2 h_i^{id}}{\partial T^2} \tag{44a}$$

$$\frac{\partial^2 H^{id}}{\partial P^2} = 0 \tag{44b}$$

$$\frac{\partial^2 H^{id}}{\partial T \partial P} = -T \sum_{i=1}^{N_C} n_i \frac{\partial^2 v_i^l}{\partial T^2} \tag{44c}$$

$$\frac{\partial^2 H^{id}}{\partial T \partial n_k} = \frac{\partial h_k^{id}}{\partial T} \tag{44d}$$

$$\frac{\partial^2 H^{id}}{\partial P \partial n_k} = v_k^l - T \frac{\partial v_k^l}{\partial T} \tag{44e}$$

$$\frac{\partial^2 H^{id}}{\partial n_l \partial n_k} = 0 \tag{44f}$$

4.2.2. Entropy

The entropy of an ideal liquid mixture is given by

$$S^{id}(T, P, n) = \sum_{i=1}^{N_C} n_i s_i^{id} - R \sum_{i=1}^{N_C} n_i \ln x_i \tag{45}$$

where the liquid mole fraction, x_i, is

$$x_i = \frac{n_i}{N} \tag{46}$$

and the total amount of moles, N, is given by (22b). The first order derivatives are

$$\frac{\partial S^{id}}{\partial T} = \sum_{i=1}^{N_C} n_i \frac{\partial s_i^{id}}{\partial T} \tag{47a}$$

$$\frac{\partial S^{id}}{\partial P} = -\sum_{i=1}^{N_C} n_i \frac{\partial v_i^l}{\partial T} \tag{47b}$$

$$\frac{\partial S^{id}}{\partial n_k} = s_k^{id} - R \ln(x_k) \tag{47c}$$

The second order derivatives are

$$\frac{\partial^2 S^{id}}{\partial T^2} = \sum_{i=1}^{N_C} n_i \frac{\partial^2 s_i^{id}}{\partial T^2} \tag{48a}$$

$$\frac{\partial^2 S^{id}}{\partial P^2} = 0 \tag{48b}$$

$$\frac{\partial^2 S^{id}}{\partial T \partial P} = -\sum_{i=1}^{N_C} n_i \frac{\partial^2 v_i^l}{\partial T^2} \tag{48c}$$

$$\frac{\partial^2 S^{id}}{\partial T \partial n_k} = \frac{\partial s_k^{id}}{\partial T} \tag{48d}$$

$$\frac{\partial^2 S^{id}}{\partial P \partial n_k} = -\frac{\partial v_k^l}{\partial T} \tag{48e}$$

$$\frac{\partial^2 S^{id}}{\partial n_l \partial n_k} = -R\left(\frac{\delta_{kl}}{n_l} - \frac{1}{N}\right) \tag{48f}$$

4.2.3. Volume

The ideal liquid mixture volume, $V^{id} = V^{id}(T, n)$, is

$$V^{id} = \sum_{i=1}^{N_C} n_i v_i^l(T) \tag{49}$$

$$\tag{50}$$

The first order derivatives are

$$\frac{\partial V^{id}}{\partial T} = \sum_{i=1}^{N_C} n_i \frac{\partial v_i^l}{\partial T} \tag{51a}$$

$$\frac{\partial V^{id}}{\partial n_k} = v_k^l \tag{51b}$$

The second order derivatives are

$$\frac{\partial^2 V^{id}}{\partial T^2} = \sum_{i=1}^{N_C} n_i \frac{\partial^2 v_i^l}{\partial T^2} \tag{52a}$$

$$\frac{\partial^2 V^{id}}{\partial T \partial n_k} = \frac{\partial v_k^l}{\partial T} \tag{52b}$$

$$\frac{\partial^2 V^{id}}{\partial n_l \partial n_k} = 0 \tag{52c}$$

5. Thermodynamic functions for real mixtures

This section presents the enthalpy, entropy and volume of a real vapor or liquid mixture. These are based on ideal gas properties and residual properties. The latter are obtained from either of the cubic equations of state, Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR)

5.1. Mixture properties

We consider a vapor or liquid phase containing N_C components with mole numbers $n = \{n_i\}_{i=1}^{N_C}$. The total amount of moles in the phase, N, and the mole fraction of the i'th component, z_i, are given by

$$N = \sum_{i=1}^{N_C} n_i \tag{53a}$$

$$z_i = \frac{n_i}{N} \tag{53b}$$

The molar enthalpy, $h = h(T, P, n)$, and entropy, $s = s(T, P, n)$, are

$$h = h^{ig} + h^R \tag{54}$$

$$s = s^{ig} + s^R \tag{55}$$

where $h^{ig} = h^{ig}(T, P, n)$ and $s^{ig} = s^{ig}(T, P, n)$ are molar ideal gas enthalpy and entropy, and $h^R(T, P, n)$ and $s^R = s^R(T, P, n)$ are molar residual enthalpy and entropy. The molar volume, $v = v(T, P, n)$, is the solution of either the Peng-Robinson or the Soave-Redlich-Kwong equations of state, both of which are in the cubic form

$$P = \frac{RT}{v - b_m} - \frac{a_m}{(v + \epsilon b_m)(v + \sigma b_m)} \tag{56}$$

where the scalars ϵ and σ are specific to each equation of state but independent of the given substances. In practice, the equation of state (56) is solved for the compressibility factor $Z = Z(T, P, n)$ in which case the molar mixture volume is

$$v = \frac{RTZ}{P} \tag{57}$$

Appendix A presents a direct and an iterative approach for solving the cubic equations of state for the compressibility factor. The mixture parameters $a_m = a_m(T, n)$ and $b_m = b_m(n)$ are obtained with van der Waals mixing rules

$$a_m = \sum_{i=1}^{N_C} \sum_{j=1}^{N_C} z_i z_j a_{ij} \tag{58a}$$

$$b_m = \sum_{i=1}^{N_C} z_i b_i \tag{58b}$$

where the mixing parameter $a_{ij} = a_{ij}(T)$ is

$$a_{ij} = (1 - k_{ij}) \sqrt{\hat{a}_{ij}} \tag{59}$$

The parameter $\hat{a}_{ij} = \hat{a}_{ij}(T) = a_i(T)a_j(T)$ is introduced for convenience and the substance specific parameters $a_i = a_i(T)$ and b_i are determined from the critical temperature, $T_{c,i}$, and critical pressure, $P_{c,i}$, of the i'th component

$$a_i = \alpha(T_{r,i}, \omega_i)\Psi \frac{R^2 T_{c,i}^2}{P_{c,i}} \tag{60a}$$

$$b_i = \Omega \frac{RT_{c,i}}{P_{c,i}} \tag{60b}$$

Table 1: Parameters in the Soave-Redlich-Kwong and the Peng-Robinson equations of state.

