SINTEF Energy Research
Gas Technology

Address:
P.O. Box 4761 Torgarden
NO-7465 Trondheim
NORWAY

Location:
Sem Sælands vei 11
Trondheim
NORWAY

www.sintef.no/energi

Memo

Volume shift for generic EOS

AUTHOR
Morten Hammer

DATE
2021-06-15

1 Introduction

The volume shift was introduced by Péneloux et al. [8],

$$c = \frac{1}{n}\sum_i c_i n_i, \tag{1}$$

where c_i is a component constant representing the component volume shift.

Different properties change when working with volume translations, see Jaubert et al. [3] for details.

The volume-shift have found application in many cubic based equations of state (t-mPR[6], PSRK[2], VTPR[1], tc-PR/tc-RK[7], . . .), and the component volume translations c_i, are often fixated to match the liquid density at $T = 0.7T_{\text{Crit}}$,

2 Volume shifts for generic EOS

The residual reduced Helmholtz function of a generic EOS is found as follows,

$$F(T, V_{\text{eos}}, \boldsymbol{n}) = \frac{A^{\text{r}}(T, V_{\text{eos}}, \boldsymbol{n})}{RT} = \int_{V_{\text{eos}}}^{\infty} \left[\frac{P(T, V'_{\text{eos}}, \boldsymbol{n})}{RT} - \frac{n}{V'_{\text{eos}}}\right] \mathrm{d}V'_{\text{eos}} \tag{2}$$

Introducing the volume shift,

$$V = V_{\text{eos}} - \sum n_i c_i = V_{\text{eos}} - C, \tag{3}$$

The residual reduced helmholtz of the volume-shifted (vs) EOS can be found, using $dV = dV_{\text{eos}}$ at constant n and T,

$$\begin{aligned}
F^{\text{vs}}(T, V, \boldsymbol{n}) &= \int_{V}^{\infty} \left[\frac{P(T, V' + C, \boldsymbol{n})}{RT} - \frac{n}{V'}\right] \mathrm{d}V' && (4)\\
&= \int_{V}^{\infty} \left[\frac{P(T, V' + C, \boldsymbol{n})}{RT} - \frac{n}{V' + C}\right] \mathrm{d}V' + n\int_{V}^{\infty} \left[\frac{1}{V' + C} - \frac{1}{V'}\right] \mathrm{d}V' && (5)\\
&= \int_{V_{\text{eos}}}^{\infty} \left[\frac{P(T, V'_{\text{eos}}, \boldsymbol{n})}{RT} - \frac{n}{V'_{\text{eos}}}\right] \mathrm{d}V'_{\text{eos}} + n\int_{V}^{\infty} \left[\frac{1}{V' + C} - \frac{1}{V'}\right] \mathrm{d}V' && (6)\\
&= F(T, V_{\text{eos}}, \boldsymbol{n}) + n \ln\left(\frac{V}{V_{\text{eos}}}\right) && (7)
\end{aligned}$$

Here we need to treat $V_{\mathrm{eos}} = V_{\mathrm{eos}}(V, \boldsymbol{n})$ with the chain rule when differentiating F^{vs}.

If we introduce F^C as the corrected residual reduced Helmholtz energy, due to the difference in ideal volume,

$$F^C(V, \boldsymbol{n}) = n \ln\left(\frac{V}{V+C}\right), \tag{8}$$

the differentials can be derived in a organized manner.

$$F_V^C = n\left(\frac{1}{V} - \frac{1}{V+C}\right) = n\left(\frac{1}{V} - \frac{1}{V_{\mathrm{eos}}}\right), \tag{9}$$

$$F_{VV}^C = n\left(-\frac{1}{V^2} + \frac{1}{(V+C)^2}\right) = n\left(-\frac{1}{V^2} + \frac{1}{V_{\mathrm{eos}}^2}\right), \tag{10}$$

$$F_i^C = \ln\left(\frac{V}{V+C}\right) - \frac{nc_i}{V+C} = \ln\left(\frac{V}{V_{\mathrm{eos}}}\right) - \frac{nc_i}{V_{\mathrm{eos}}}, \tag{11}$$

$$F_{ij}^C = -\frac{(c_j + c_i)}{V+C} + \frac{nc_ic_j}{(V+C)^2} = -\frac{(c_j + c_i)}{V_{\mathrm{eos}}} + \frac{nc_ic_j}{V_{\mathrm{eos}}^2}, \tag{12}$$

$$F_{Vi}^C = \frac{1}{V} - \frac{1}{V+C} + \frac{nc_i}{(V+C)^2} = \frac{1}{V} - \frac{1}{V_{\mathrm{eos}}} + \frac{nc_i}{V_{\mathrm{eos}}^2} \tag{13}$$

