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Memo

Wong-Sandler equation of state

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1 Introduction

Derivation of the Wong-Sandler first and second differentials needed for thermopack implementation[5]. The appendix of the Wong-Sandler paper contain parameter definitions and first order differentials with respect to mole numbers for the Peng-Robinson equation of state.

2 Infinite pressure limit of the equations of state

To determine the C parameter of equation A3 and A4, the pressure limit of the equation of state must be found.

$$P = \frac{nRT}{V-B} - \frac{A}{(V-B(T)m_1)(V-B(T)m_2)} \tag{1}$$

The residual Helmholtz function, F, becomes

$$F(T,V,\boldsymbol{n}) = n\left[\ln\left(\frac{V}{V-B}\right) - \frac{A}{(m_1-m_2)BRT}\ln\left(\frac{V-m_2B}{V-m_1B}\right)\right]. \tag{2}$$

In order to find the pressure limit, we use that,

$$F(T,P,\boldsymbol{n}) = F(T,V,\boldsymbol{n}) - \ln(Z), \tag{3}$$

Table 1: Different equations of state

Year:	Name:	Functional form:
1873	Van der Waals	$P = \frac{RT}{v-b} - \frac{a}{v^2}$
1949	Redlich Kwong	$P = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)}$
1972	Soave Redlich Kwong	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)}$
1976	Peng Robinson	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+b(v-b)}$
1980	Schmidt-Wensel	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v^2+(1+3c)bv-3cb^2}$
1982	Patel Teja	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+c(v-b)}$
1987	Yu-Lu	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v(v+b)+b(3v+c)}$
1987	Trebble-Bishnoi	$P = \frac{RT}{v-b} - \frac{\alpha(T)a}{v^2+(b(T)+c)v-b(T)c-d^2}$

Table 2: Equation of state parameters

Name:	m_1	m_2
Van der Waals:	0	0
Redlich Kwong:	0	-1
Soave Redlich Kwong:	0	-1
Peng Robinson:	-1+$\sqrt{2}$	-1-$\sqrt{2}$
Schmidt-Wensel	$\frac{-1-3w+\sqrt{1+18w+9w^2}}{2}$	$\frac{-1-3w-\sqrt{1+18w+9w^2}}{2}$
Patel Teja:	$\frac{-b-c+\sqrt{b^2+2bc+c^2+4bc}}{2b}$	$\frac{-b-c-\sqrt{b^2+2bc+c^2+4bc}}{2b}$
Yu-Lu	$\frac{-c-3b+\sqrt{c^2+2bc+9b^2}}{2b}$	$\frac{-c-3b-\sqrt{c^2+2bc+9b^2}}{2b}$
Trebble-Bishnoi	$\frac{-b(T)-c+\sqrt{b(T)^2+6b(T)c+c^2+4d}}{2b(T)}$	$\frac{-b(T)-c-\sqrt{b(T)^2+6b(T)c+c^2+4d}}{2b(T)}$

where $Z = PV/(nRT)$. We then get,

$$F(T,P,\boldsymbol{n}) = n\left[-\ln\left(\frac{P\left(V-B\right)}{nRT}\right) - \frac{A}{\left(m_1-m_2\right)BRT}\ln\left(\frac{V-m_2B}{V-m_1B}\right)\right]. \tag{4}$$

From 1 we see

$$\lim_{P\to\infty}\frac{P\left(V-B\right)}{nRT} = 1 \tag{5}$$

We therefore get

$$\lim_{P\to\infty}F(T,P,\boldsymbol{n}) = \frac{nA}{BRT}\frac{1}{\left(m_1-m_2\right)}\ln\left(\frac{B-m_1B}{B-m_2B}\right) = \frac{nAC}{BRT}, \tag{6}$$

where C is given as follows,

$$C = \frac{1}{\left(m_1-m_2\right)}\ln\left(\frac{1-m_1}{1-m_2}\right). \tag{7}$$

3 The Wong-Sandler mixing rule

The Wong-Sandler mixing rule give a relation between the B and A parameter of the equation of state. In effect the B parameter become temperature dependent.