Eq.	ϵ	σ	Ω	Ψ
SRK	1	0	0.08664	0.42748
PR	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07779	0.45724

where $\alpha(T_{r,i}, \omega_i)$ is a function of the reduced temperature, $T_{r,i} = T/T_{c,i}$, and the acentric factor, ω_i, given by

$$\alpha(T_{r,i}, \omega_i) = \left(1 + m(\omega_i)(1 - T_{r,i}^{1/2})\right)^2 \tag{61}$$

The scalars Ψ and Ω are related to the equation of state parameters, ϵ and σ, and their values are shown in Table 1. The function $m(\omega_i)$ is a second order polynomium in the acentric factor, ω_i, for the Peng-Robinson and Soave-Redlich-Kwong equations of state and is given by

$$m_{\mathrm{SRK}}(\omega_i) = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \tag{62a}$$

$$m_{\mathrm{PR}}(\omega_i) = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{62b}$$

The cubic equation of state (56) is solved for the compressibility factor $Z = Z(T, P, n)$ and is therefore rewritten using the third order polynomial $q = q(Z)$

$$q = Z^3 + \sum_{m=0}^{2} d_m Z^m = 0 \tag{63}$$

where the polynomial coefficients $\{d_m = d_m(A, B)\}_{m=0}^2$ are

$$d_2 = B(\epsilon + \sigma - 1) - 1 \tag{64a}$$

$$d_1 = A - B(\epsilon + \sigma) + B^2(\epsilon\sigma - \epsilon - \sigma) \tag{64b}$$

$$d_0 = -\left(AB + \left(B^2 + B^3\right)\epsilon\sigma\right) \tag{64c}$$

The dimensionless quantities $A = A(T, P, n)$ and $B = B(T, P, n)$ are introduced for convenience and are given by

$$A = \frac{Pa_m}{R^2T^2} \tag{65a}$$

$$B = \frac{Pb_m}{RT} \tag{65b}$$

5.2. Residual enthalpy and entropy

The molar residual enthalpy and entropy are given in terms of the four auxiliary functions $f = f(Z, B)$, $g_h = g_h(T, n)$, $g_s = g_s(T, n)$ and $g_z = g_z(Z, B)$

$$h^R = h^R(T, P, n) = RT(Z - 1) + \frac{1}{\epsilon - \sigma} g_h f \tag{66a}$$

$$s^R = s^R(T, P, n) = Rg_z + \frac{1}{\epsilon - \sigma} g_s f \tag{66b}$$

The auxiliary functions, $f = f(Z, B)$, $g_h = g_h(T, n)$, $g_s = g_s(T, n)$ and $g_z = g_z(Z, B)$, are

$$f = \ln\left(\frac{Z + \epsilon B}{Z + \sigma B}\right) \tag{67a}$$

$$g_h = T g_s - \frac{a_m}{b_m} \tag{67b}$$

$$g_s = \frac{1}{b_m}\frac{\partial a_m}{\partial T} \tag{67c}$$

$$g_z = \ln(Z - B) \tag{67d}$$

The function $f = f(Z, B)$ depends on the equation of state parameters, ϵ and σ, whereas $g_h = g_h(T, n)$, $g_s = g_s(T, n)$ and $g_z = g_z(Z, B)$ do not. The first order derivatives of the residual enthalpy, $h^R = h^R(T, P, n)$, are

$$\frac{\partial h^R}{\partial T} = R(Z-1) + RT\frac{\partial Z}{\partial T} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_h}{\partial T} f + g_h \frac{\partial f}{\partial T}\right) \tag{68a}$$

$$\frac{\partial h^R}{\partial P} = RT\frac{\partial Z}{\partial P} + \frac{1}{\epsilon - \sigma} g_h \frac{\partial f}{\partial P} \tag{68b}$$

$$\frac{\partial h^R}{\partial n_k} = RT\frac{\partial Z}{\partial n_k} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_s}{\partial n_k} f + g_h \frac{\partial f}{\partial n_k}\right) \tag{68c}$$

The second order derivatives are

$$\frac{\partial^2 h^R}{\partial T^2} = 2R\frac{\partial Z}{\partial T} + RT\frac{\partial^2 Z}{\partial T^2} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial^2 g_h}{\partial T^2} f + 2\frac{\partial g_h}{\partial T}\frac{\partial f}{\partial T} + g_h \frac{\partial^2 f}{\partial T^2}\right) \tag{69a}$$

$$\frac{\partial^2 h^R}{\partial P^2} = RT\frac{\partial^2 Z}{\partial P^2} + \frac{1}{\epsilon - \sigma} g_h \frac{\partial^2 f}{\partial P^2} \tag{69b}$$

$$\frac{\partial^2 h^R}{\partial T \partial P} = R\frac{\partial Z}{\partial P} + RT\frac{\partial^2 Z}{\partial T \partial P} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_h}{\partial T}\frac{\partial f}{\partial P} + g_h \frac{\partial^2 f}{\partial T \partial P}\right) \tag{69c}$$

$$\frac{\partial^2 h^R}{\partial T \partial n_k} = R\frac{\partial Z}{\partial n_k} + RT\frac{\partial^2 Z}{\partial T \partial n_k} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial^2 g_h}{\partial T \partial n_k} f + \frac{\partial g_h}{\partial T}\frac{\partial f}{\partial n_k} + \frac{\partial g_h}{\partial n_k}\frac{\partial f}{\partial T} + g_h \frac{\partial^2 f}{\partial T \partial n_k}\right) \tag{69d}$$

$$\frac{\partial^2 h^R}{\partial P \partial n_k} = RT\frac{\partial^2 Z}{\partial P \partial n_k} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_h}{\partial n_k}\frac{\partial f}{\partial P} + g_h \frac{\partial^2 f}{\partial P \partial n_k}\right) \tag{69e}$$

$$\frac{\partial^2 h^R}{\partial n_l \partial n_k} = RT\frac{\partial^2 Z}{\partial n_l \partial n_k} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial^2 g_h}{\partial n_l \partial n_k} f + \frac{\partial g_h}{\partial n_k}\frac{\partial f}{\partial n_l} + \frac{\partial g_h}{\partial n_l}\frac{\partial f}{\partial n_k} + g_h \frac{\partial^2 f}{\partial n_l \partial n_k}\right) \tag{69f}$$

The first order derivatives of the residual entropy, $s^R = s^R(T, P, n)$, are

$$\frac{\partial s^R}{\partial T} = R\frac{\partial g_z}{\partial T} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_s}{\partial T} f + g_s \frac{\partial f}{\partial T}\right) \tag{70a}$$

$$\frac{\partial s^R}{\partial P} = R\frac{\partial g_z}{\partial P} + \frac{1}{\epsilon - \sigma} g_s \frac{\partial f}{\partial P} \tag{70b}$$

$$\frac{\partial s^R}{\partial n_k} = R\frac{\partial g_z}{\partial n_k} + \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_s}{\partial n_k} f + g_s \frac{\partial f}{\partial n_k}\right) \tag{70c}$$