In addition the compositional differentials change since $V_{\mathrm{eos}} = V + C$,

$$F_i^{\mathrm{eos}} = F_i^{\mathrm{eos}} + F_{V_{\mathrm{eos}}}^{\mathrm{eos}} c_i, \tag{14}$$

$$F_{Ti}^{\mathrm{eos}} = F_{Ti}^{\mathrm{eos}} + F_{TV_{\mathrm{eos}}}^{\mathrm{eos}} c_i, \tag{15}$$

$$F_{ij}^{\mathrm{eos}} = F_{ij}^{\mathrm{eos}} + F_{iV_{\mathrm{eos}}}^{\mathrm{eos}} c_j + F_{V_{\mathrm{eos}}j}^{\mathrm{eos}} c_i + F_{V_{\mathrm{eos}}V_{\mathrm{eos}}}^{\mathrm{eos}} c_ic_j. \tag{16}$$

2.1 Test of the fugacity coefficient

Let us test this for the fugacity coefficient. It is defined as

$$\ln \hat{\varphi}_i^{\mathrm{vs}} = \left(\frac{\partial F^{\mathrm{vs}}}{\partial n_i}\right)_{T,V,n_j} - \ln(Z) = F_{n_i}^{\mathrm{vs}} - \ln(Z) \tag{17}$$

Differentiating F^{vs},

$$F_{n_i}^{\mathrm{vs}} = F_{n_i} + F_{V_{\mathrm{eos}}} c_i + \ln\left(\frac{V}{V_{\mathrm{eos}}}\right) - \frac{nc_i}{V_{\mathrm{eos}}} = F_{n_i} + \ln\left(\frac{V}{V_{\mathrm{eos}}}\right) - \frac{Pc_i}{RT} \tag{18}$$

Combining Equation 17 and 18, we get

$$\ln \hat{\varphi}_i^{\mathrm{vs}} = F_{n_i} + \ln\left(\frac{V}{V_{\mathrm{eos}}}\right) - \frac{Pc_i}{RT} - \ln\left(\frac{PV}{nRT}\right) \tag{19}$$

$$= F_{n_i} - \ln\left(\frac{PV_{\mathrm{eos}}}{nRT}\right) - \frac{Pc_i}{RT} \tag{20}$$

$$= \ln \hat{\varphi}_i - \frac{Pc_i}{RT} \tag{21}$$

which is the same result as reported by Péneloux et al.

3 Correlations used for c_i

The c_i for the SRK EOS is calculated from the following equation:

$$c_i = 0.40768 \frac{RT_{c_i}}{P_{c_i}} \left(0.29441 - Z_{\mathrm{RA}}\right) \tag{22}$$

Z_{RA} are tabulated in TPlib. Reid et al. [10] also correlate Z_{RA} as follows:

$$Z_{\mathrm{RA}} = 0.29056 - 0.08775\omega \tag{23}$$

Jhaveri and Youngren [4] have developed different paramaters for the PR EOS:

$$c_i^{\mathrm{PR}} = 0.50033 \frac{RT_{c_i}}{P_{c_i}} \left(0.25969 - Z_{\mathrm{RA}}\right) \tag{24}$$

4 Temperature dependent volume shift

Temperature dependent volume translation are known to give supercritical iso-therm crossings [9] and possibly un-physical behaviour [5] and must be executed with care. In some cases it can be used as a simple remedy to improve liquid density predictions.