Table 3: Equation of state C-parameter

EOS	C
Van der Waals	-1
Redlich Kwong	-ln 2
Soave Redlich Kwong	-ln 2
Peng Robinson	$\frac{1}{\sqrt{2}} \ln\left(\sqrt{2}-1\right)$
Otherwise	Use Eq. 7

$$B = \frac{Q}{n - D} \tag{8}$$

$$\Updownarrow$$

$$B(n - D) = Q \tag{9}$$

$$\frac{A}{RT} = BD \tag{10}$$

$$\Updownarrow$$

$$A = BDRT \tag{11}$$

Q is defined as follows,

$$Q = \sum_i \sum_j n_i n_j \left(b - \frac{a}{RT}\right)_{ij}, \tag{12}$$

where

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i(T)}{RT}\right) + \left(b_j - \frac{a_j(T)}{RT}\right)}{2} \left(1 - k_{ij}\left(T\right)\right), \tag{13}$$

and

$$a_i(T) = \tilde{a}_i \alpha(T), \tag{14}$$

To simplify the differentials, we introduce r_i,

$$r_i = \left(b_i - \frac{a_i(T)}{RT}\right), \tag{15}$$

$$r_{i,T} = -\frac{a_{i,T}}{RT} + \frac{a_i}{RT^2}, \tag{16}$$

$$r_{i,TT} = -\frac{a_{i,TT}}{RT} + \frac{2a_{i,T}}{RT^2} - \frac{2a_i}{RT^3}. \tag{17}$$

$$\tag{18}$$

D is defined as,

$$D = \sum_i n_i \frac{a_i}{b_i RT} + \frac{A_{\infty}^{\mathrm{E}}}{CRT} \tag{19}$$

4 Partial differentials

4.1 Temperature differentials

Differentiating 9 with respect to T gives:

$$B_T(n-D) - BD_T = Q_T \tag{20}$$

$$\Updownarrow$$

$$B_T = \frac{Q_T + BD_T}{n-D} \tag{21}$$

Further differentiating 20 with respect to T gives:

$$B_{TT}(n-D) - 2B_TD_T - BD_{TT} = Q_{TT} \tag{22}$$

$$\Updownarrow$$

$$B_{TT} = \frac{Q_{TT} + 2B_TD_T + BD_{TT}}{n-D} \tag{23}$$

Differentiating 11 with respect to T gives:

$$A_T = B_TDRT + BD_TRT + BDR \tag{24}$$

$$\tag{25}$$

Further differentiating 24 with respect to T gives:

$$A_{TT} = B_{TT}DRT + 2B_TD_TRT + 2B_TDR + 2BD_TR + BD_{TT}RT \tag{26}$$

Differentiating 12, gives,

$$Q_T = \sum_i\sum_j n_in_j \left(\frac{(r_{i,T} + r_{j,T})(1-k_{ij})}{2} - \frac{r_i + r_j}{2}k_{ij,T}\right), \tag{27}$$

$$Q_{TT} = \sum_i\sum_j n_in_j \left(\frac{(r_{i,TT} + r_{j,TT})(1-k_{ij})}{2} - (r_{i,T} + r_{j,T})\, k_{ij,T}\right. \tag{28}$$

$$\left. - \frac{r_i + r_j}{2}k_{ij,TT}\right), \tag{29}$$

Differentiating 19, gives,

$$D_TRT + DR = \sum_i n_i \frac{a_{i,T}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,T}}{C}, \tag{30}$$

$$\Updownarrow$$

$$D_T = \frac{\sum_i n_i \frac{a_{i,T}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,T}}{C} - DR}{RT}. \tag{31}$$

Differentiating 30 further gives,

$$D_{TT}RT + 2D_TR = \sum_i n_i \frac{a_{i,TT}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,TT}}{C}, \tag{32}$$

$$\Updownarrow$$

$$D_{TT} = \frac{\sum_i n_i \frac{a_{i,TT}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,TT}}{C} - 2D_TR}{RT}. \tag{33}$$

4.2 Mole number differentials

Differentiating 9 with respect to n_i gives:

$$B_i(n-D) + B(1-D_i) = Q_i \tag{34}$$

$$\Updownarrow$$

$$B_i = \frac{Q_i + B(D_i - 1)}{n - D} \tag{35}$$

Further differentiating 34 with respect to n_j gives:

$$B_{ij}(n-D) + B_i(1-D_j) + B_j(1-D_i) - BD_{ij} = Q_{ij} \tag{36}$$

$$\Updownarrow$$

$$\frac{Q_{ij} + B_i(D_j - 1) + B_j(D_i - 1) + BD_{ij}}{n - D} = B_{ij} \tag{37}$$