The second order derivatives are

$$\frac{\partial^2 s^R}{\partial T^2} = R\frac{\partial^2 g_z}{\partial T^2} + \frac{1}{\epsilon-\sigma}\left(\frac{\partial^2 g_s}{\partial T^2} f + 2\frac{\partial g_s}{\partial T}\frac{\partial f}{\partial T} + g_s\frac{\partial^2 f}{\partial T^2}\right) \tag{71a}$$

$$\frac{\partial^2 s^R}{\partial P^2} = R\frac{\partial^2 g_z}{\partial T^2} + \frac{1}{\epsilon-\sigma} g_s\frac{\partial^2 f}{\partial P^2} \tag{71b}$$

$$\frac{\partial^2 s^R}{\partial T\partial P} = R\frac{\partial^2 g_z}{\partial T\partial P} + \frac{1}{\epsilon-\sigma}\left(\frac{\partial g_s}{\partial T}\frac{\partial f}{\partial P} + g_s\frac{\partial^2 f}{\partial T\partial P}\right) \tag{71c}$$

$$\frac{\partial^2 s^R}{\partial T\partial n_k} = R\frac{\partial^2 g_z}{\partial T\partial n_k} + \frac{1}{\epsilon-\sigma}\left(\frac{\partial^2 g_s}{\partial T\partial n_k} f + \frac{\partial g_s}{\partial T}\frac{\partial f}{\partial n_k} + \frac{\partial g_s}{\partial n_k}\frac{\partial f}{\partial T} + g_s\frac{\partial^2 f}{\partial T\partial n_k}\right) \tag{71d}$$

$$\frac{\partial^2 s^R}{\partial P\partial n_k} = R\frac{\partial^2 g_z}{\partial P\partial n_k} + \frac{1}{\epsilon-\sigma}\left(\frac{\partial g_s}{\partial n_k}\frac{\partial f}{\partial P} + g_s\frac{\partial^2 f}{\partial P\partial n_k}\right) \tag{71e}$$

$$\frac{\partial^2 s^R}{\partial n_l\partial n_k} = R\frac{\partial^2 g_z}{\partial n_l\partial n_k} + \frac{1}{\epsilon-\sigma}\left(\frac{\partial^2 g_s}{\partial n_l\partial n_k} f + \frac{\partial g_s}{\partial n_k}\frac{\partial f}{\partial n_l} + \frac{\partial g_s}{\partial n_l}\frac{\partial f}{\partial n_k} + g_s\frac{\partial^2 f}{\partial n_l\partial n_k}\right) \tag{71f}$$

5.3. Fugacity coefficients

In this report we also present an explicit expression for the logarithmic fugacity coefficients $\{\ln\phi_i\}_{i=1}^{N_C}$ derived from the residual properties (66). The expression for the fugacity coefficients is obtained using the auxiliary functions $f = f(Z,B)$, $g_z = g_z(Z,B)$ and $g_{\phi,i} = g_{\phi,i}(T,n)$

$$\ln\phi_i = (Z-1)\frac{b_i}{b_m} - g_z - \frac{1}{\epsilon-\sigma} g_{\phi,i} f \tag{72}$$

where the auxiliary function $g_{\phi,i} = g_{\phi,i}(T,n)$ is

$$g_{\phi,i} = \frac{1}{RTb_m}\left(2\sum_{j=1}^{N_C} z_j a_{ij} - a_m\frac{b_i}{b_m}\right) \tag{73}$$

The first order derivatives are

$$\frac{\partial\ln\phi_i}{\partial T} = \frac{\partial Z}{\partial T}\frac{b_i}{b_m} - \frac{\partial g_z}{\partial T} - \frac{1}{\epsilon-\sigma}\left(\frac{\partial g_{\phi,i}}{\partial T} f + g_{\phi,i}\frac{\partial f}{\partial T}\right) \tag{74a}$$

$$\frac{\partial\ln\phi_i}{\partial P} = \frac{\partial Z}{\partial P}\frac{b_i}{b_m} - \frac{\partial g_z}{\partial P} - \frac{1}{\epsilon-\sigma} g_{\phi,i}\frac{\partial f}{\partial P} \tag{74b}$$

$$\frac{\partial\ln\phi_i}{\partial n_k} = \frac{\partial Z}{\partial n_k}\frac{b_i}{b_m} - (Z-1)\frac{b_i}{b_m^2}\frac{\partial b_m}{\partial n_k} - \frac{\partial g_z}{\partial n_k} - \frac{1}{(\epsilon-\sigma)}\left(\frac{\partial g_{\phi,i}}{\partial n_k} f + g_{\phi,i}\frac{df}{dn_k}\right) \tag{74c}$$

The second order derivatives are

$$\frac{\partial^2 \ln \phi_i}{\partial T^2} = \frac{\partial^2 Z}{\partial T^2}\frac{b_i}{b_m} - \frac{\partial^2 g_z}{\partial T^2} - \frac{1}{\epsilon - \sigma}\left(\frac{\partial^2 g_{\phi,i}}{\partial T^2} f + 2\frac{\partial g_{\phi,i}}{\partial T}\frac{\partial f}{\partial T} + g_{\phi,i}\frac{\partial^2 f}{\partial T^2}\right) \tag{75a}$$

$$\frac{\partial^2 \ln \phi_i}{\partial P^2} = \frac{\partial^2 Z}{\partial P^2}\frac{b_i}{b_m} - \frac{\partial^2 g_z}{\partial P^2} - \frac{1}{\epsilon - \sigma} g_{\phi,i}\frac{\partial^2 f}{\partial P^2} \tag{75b}$$

$$\frac{\partial^2 \ln \phi_i}{\partial T \partial P} = \frac{\partial^2 Z}{\partial T \partial P}\frac{b_i}{b_m} - \frac{\partial^2 g_z}{\partial T \partial P} - \frac{1}{\epsilon - \sigma}\left(\frac{\partial g_{\phi,i}}{\partial T}\frac{\partial f}{\partial P} + g_{\phi,i}\frac{\partial^2 f}{\partial T \partial P}\right) \tag{75c}$$

$$\begin{aligned}\frac{\partial^2 \ln \phi_i}{\partial T \partial n_k} = {} & \frac{\partial^2 Z}{\partial T \partial n_k}\frac{b_i}{b_m} - \frac{\partial Z}{\partial T}\frac{b_i}{b_m^2}\frac{\partial b_m}{\partial n_k} - \frac{\partial^2 g_z}{\partial T \partial n_k} \\ & - \frac{1}{(\epsilon - \sigma)}\left(\frac{\partial^2 g_{\phi,i}}{\partial T \partial n_k} f + \frac{\partial g_{\phi,i}}{\partial T}\frac{df}{dn_k} + \frac{\partial g_{\phi,i}}{\partial n_k}\frac{df}{dT} + g_{\phi,i}\frac{\partial^2 f}{\partial T \partial n_k}\right)\end{aligned} \tag{75d}$$

$$\begin{aligned}\frac{\partial^2 \ln \phi_i}{\partial P \partial n_k} = {} & \frac{\partial^2 Z}{\partial P \partial n_k}\frac{b_i}{b_m} - \frac{\partial Z}{\partial P}\frac{b_i}{b_m^2}\frac{\partial b_m}{\partial n_k} - \frac{\partial^2 g_z}{\partial P \partial n_k} \\ & - \frac{1}{(\epsilon - \sigma)}\left(\frac{\partial g_{\phi,i}}{\partial n_k}\frac{df}{dP} + g_{\phi,i}\frac{\partial^2 f}{\partial P \partial n_k}\right)\end{aligned} \tag{75e}$$

$$\begin{aligned}\frac{\partial^2 \ln \phi_i}{\partial n_l \partial n_k} = {} & \frac{\partial^2 Z}{\partial n_l \partial n_k}\frac{b_i}{b_m} - \left(\frac{\partial Z}{\partial n_k}\frac{\partial b_m}{\partial n_l} + \frac{\partial Z}{\partial n_l}\frac{\partial Z}{\partial n_k}\right)\frac{b_i}{b_m^2} + (Z-1)\frac{b_i}{b_m^2}\left(\frac{2}{b_m}\frac{\partial b_m}{\partial n_k}\frac{\partial b_m}{\partial n_l} - \frac{\partial^2 b_m}{\partial n_l \partial n_k}\right) \\ & - \frac{\partial^2 g_z}{\partial n_l \partial n_k} - \frac{1}{(\epsilon - \sigma)}\left(\frac{\partial^2 g_{\phi,i}}{\partial n_l \partial n_k} f + \frac{\partial g_{\phi,i}}{\partial n_k}\frac{df}{dn_l} + \frac{\partial g_{\phi,i}}{\partial n_l}\frac{df}{dn_k} + g_{\phi,i}\frac{\partial^2 f}{\partial n_l \partial n_k}\right)\end{aligned} \tag{75f}$$