In this case the F^C function becomes,

$$F^C(V, \boldsymbol{n}, T) = n \ln \left(\frac{V}{V + C(\boldsymbol{n}, T)} \right), \tag{25}$$

and the temperature differentials become,

$$F_T^C = -\frac{nC_T}{V + C} = -\frac{nC_T}{V_{\mathrm{eos}}}, \tag{26}$$

$$F_{TT}^C = -\frac{nC_{TT}}{V + C} + \frac{nC_T^2}{(V + C)^2} = -\frac{nC_{TT}}{V_{\mathrm{eos}}} + \frac{nC_T^2}{V_{\mathrm{eos}}^2}, \tag{27}$$

$$F_{VT}^C = \frac{nC_T}{(V + C)^2} = \frac{nC_T}{V_{\mathrm{eos}}^2}, \tag{28}$$

$$F_{iT}^C = -\frac{C_T}{V + C} - \frac{nc_{iT}}{V + C} + \frac{nC_T c_i}{(V + C)^2} = -\frac{(C_T + nc_{iT})}{V_{\mathrm{eos}}} + \frac{nC_T c_i}{V_{\mathrm{eos}}^2}. \tag{29}$$

In addition the compositional and temperature differentials change since $V_{\mathrm{eos}} = V + C(\boldsymbol{n}, T)$,

$$F_T^{\mathrm{eos}} = F_T^{\mathrm{eos}} + F_{V_{\mathrm{eos}}}^{\mathrm{eos}} C_T, \tag{30}$$

$$F_{TT}^{\mathrm{eos}} = F_{TT}^{\mathrm{eos}} + 2F_{TV_{\mathrm{eos}}}^{\mathrm{eos}} C_T + F_{V_{\mathrm{eos}}V_{\mathrm{eos}}}^{\mathrm{eos}} C_T^2 + F_{V_{\mathrm{eos}}}^{\mathrm{eos}} C_{TT}, \tag{31}$$

$$F_{VT}^{\mathrm{eos}} = F_{VT}^{\mathrm{eos}} + F_{V_{\mathrm{eos}}V_{\mathrm{eos}}}^{\mathrm{eos}} C_T, \tag{32}$$

$$F_{Ti}^{\mathrm{eos}} = F_{Ti}^{\mathrm{eos}} + F_{TV_{\mathrm{eos}}}^{\mathrm{eos}} c_i + F_{V_{\mathrm{eos}}V_{\mathrm{eos}}}^{\mathrm{eos}} C_T c_i + F_{V_{\mathrm{eos}}i}^{\mathrm{eos}} C_T + F_{V_{\mathrm{eos}}}^{\mathrm{eos}} c_{T,i}. \tag{33}$$

While F_i^{eos} and F_{ij}^{eos} are unchanged from (14) and (16) respectively.

References

[1] Eileen Collinet and Jürgen Gmehling. Prediction of phase equilibria with strong electrolytes with the help of the volume translated Peng-Robinson group contribution equation of state (VTPR). *Fluid Phase Equilibria*, 246(1-2):111 – 118, 2006.

[2] K. Fischer and J. Gmehling. Further development, status and results of the PSRK method for the prediction of vapor-liquid equilibria and gas solubilities. *Fluid Phase Equilibria*, 121(1-2):185 – 206, 1996.

[3] Jean-Noël Jaubert, Romain Privat, Yohann [Le Guennec], and Lucie Coniglio. Note on the properties altered by application of a péneloux–type volume translation to an equation of state. *Fluid Phase Equilibria*, 419:88 – 95, 2016.

[4] B. S. Jhaveri and G. K. Youngren. Three-parameter modification of the peng-robinson equation of state to improve volumetric predictions. *SPE Reservoir Engineering*, 8:1033 – 1040, 1988.

[5] Vladimir Kalikhman, Daniel Kost, and Ilya Polishuk. About the physical validity of attaching the repulsive terms of analytical EOS models by temperature dependencies. *Fluid Phase Equilibria*, 293(2):164 – 167, 2010.

[6] Aris Kordas, Kostis Magoulas, Sofia Stamataki, and Dimitrios Tassios. Methane-hydrocarbon interaction parameters correlation for the Peng-Robinson and the t-mPR equation of state. *Fluid Phase Equilibria*, 112(1):33 – 44, 1995.

[7] Yohann Le Guennec, Romain Privat, and Jean-Noël Jaubert. Development of the translated-consistent tc-PR and tc-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub-and super-critical domains. *Fluid Phase Equilibria*, 429:301–312, 2016.

[8] André Péneloux, Evelyne Rauzy, and Richard Fréze. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilibria*, 8(1):7 – 23, 1982.

[9] Oliver Pfohl. Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties. *Fluid Phase Equilibria*, 163(1):157 – 159, 1999.

[10] R. C. Reid, J. M. Prausnitz, and B. E. Poling. *The properties of gases & liquids*. McGraw-Hill, Inc., USA, 4 edition, 1987.