Differentiating 11 with respect to n_i gives:

$$A_i = RT\left(B_i D + BD_i\right) \tag{38}$$

$$\tag{39}$$

Further differentiating 38 with respect to n_j gives:

$$A_{ij} = RT\left(B_{ij}D + B_i D_j + B_j D_i + BD_{ij}\right) \tag{40}$$

Differentiating 12, with respect to n_i and thereafter n_j gives,

$$Q_i = 2\sum_j n_j \left(b - \frac{a}{RT}\right)_{ij}, \tag{41}$$

$$Q_{ij} = 2\left(b - \frac{a}{RT}\right)_{ij}. \tag{42}$$

Differentiating Equation 19 with respect to n_i gives,

$$D_i RT = \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}_{\infty,i}}{C}. \tag{43}$$

Differentiating 43 further with respect to n_j gives,

$$D_{ij} RT = \frac{A^{\mathrm{E}}_{\infty,ij}}{C}. \tag{44}$$

4.3 Cross differentials

Differentiating 34 with respect to T gives:

$$B_{iT}(n-D) - B_i D_T + B_T(1-D_i) - BD_{iT} = Q_{iT} \tag{45}$$

$$\Updownarrow$$

$$\frac{Q_{iT} + B_i D_T + B_T(D_i - 1) + BD_{iT}}{n - D} = B_{iT} \tag{46}$$

Differentiating 38 with respect to T gives:

$$A_{iT} = R\left(B_{iT}DT + B_i D_T T + B_i D + B_T D_i T + BD_{iT}T + BD_i\right) \tag{47}$$

$$\tag{48}$$

Differentiating 41, with respect to T gives,

$$Q_{iT} = 2\sum_j n_j \left(\frac{(r_{i,T} + r_{j,T})(1 - k_{ij})}{2} - \frac{r_i + r_j}{2} k_{ij,T} \right). \tag{49}$$

$$\tag{50}$$

Differentiating Equation 43 with respect to T gives,

$$D_{iT} RT + D_i R = \frac{a_{i,T}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,iT}}{C}. \tag{51}$$

$$\Updownarrow$$

$$D_{iT} = \frac{\frac{a_{i,T}}{b_i} + \frac{A^{\mathrm{E}}_{\infty,iT}}{C} - D_i R}{RT}. \tag{52}$$

5 The NRTL infinite free energy model

The NRTL model [2]:

$$\frac{A^{\mathrm{E}}_{\infty}}{RT} = \sum_i n_i \left(\frac{\sum_j n_j \tau_{ji} g_{ji}}{\sum_k n_k g_{ki}} \right), \tag{53}$$

where

$$g_{ij}(T) = \exp\left(-\alpha_{ij} \tau_{ij}(T)\right). \tag{54}$$

Looking at the NRTL model it is very similar to the Huron-Vidal model (HV) [1],

$$\frac{G^{\mathrm{E}}_{\infty}}{RT} = \sum_i n_i \left(\frac{\sum_j n_j b_j \tau_{ji} g_{ji}}{\sum_k n_k b_k g_{ki}} \right). \tag{55}$$

Comparing equation 55 and equation 53, the substitution $b_j g^{\mathrm{HV}}_{ji} = g^{\mathrm{NRTL}}_{ji}$ can be made, that lets us reuse the existing HV implementation. For the combination of NRTL for some binaries and simple van der Waals mixing for other binaries, the following can be done,

$$g_{ji} = b_j, \tag{56}$$

$$\beta_{ii} = \frac{a_i}{b_i} C, \tag{57}$$

$$\beta_{ji} = -\frac{\sqrt{b_i b_j}}{b_{ij}} \sqrt{\beta_{ii} \beta_{jj}} (1 - k_{ij}), \tag{58}$$

$$\tau_{ji} = \frac{\beta_{ji} - \beta_{ii}}{RT}. \tag{59}$$

This follows from the relations for HV described in [4].

Alternatively the relations developed by [3], can be used.

5.1 Differentials

Follows the approach above, the differentials are already available from [4].

References

[1] Marie-José Huron and Jean Vidal. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria*, 3(4):255 – 271, 1979.

[2] Henri Renon and J. M. Prausnitz. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE Journal*, 14(1):135–144, 1968.

[3] Chorng H. Twu, Wayne D. Sim, and Vince Tassone. Liquid activity coefficient model for CEOS/A^E mixing rules. *Fluid Phase Equilibria*, 183-184:65–74, 2001. Proceedings of the fourteenth symposium on thermophysical properties.

[4] Ø. Wilhelmsen, G. Skaugen, and M. Hammer. Flexible thermodynamic workbench for CCS thermodynamics - Update 2013. Technical Report DA1301, SINTEF Energy, 2013.

[5] D. S. H. Wong and S. I. Sandler. A theoretically correct mixing rule for cubic equations of state. *AIChE Journal*, 38(5):671–680, 1992.