5.4. Auxiliary functions

Note on nomenclature: *In order to keep the derivative information brief we introduce the auxiliary variables w_1 and w_2. Each of these variables are a placeholder for either temperature, T, pressure, P, or a mole number, n_k. We will use these auxiliary variables in cases where the structure of the derivative equations do not depend on the type of variable.*

The first order derivatives of $f = f(Z, B)$ with respect to temperature, pressure and mole numbers are expressed through the derivatives with respect to the compressibility factor $Z = Z(T, P, n)$ and $B = B(T, P, n)$

$$\frac{\partial f}{\partial w_1} = \frac{\partial f}{\partial Z}\frac{\partial Z}{\partial w_1} + \frac{\partial f}{\partial B}\frac{\partial B}{\partial w_1}, \quad w_1 \in \{T, P, n_k\} \tag{76}$$

The second order temperature, pressure and composition derivatives are

$$\begin{aligned}\frac{\partial^2 f}{\partial {w_1}^2} = {} & \frac{\partial^2 f}{\partial Z^2}\left(\frac{\partial Z}{\partial w_1}\right)^2 + \frac{\partial f}{\partial Z}\frac{\partial^2 Z}{\partial {w_1}^2} + 2\frac{\partial^2 f}{\partial Z \partial B}\frac{\partial Z}{\partial w_1}\frac{\partial B}{\partial w_1} \\ & + \frac{\partial^2 f}{\partial B^2}\left(\frac{\partial B}{\partial w_1}\right)^2 + \frac{\partial f}{\partial B}\frac{\partial^2 B}{\partial {w_1}^2}\end{aligned} \tag{77a}$$

$$\begin{aligned}\frac{\partial^2 f}{\partial w_1 \partial w_2} = {} & \frac{\partial^2 f}{\partial Z^2}\frac{\partial Z}{\partial w_1}\frac{\partial Z}{\partial w_2} + \frac{\partial^2 f}{\partial B^2}\frac{\partial B}{\partial T}\frac{\partial B}{\partial w_2} + \frac{\partial f}{\partial Z}\frac{\partial^2 Z}{\partial w_1 \partial w_2} \\ & + \frac{\partial f}{\partial B}\frac{\partial^2 B}{\partial w_1 \partial w_2} + \frac{\partial^2 f}{\partial Z \partial B}\left(\frac{\partial Z}{\partial w_1}\frac{\partial B}{\partial w_2} + \frac{\partial Z}{\partial w_2}\frac{\partial B}{\partial w_1}\right)\end{aligned} \tag{77b}$$

where $w_1 \in \{T, P, n_k\}$ and $w_2 \in \{T, P, n_l\}$. **Note:** w_1 and w_2 can represent *different* mole numbers, n_k and n_l, respectively. The first order derivatives of $f = f(Z, B)$ with respect to the compressibility factor Z and B are

$$\frac{\partial f}{\partial Z} = \frac{1}{Z + \epsilon B} - \frac{1}{Z + \sigma B} \tag{78a}$$

$$\frac{\partial f}{\partial B} = \frac{\epsilon}{Z + \epsilon B} - \frac{\sigma}{Z + \sigma B} \tag{78b}$$

The second order derivatives are

$$\frac{\partial^2 f}{\partial Z^2} = -\frac{1}{(Z + \epsilon B)^2} + \frac{1}{(Z + \sigma B)^2} \tag{79a}$$

$$\frac{\partial^2 f}{\partial B^2} = -\left(\frac{\epsilon}{Z + \epsilon B}\right)^2 + \left(\frac{\sigma}{Z + \sigma B}\right)^2 \tag{79b}$$

$$\frac{\partial^2 f}{\partial Z \partial B} = -\frac{\epsilon}{(Z + \epsilon B)^2} + \frac{\sigma}{(Z + \sigma B)^2} \tag{79c}$$

The first order derivatives of $g_h = g_h(T, n)$ are

$$\frac{\partial g_h}{\partial T} = T \frac{\partial g_s}{\partial T} \tag{80a}$$

$$\frac{\partial g_h}{\partial n_k} = T \frac{\partial g_s}{\partial n_k} - \frac{1}{b_m}\left(\frac{\partial a_m}{\partial n_k} - \frac{a_m}{b_m}\frac{\partial b_m}{\partial n_k}\right) \tag{80b}$$

The second order derivatives are

$$\frac{\partial^2 g_h}{\partial T^2} = \frac{\partial g_s}{\partial T} + T \frac{\partial^2 g_s}{\partial T^2} \tag{81a}$$

$$\frac{\partial^2 g_h}{\partial T \partial n_k} = T \frac{\partial^2 g_s}{\partial T \partial n_k} \tag{81b}$$

$$\begin{aligned} \frac{\partial^2 g_h}{\partial n_l \partial n_k} = {} & T \frac{\partial^2 g_s}{\partial n_l \partial n_k} - \frac{1}{b_m}\frac{\partial^2 a_m}{\partial n_l \partial n_k} \\ & + \frac{1}{b_m^2}\left(\frac{\partial a_m}{\partial n_l}\frac{\partial b_m}{\partial n_k} + \frac{\partial a_m}{\partial n_k}\frac{\partial b_m}{\partial n_l} + a_m\left(\frac{-2}{b_m}\frac{\partial b_m}{\partial n_l}\frac{\partial b_m}{\partial n_k} + \frac{\partial^2 b_m}{\partial n_l \partial n_k}\right)\right) \end{aligned} \tag{81c}$$

The first order derivatives of $g_s = g_s(T, n)$ are

$$\frac{\partial g_s}{\partial T} = \frac{1}{b_m}\frac{\partial^2 a_m}{\partial T^2} \tag{82a}$$

$$\frac{\partial g_s}{\partial n_k} = \frac{1}{b_m}\frac{\partial^2 a_m}{\partial T \partial n_k} - \frac{1}{b_m^2}\frac{\partial b_m}{\partial n_k}\frac{\partial a_m}{\partial T} \tag{82b}$$

The second order derivatives are

$$\frac{\partial^2 g_s}{\partial T^2} = \frac{1}{b_m}\frac{\partial^3 a_m}{\partial T^3} \tag{83a}$$

$$\frac{\partial^2 g_s}{\partial T \partial n_k} = \frac{1}{b_m}\frac{\partial^3 a_m}{\partial T^2 \partial n_k} - \frac{1}{b_m^2}\frac{\partial b_m}{\partial n_k}\frac{\partial^2 a_m}{\partial T^2} \tag{83b}$$

$$\begin{aligned}\frac{\partial^2 g_s}{\partial n_l \partial n_k} = \frac{1}{b_m^2}\Bigg[&\left(\frac{2}{b_m}\frac{\partial b_m}{\partial n_l}\frac{\partial b_m}{\partial n_k} - \frac{\partial^2 b_m}{\partial n_l \partial n_k}\right)\frac{\partial a_m}{\partial T} \\ &- \frac{\partial b_m}{\partial n_k}\frac{\partial^2 a_m}{\partial T \partial n_l} - \frac{\partial b_m}{\partial n_l}\frac{\partial^2 a_m}{\partial T \partial n_k} + b_m \frac{\partial^3 a_m}{\partial T \partial n_m \partial n_k}\Bigg]\end{aligned} \tag{83c}$$

The first order derivatives of $g_z = g_z(Z, B)$ with respect to temperature, pressure and mole numbers are expressed through the derivative with respect to the compressibility factor $Z = Z(T, P, n)$ and $B = B(T, P, n)$

$$\frac{\partial g_z}{\partial w_1} = \frac{\partial g_z}{\partial Z}\frac{\partial Z}{\partial w_1} + \frac{\partial g_z}{\partial B}\frac{\partial B}{\partial w_1}, \quad w_1 \in \{T, P, n_k\} \tag{84}$$

The second order temperature, pressure and composition derivatives are

$$\begin{aligned}\frac{\partial^2 g_z}{\partial {w_1}^2} = &\frac{\partial^2 g_z}{\partial Z^2}\left(\frac{\partial Z}{\partial w_1}\right)^2 + \frac{\partial g_z}{\partial Z}\frac{\partial^2 Z}{\partial {w_1}^2} + 2\frac{\partial^2 g_z}{\partial Z \partial B}\frac{\partial Z}{\partial w_1}\frac{\partial B}{\partial w_1} \\ &+ \frac{\partial^2 g_z}{\partial B^2}\left(\frac{\partial B}{\partial w_1}\right)^2 + \frac{\partial g_z}{\partial B}\frac{\partial^2 B}{\partial {w_1}^2}\end{aligned} \tag{85a}$$

$$\begin{aligned}\frac{\partial^2 g_z}{\partial w_1 \partial w_2} = &\frac{\partial^2 g_z}{\partial Z^2}\frac{\partial Z}{\partial w_1}\frac{\partial Z}{\partial w_2} + \frac{\partial^2 g_z}{\partial B^2}\frac{\partial B}{\partial T}\frac{\partial B}{\partial w_2} + \frac{\partial g_z}{\partial Z}\frac{\partial^2 Z}{\partial w_1 \partial w_2} \\ &+ \frac{\partial g_z}{\partial B}\frac{\partial^2 B}{\partial w_1 \partial w_2} + \frac{\partial^2 g_z}{\partial Z \partial B}\left(\frac{\partial Z}{\partial w_1}\frac{\partial B}{\partial w_2} + \frac{\partial Z}{\partial w_2}\frac{\partial B}{\partial w_1}\right)\end{aligned} \tag{85b}$$

where $w_1 \in \{T, P, n_k\}$ and $w_2 \in \{T, P, n_l\}$. **Note:** these derivative equations are structurally identical to the derivatives of f (76)-(77). The first order derivatives of $g_z = g_z(Z, B)$ with respect to the compressibility factor Z and B are

$$\frac{\partial g_z}{\partial Z} = \frac{1}{Z - B} \tag{86a}$$

$$\frac{\partial g_z}{\partial B} = -\frac{1}{Z - B} \tag{86b}$$

The second order derivatives are

$$\frac{\partial^2 g_z}{\partial Z^2} = -\frac{1}{(Z - B)^2} \tag{87a}$$

$$\frac{\partial^2 g_z}{\partial Z^2} = \frac{1}{(Z - B)^2} \tag{87b}$$

$$\frac{\partial^2 g_z}{\partial Z \partial B} = \frac{1}{(Z - B)^2} \tag{87c}$$

The first order derivatives of the auxiliary function $g_{\phi,i} = g_{\phi,i}(T, n)$ are

$$\frac{\partial g_{\phi,i}}{\partial T} = \frac{1}{T}\left(\frac{1}{Rb_m}\left(2\sum_{j=1}^{N_C} z_j \frac{\partial a_{ij}}{\partial T} - \frac{\partial a_m}{\partial T}\frac{b_i}{b_m}\right) - g_{\phi,i}\right) \tag{88a}$$

$$\frac{\partial g_{\phi,i}}{\partial n_k} = \frac{1}{b_m}\left[\left(\frac{2}{N}\left(a_{ik} - \sum_{j=1}^{N_C} x_j a_{ij}\right) - \frac{b_i}{b_m}\left(\frac{\partial a_m}{\partial n_k} - \frac{1}{b_m}\frac{\partial b_m}{\partial n_k}\right)\right) - \frac{\partial b_m}{\partial n_k} g_{\phi,i} + \frac{1}{RT}\right] \tag{88b}$$

The second order derivatives are

$$\frac{\partial^2 g_{\phi,i}}{\partial T^2} = \frac{1}{T}\left(\frac{1}{Rb_m}\left(2\sum_{j=1}^{N_C} z_j \frac{\partial^2 a_{ij}}{\partial T^2} - \frac{\partial^2 a_m}{\partial T^2}\frac{b_i}{b_m}\right) - 2\frac{\partial g_{\phi,i}}{\partial T}\right) \tag{89a}$$

$$\begin{aligned}\frac{\partial^2 g_{\phi,i}}{\partial T \partial n_k} = &-\frac{1}{T}\left(\frac{\partial g_{\phi,i}}{\partial n_k} + \frac{1}{b_m}\frac{\partial b_m}{\partial n_k} g_{\phi,i}\right) \\ &+ \frac{1}{b_m}\left[-\frac{\partial b_m}{\partial n_k}\frac{\partial g_{\phi,i}}{\partial T} + \frac{1}{RT}\left(\frac{2}{N}\left(\frac{\partial a_{ik}}{\partial T} - \sum_{j=1}^{N_C} x_j \frac{\partial a_{ij}}{\partial T}\right) - \frac{1}{b_m}\left(\frac{\partial^2 a_m}{\partial T \partial n_k} - \frac{1}{b_m}\frac{\partial b_m}{\partial n_k}\right) b_i\right)\right],\end{aligned} \tag{89b}$$

$$\begin{aligned}\frac{\partial^2 g_{\phi,i}}{\partial n_l \partial n_k} = &-\frac{1}{b_m}\left(\frac{\partial g_{\phi,i}}{\partial n_l}\frac{\partial b_m}{\partial n_k} + \frac{\partial b_m}{\partial n_l}\frac{\partial g_{\phi,i}}{\partial n_k} + \frac{\partial^2 b_m}{\partial n_l \partial n_k}\right) + \frac{1}{RT}\frac{1}{b_m}\left[\frac{2}{N^2}\left(2\sum_{j=1}^{N_C} x_j a_{ij} - a_{il} - a_{ik}\right)\right. \\ &\left. - \frac{1}{b_m}\left\{\frac{\partial^2 a_m}{\partial n_l \partial n_k} - \frac{\partial a_m}{\partial n_k}\frac{1}{b_m}\frac{\partial b_m}{\partial n_l} - \frac{1}{b_m^2}\left[\left(\frac{\partial a_m}{\partial n_l} - 2a_m\frac{1}{b_m}\frac{\partial b_m}{\partial n_l}\right)\frac{\partial b_m}{\partial n_k} + a_m\frac{\partial^2 b_m}{\partial n_l \partial n_k}\right]\right\} b_i\right]\end{aligned} \tag{89c}$$

5.5. Compressibility factor

The compressibility factor is implicitly defined by the cubic equation (63) for a given temperature pressure and composition. The first order derivatives of the compressibility factor $Z = Z(T, P, n)$ are given in terms of the derivatives of the polynomium $q = q(Z)$ given in (63)-(64).

$$\frac{\partial Z}{\partial w_1} = -\left(\frac{\partial q}{\partial Z}\right)^{-1}\frac{\partial q}{\partial w_1}, \quad w_1 \in \{T, P, n_k\} \tag{90a}$$

The second order derivatives are

$$\frac{\partial^2 Z}{\partial {w_1}^2} = -\left(\frac{\partial q}{\partial Z}\right)^{-1}\left(\frac{\partial^2 q}{\partial {w_1}^2} + \frac{\partial^2 q}{\partial Z^2}\left(\frac{\partial Z}{\partial w_1}\right)^2 + 2\frac{\partial^2 q}{\partial w_1 \partial Z}\frac{\partial Z}{\partial w_1}\right) \tag{91a}$$

$$\frac{\partial^2 Z}{\partial w_1 \partial w_2} = -\left(\frac{\partial q}{\partial Z}\right)^{-1}\left(\frac{\partial^2 q}{\partial w_1 \partial w_2} + \frac{\partial^2 q}{\partial Z^2}\frac{\partial Z}{\partial w_1}\frac{\partial Z}{\partial w_2} + \frac{\partial^2 q}{\partial w_1 \partial Z}\frac{\partial Z}{\partial w_2} + \frac{\partial^2 q}{\partial w_2 \partial Z}\frac{\partial Z}{\partial w_1}\right) \tag{91b}$$

where $w_1 \in \{T, P, n_k\}$ and $w_2 \in \{T, P, n_l\}$. The first order derivatives of the cubic polynomium $q = q(Z)$ are expressed through the derivatives of the polynomial coefficients $\{d_m = d_m(A, B)\}_{m=0}^2$

$$\frac{\partial q}{\partial Z} = 3Z^2 + \sum_{m=1}^{2} m d_m Z^{m-1} \tag{92a}$$

$$\frac{\partial q}{\partial w_1} = \sum_{m=0}^{2}\frac{\partial d_m}{\partial w_1} Z^m, \quad w_1 \in \{T, P, n_k\} \tag{92b}$$

The second order derivatives are

$$\frac{\partial^2 q}{\partial Z^2} = 6Z + 2d_2 \tag{93a}$$

$$\frac{\partial^2 q}{\partial Z \partial w_1} = \sum_{m=1}^{2} m \frac{\partial d_m}{\partial w_1} Z^{m-1} \tag{93b}$$

$$\frac{\partial^2 q}{\partial {w_1}^2} = \sum_{m=0}^{2} \frac{\partial^2 d_m}{\partial {w_1}^2} Z^m \tag{93c}$$

$$\frac{\partial^2 q}{\partial w_1 \partial w_2} = \sum_{m=0}^{2} \frac{\partial^2 d_m}{\partial w_1 \partial w_2} Z^m \tag{93d}$$

where $w_1 \in \{T, P, n_k\}$ and $w_2 \in \{T, P, n_l\}$.

5.6. Polynomial coefficients

The temperature, pressure and composition derivatives of the polynomial coefficients are expressed through the derivatives with respect to $A = A(T, P, n)$ and $B = B(T, P, n)$. The first order derivatives of $\{d_m = d_m(A, B)\}_{k=0}^{2}$ are

$$\frac{\partial d_m}{\partial w_1} = \frac{\partial d_m}{\partial A}\frac{\partial A}{\partial w_1} + \frac{\partial d_m}{\partial B}\frac{\partial B}{\partial w_1}, \quad w_1 \in \{T, P, n_k\} \tag{94}$$

The second order derivatives are

$$\begin{aligned} \frac{\partial^2 d_m}{\partial {w_1}^2} = {} & \frac{\partial^2 d_m}{\partial A^2}\left(\frac{\partial A}{\partial w_1}\right)^2 + \frac{\partial d_m}{\partial A}\frac{\partial^2 A}{\partial {w_1}^2} + 2\frac{\partial^2 d_m}{\partial A \partial B}\frac{\partial A}{\partial w_1}\frac{\partial B}{\partial w_1} \\ & + \frac{\partial^2 d_m}{\partial B^2}\left(\frac{\partial B}{\partial w_1}\right)^2 + \frac{\partial d_m}{\partial B}\frac{\partial^2 B}{\partial {w_1}^2} \end{aligned} \tag{95a}$$

$$\begin{aligned} \frac{\partial^2 d_m}{\partial w_1 \partial w_2} = {} & \frac{\partial^2 d_m}{\partial A^2}\frac{\partial A}{\partial w_1}\frac{\partial A}{\partial w_2} + \frac{\partial^2 d_m}{\partial B^2}\frac{\partial B}{\partial w_1}\frac{\partial B}{\partial w_2} + \frac{\partial d_m}{\partial A}\frac{\partial^2 A}{\partial w_1 \partial w_2} \\ & + \frac{\partial d_m}{\partial B}\frac{\partial^2 B}{\partial w_1 \partial w_2} + \frac{\partial^2 d_m}{\partial A \partial B}\left(\frac{\partial A}{\partial w_1}\frac{\partial B}{\partial w_2} + \frac{\partial A}{\partial w_2}\frac{\partial B}{\partial w_1}\right) \end{aligned} \tag{95b}$$

where $w_1 \in \{T, P, n_k\}$ and $w_2 \in \{T, P, n_l\}$. **Note**: w_1 and w_2 can represent *different* mole numbers, n_k and n_l, respectively. The first order derivatives of the polynomial coefficient $d_2 = d_2(A, B)$ with respect to A and B are

$$\frac{\partial d_2}{\partial A} = 0 \tag{96a}$$

$$\frac{\partial d_2}{\partial B} = (\epsilon + \sigma - 1) \tag{96b}$$

The second order derivatives are

$$\frac{\partial^2 d_2}{\partial A^2} = 0 \tag{97a}$$

$$\frac{\partial^2 d_2}{\partial B^2} = 0 \tag{97b}$$

$$\frac{\partial^2 d_2}{\partial A \partial B} = 0 \tag{97c}$$

The first order derivatives of $d_1 = d_1(A, B)$ are

$$\frac{\partial d_1}{\partial A} = 1 \tag{98a}$$

$$\frac{\partial d_1}{\partial B} = -(\epsilon + \sigma) + 2(\epsilon\sigma - \epsilon - \sigma)B \tag{98b}$$

The second order derivatives are

$$\frac{\partial^2 d_1}{\partial A^2} = 0 \tag{99a}$$

$$\frac{\partial^2 d_1}{\partial B^2} = 2(\epsilon\sigma - \epsilon - \sigma) \tag{99b}$$

$$\frac{\partial^2 d_1}{\partial A \partial B} = 0 \tag{99c}$$

The first order derivatives of $d_0 = d_0(A, B)$ are

$$\frac{\partial d_0}{\partial A} = -B \tag{100a}$$

$$\frac{\partial d_0}{\partial B} = -\left(A + \epsilon\sigma(2B + 3B^2)\right) \tag{100b}$$

The second order derivatives are

$$\frac{\partial^2 d_0}{\partial A^2} = 0 \tag{101a}$$

$$\frac{\partial^2 d_0}{\partial B^2} = -\epsilon\sigma(2 + 6B) \tag{101b}$$

$$\frac{\partial^2 d_0}{\partial A \partial B} = -1 \tag{101c}$$

5.7. The quantities A and B

The first order derivatives of $A = A(T, P, n)$ are given in terms of the derivatives of the mixing parameter $a_m = a_m(T, n)$

$$\frac{\partial A}{\partial T} = \frac{\partial a_m}{\partial T}\frac{P}{R^2T^2} - \frac{2}{T}A \tag{102a}$$

$$\frac{\partial A}{\partial P} = \frac{a_m}{R^2T^2} \tag{102b}$$

$$\frac{\partial A}{\partial n_k} = \frac{\partial a_m}{\partial n_k}\frac{P}{R^2T^2} \tag{102c}$$

The second order derivatives are

$$\frac{\partial^2 A}{\partial T^2} = \frac{P}{R^2T^2}\left(\frac{\partial^2 a_m}{\partial T^2} - \frac{1}{T}\frac{\partial a_m}{\partial T}\right) - \frac{3}{T}\frac{\partial A}{\partial T} \tag{103a}$$

$$\frac{\partial^2 A}{\partial P^2} = 0 \tag{103b}$$

$$\frac{\partial^2 A}{\partial T \partial P} = \frac{\partial a_m}{\partial T}\frac{1}{R^2T^2} - \frac{2}{T}\frac{\partial A}{\partial P} \tag{103c}$$

$$\frac{\partial^2 A}{\partial T \partial n_k} = \frac{\partial^2 a_m}{\partial T \partial n_k}\frac{P}{R^2T^2} - \frac{2}{T}\frac{\partial A}{\partial n_k} \tag{103d}$$

$$\frac{\partial^2 A}{\partial P \partial n_k} = \frac{\partial a_m}{\partial n_k}\frac{1}{R^2T^2} \tag{103e}$$

$$\frac{\partial^2 A}{\partial n_l \partial n_k} = \frac{\partial^2 a_m}{\partial n_l \partial n_k}\frac{P}{R^2T^2} \tag{103f}$$

The first order derivatives of $B = B(T, P, n)$ are given in terms of the derivatives of the mixing parameter $b_m = b_m(n)$

$$\frac{\partial B}{\partial T} = -\frac{b_m P}{RT^2} \tag{104a}$$

$$\frac{\partial B}{\partial P} = \frac{b_m}{RT} \tag{104b}$$

$$\frac{\partial B}{\partial n_k} = \frac{\partial b_m}{\partial n_k}\frac{P}{RT} \tag{104c}$$

The second order derivatives are

$$\frac{\partial^2 B}{\partial T^2} = 2\frac{b_m P}{RT^3} \tag{105a}$$

$$\frac{\partial^2 B}{\partial P^2} = 0 \tag{105b}$$

$$\frac{\partial^2 B}{\partial T \partial P} = -\frac{b_m}{RT^2} \tag{105c}$$

$$\frac{\partial^2 B}{\partial T \partial n_k} = -\frac{\partial b_m}{\partial n_k}\frac{P}{RT^2} \tag{105d}$$

$$\frac{\partial^2 B}{\partial P \partial n_k} = \frac{\partial b_m}{\partial n_k}\frac{1}{RT} \tag{105e}$$

$$\frac{\partial^2 B}{\partial n_l \partial n_k} = \frac{\partial^2 b_m}{\partial n_l \partial n_k}\frac{P}{RT} \tag{105f}$$

5.8. Mixing parameters

The derivatives of the mixing parameters $a_m = a_m(T, n)$ exploit the symmetry of $a_{ij} = a_{ij}(T) = a_{ji}(T)$. The first order derivatives are

$$\frac{\partial a_m}{\partial T} = \sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i z_j \frac{\partial a_{ij}}{\partial T} \tag{106a}$$

$$\frac{\partial a_m}{\partial n_k} = \frac{2}{N}\left(\sum_{i=1}^{N_C} z_i a_{ik} - a_m\right) \tag{106b}$$

The second order derivatives are

$$\frac{\partial^2 a_m}{\partial T^2} = \sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i z_j \frac{\partial^2 a_{ij}}{\partial T^2} \tag{107a}$$

$$\frac{\partial^2 a_m}{\partial T \partial n_k} = \frac{2}{N}\left(\sum_{i=1}^{N_C} z_i \frac{\partial a_{ik}}{\partial T} - \frac{\partial a_m}{\partial T}\right) \tag{107b}$$

$$\frac{\partial^2 a_m}{\partial n_l \partial n_k} = \frac{1}{N}\left(a_{kl} + a_m - \frac{\partial a_m}{\partial n_k} - \frac{\partial a_m}{\partial n_k}\right) \tag{107c}$$

The relevant third order derivatives are

$$\frac{\partial^3 a_m}{\partial T^3} = \sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i z_j \frac{\partial^3 a_{ij}}{\partial T^3} \tag{108a}$$

$$\frac{\partial^3 a_m}{\partial T^2 \partial n_k} = \frac{2}{N}\left(\sum_{i=1}^{N_C} z_i \frac{\partial^2 a_{ik}}{\partial T^2} - \frac{\partial^2 a_m}{\partial T^2}\right) \tag{108b}$$

$$\frac{\partial^3 a_m}{\partial T \partial n_l \partial n_k} = \frac{1}{N}\left(\frac{\partial a_{kl}}{\partial T} + \frac{\partial a_m}{\partial T} - \frac{\partial^2 a_m}{\partial T \partial n_k} - \frac{\partial^2 a_m}{\partial T \partial n_k}\right) \tag{108c}$$

The derivatives of the mixing parameter $b_m = b_m(n)$ are

$$\frac{\partial b_m}{\partial n_k} = \frac{b_k - b_m}{N} \tag{109a}$$

$$\frac{\partial^2 b_m}{\partial n_l \partial n_k} = \frac{2b_m - b_l - b_k}{N^2} \tag{109b}$$

The derivatives of $a_{ij} = a_{ij}(T)$ are given in terms of the derivatives of the auxiliary function $\hat{a}_{ij} = \hat{a}_{ij}(T)$

$$\frac{\partial a_{ij}}{\partial T} = \frac{1 - k_{ij}}{2\sqrt{\hat{a}_{ij}}} \frac{\partial \hat{a}_{ij}}{\partial T} \tag{110a}$$

$$\frac{\partial^2 a_{ij}}{\partial T^2} = \frac{1}{2}\frac{1 - k_{ij}}{\sqrt{\hat{a}_{ij}}}\left(\frac{\partial^2 \hat{a}_{ij}}{\partial T^2} - \frac{1}{2\hat{a}_{ij}}\left(\frac{\partial \hat{a}_{ij}}{\partial T}\right)^2\right) \tag{110b}$$

$$\frac{\partial^3 a_{ij}}{\partial T^3} = -\frac{1 - k_{ij}}{4\sqrt{\hat{a}_{ij}}}\left(\frac{1}{\hat{a}_{ij}}\frac{\partial^2 \hat{a}_{ij}}{\partial T^2} + 2\frac{\partial^3 \hat{a}_{ij}}{\partial T^3}\right) + \frac{1}{2\hat{a}_{ij}}\left(\frac{1}{\hat{a}_{ij}}\frac{\partial \hat{a}_{ij}}{\partial T}\frac{\partial a_{ij}}{\partial T} - \frac{\partial^2 a_{ij}}{\partial T^2}\right) \tag{110c}$$

The derivatives of the auxiliary function $\hat{a}_{ij} = \hat{a}_{ij}(T)$ are given in terms of derivatives of the pure component properties $a_i = a_i(T)$

$$\frac{\partial \hat{a}_{ij}}{\partial T} = \frac{\partial a_i}{\partial T} a_j + a_i \frac{\partial a_j}{\partial T} \tag{111a}$$

$$\frac{\partial^2 \hat{a}_{ij}}{\partial T^2} = \frac{\partial^2 a_i}{\partial T^2} a_j + 2\frac{\partial a_i}{\partial T}\frac{\partial a_j}{\partial T} + a_i \frac{\partial^2 a_j}{\partial T^2} \tag{111b}$$

$$\frac{\partial^3 \hat{a}_{ij}}{\partial T^3} = \frac{\partial^3 a_i}{\partial T^3} a_j + 3\frac{\partial^2 a_i}{\partial T^2}\frac{\partial a_j}{\partial T} + 3\frac{\partial a_i}{\partial T}\frac{\partial^2 a_j}{\partial T^2} + a_i \frac{\partial^3 a_j}{\partial T^3} \tag{111c}$$

5.9. Pure component properties

The pure component parameters $a_i = a_i(T)$ are directly proportional to $\alpha = \alpha(T_{r,i}, \omega_i)$ and as such their derivatives are

$$\frac{\partial a_i}{\partial T} = \frac{\partial \alpha}{\partial T} \Psi \frac{R^2 T_{c,i}^2}{P_{c,i}} \tag{112a}$$

$$\frac{\partial^2 a_i}{\partial T^2} = \frac{\partial^2 \alpha}{\partial T^2} \Psi \frac{R^2 T_{c,i}^2}{P_{c,i}} \tag{112b}$$

$$\frac{\partial^3 a_i}{\partial T^3} = \frac{\partial^3 \alpha}{\partial T^3} \Psi \frac{R^2 T_{c,i}^2}{P_{c,i}} \tag{112c}$$

The derivatives of $\alpha = \alpha(T_{r,i}, \omega_i)$ are

$$\frac{\partial \alpha}{\partial T} = -\alpha \frac{m(\omega_i)}{\sqrt{\alpha T T_{c,i}}} \tag{113a}$$

$$\frac{\partial^2 \alpha}{\partial T^2} = -\frac{1}{2}\frac{\partial \alpha}{\partial T}\left(\frac{1}{T} - \frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right) \tag{113b}$$

$$\frac{\partial^3 \alpha}{\partial T^3} = -\frac{1}{2}\left[\frac{\partial^2 \alpha}{\partial T^2}\left(\frac{1}{T} - \frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right) + \frac{\partial \alpha}{\partial T}\left(\left(\frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right)^2 - \frac{1}{\alpha}\frac{\partial^2 \alpha}{\partial T^2} - \frac{1}{T^2}\right)\right] \tag{113c}$$

Appendix A. Solution of cubic equations

There exists a number of approaches for solving the cubic equation of state (56) for the roots when pressure and temperature are given. These approaches are either direct approaches that use explicit formula for computing the roots, iterative approaches that approximate the roots of interest or a combination of both where the direct solution is refined by an iterative approach in order to remove imprecision arising from rounding errors. In this work we use an iterative approach as described by Smith et al. (2005) and compare to Cardano's approach which is briefly described by Monroy-Loperena (2012). The equation of state (56) is rewritten in terms of the compressibility factor $Z = PV/(RT)$

$$\begin{aligned} &Z^3 - Z^2\left(1 - B(\epsilon + \sigma - 1)\right) \\ &\quad - Z\left(\epsilon + \sigma - B(\epsilon\sigma - \epsilon - \sigma) - A/B\right)B \\ &\quad - \left(A + B(1 + B)\epsilon\sigma\right)B = 0, \end{aligned} \tag{A.1}$$

where A and B are given by

$$A = \frac{a_m(T,n)P}{R^2T^2} \tag{A.2}$$

$$B = \frac{Pb_m(n)}{RT} \tag{A.3}$$

The equation of state (A.1) is written compactly

$$q(Z) = Z^3 + d_1Z^2 + d_2Z + d_3 = 0 \tag{A.4}$$

Cardano's direct approach

The number of real roots are determined by the two quantities Q and R

$$Q = (d_1^2 - 3d_2)/9 \tag{A.5}$$

$$R = (2d_1^3 - 9d_1d_2 + 27d_3)/54 \tag{A.6}$$

There are three real roots if $R^2 \leq Q^3$. In that case, the roots are found by the formula

$$Z_1 = -2\sqrt{Q}\cos(\theta/3) - d_1/3 \tag{A.7a}$$

$$Z_2 = -2\sqrt{Q}\cos((\theta + 2\pi)/3) - d_1/3 \tag{A.7b}$$

$$Z_3 = -2\sqrt{Q}\cos((\theta - 2\pi)/3) - d_1/3 \tag{A.7c}$$

where θ is computed by

$$\theta = \arccos(R/\sqrt{Q^3}) \tag{A.8}$$

If $R^2 > Q^3$, there is one real root and two complex conjugate roots that are given by

$$Z_1 = (S + T) - d_1/3 \tag{A.9a}$$

$$Z_2 = -1/2(S + T) - d_1/3 + i\sqrt{3}/2(S - T) \tag{A.9b}$$

$$Z_3 = -1/2(S + T) - d_1/3 - i\sqrt{3}/2(S - T) \tag{A.9c}$$

where

$$S = -\text{sgn}(R)\left(|R| + \sqrt{R^2 - Q^3}\right)^{1/3} \tag{A.10}$$

$$T = \begin{cases} Q/S & (S \neq 0) \\ 0 & (S = 0) \end{cases} \tag{A.11}$$

In the case of multiple roots, the smallest represents the liquid phase compressibility factor, $Z^l = \min\{Z_1, Z_2, Z_3\}$, and the largest is vapor phase compressibility factor, $Z^v = \max\{Z_1, Z_2, Z_3\}$.

An iterative Newton approach

The approach described here uses Newton iterations to solve the cubic equation (A.1). It is possible to use higher-order methods as discussed by Olivera-Fuentes (1993), due to the cubic nature of the equation. In the Newton approach, an initial guess, Z_0, is iteratively improved by

$$Z_{k+1} = Z_k - q(Z_k)/q'(Z_k) \tag{A.12}$$

$$q'(Z_k) = 3Z_k^2 + 2d_1Z_k + d_2 \tag{A.13}$$

The iterative sequence is terminated when both of the following criteria are satisfied

$$|Z_{k+1} - Z_k| < \epsilon \tag{A.14}$$

$$|Z_{k+1}^3 + d_1 z_{k+1}^2 + d_2 Z_{k+1} + d_3| < \epsilon \tag{A.15}$$

Once the sequence is terminated, a single root has been found. The following initial estimates are used, depending on whether the compressibility factor of the vapor phase, Z^v, or of the liquid phase, Z^l, is sought

$$Z_0^v = 1 \tag{A.16}$$

$$Z_0^l = B \tag{A.17}$$

References

Monroy-Loperena, R., 2012. A note on the analytical solution of cubic equations of state in process simulation. Industrial & Engineering Chemistry Research 51, 6972–6976.

Olivera-Fuentes, C., 1993. The optimal solution of cubic equations of state. Latin American Applied Research 23, 243–256.

Smith, J.M., Van Ness, H.C., Abbott, M.M., 2005. Introduction to Chemical Engineering Thermodynamics. 7th ed., McGraw-Hill, New York, NY.

Thomson, G., 1996. The DIPPR® databases. International Journal of Thermophysics 17, 223–232.