SINTEF

Memo

Testing the Lee-Kesler equation of state implementation in ThermoPack

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1 Introduction

Modifications of the work by Jørgen Røysland Aarnes on the Lee-Kesler equation of state (EoS) [1].

2 The Lee-Kesler model

The corresponding state method weigh the properties of two separate equations of state as follows,

$$M = M^{(0)} + \frac{\omega_M}{\omega^{(r)}}(M^{(r)} - M^{(0)}), \tag{2.1}$$

where, $\omega_M = \omega_M(\mathbf{n})$. M is z, A^R, S^R, H^R or any property that can be derived from these without using mole number differentials.

The binary interaction parameters of Plöcker et al. [2] is implemented, and used for the testing of the Lee-Kelser EoS.

2.1 Residual Gibbs energy

The residual Gibbs energy, G^R, or the mixture fugacity coefficient, $\ln \Phi_M$, for the reference and simple fluid was not included in the memo by Jørgen.

$$\ln \Phi_M = \frac{G^R(T, P, \mathbf{n})}{RT} = \frac{A^R(T, V, \mathbf{n})}{RT} + n\left(z - 1 - \ln(z)\right) \tag{2.2}$$

$$\left(\frac{\partial \ln \Phi_M}{\partial T}\right)_{P, \mathbf{n}} = -\frac{H^R}{RT^2} \tag{2.3}$$

$$\left(\frac{\partial \ln \Phi_M}{\partial P}\right)_{T, \mathbf{n}} = \frac{V^R}{RT} = \frac{V - V^{ig}}{RT} = n\frac{(z-1)}{P} \tag{2.4}$$

$$\ln \phi_i = \left(\frac{\partial \ln \Phi_M}{\partial n_i}\right)_{T, P} = \frac{1}{RT}\left(\frac{\partial A^R}{\partial n_i}\right)_{T, V} - \ln z \tag{2.5}$$

$$\tag{2.6}$$

2.2 The fugacities and differentials

Knowing the residual Gibbs energy, for the simple and reference fluid, the combined fugacities can be derived. The mixture fugacity become

$$\ln \Phi_M = \ln \Phi_M^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\ln \Phi_M^{(r)} - \ln \Phi_M^{(0)}\right). \tag{2.7}$$

The component fugacities become

$$\ln \phi_i = \ln \phi_i^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\ln \phi_i^{(r)} - \ln \phi_i^{(0)}\right) + \frac{1}{\omega^{(r)}}\left(\frac{\partial \omega_M}{\partial n_i}\right)\left(\ln \Phi_M^{(r)} - \ln \Phi_M^{(0)}\right). \tag{2.8}$$

Further the differentials become

$$\left(\frac{\partial \ln \phi_i}{\partial T}\right)_P = \left(\frac{\partial \ln \phi_i}{\partial T}\right)_P^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\left(\frac{\partial \ln \phi_i}{\partial T}\right)_P^{(r)} - \left(\frac{\partial \ln \phi_i}{\partial T}\right)_P^{(0)}\right) \tag{2.9}$$

$$+ \frac{1}{\omega^{(r)}}\left(\frac{\partial \omega_M}{\partial n_i}\right)\left(\left(\frac{\partial \ln \Phi_M}{\partial T}\right)_P^{(r)} - \left(\frac{\partial \ln \Phi_M}{\partial T}\right)_P^{(0)}\right), \tag{2.10}$$

$$\left(\frac{\partial \ln \phi_i}{\partial P}\right)_T = \left(\frac{\partial \ln \phi_i}{\partial P}\right)_T^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\left(\frac{\partial \ln \phi_i}{\partial P}\right)_T^{(r)} - \left(\frac{\partial \ln \phi_i}{\partial P}\right)_T^{(0)}\right) \tag{2.11}$$

$$+ \frac{1}{\omega^{(r)}}\left(\frac{\partial \omega_M}{\partial n_i}\right)\left(\left(\frac{\partial \ln \Phi_M}{\partial P}\right)_T^{(r)} - \left(\frac{\partial \ln \Phi_M}{\partial P}\right)_T^{(0)}\right), \tag{2.12}$$

$$\ln \phi_{ij} = \ln \phi_{ij}^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\ln \phi_{ij}^{(r)} - \ln \phi_{ij}^{(0)}\right) + \frac{1}{\omega^{(r)}}\left(\frac{\partial \omega_M}{\partial n_i}\right)\left(\ln \phi_j^{(r)} - \ln \phi_j^{(0)}\right) \tag{2.13}$$

$$+ \frac{1}{\omega^{(r)}}\left(\frac{\partial^2 \omega_M}{\partial n_i \partial n_j}\right)\left(\ln \Phi_M^{(r)} - \ln \Phi_M^{(0)}\right). \tag{2.14}$$

$$\tag{2.15}$$

2.3 The residual entropy, enthalpy and differentials

The combined residual entropy and enthalpy differentials will have the same terms, so only the entropy and differentials are given. The combined entropy is given as follows,

$$S^R(T, P, \mathbf{n}) = S^R(T, P, \mathbf{n})^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(S^R(T, P, \mathbf{n})^{(r)} - S^R(T, P, \mathbf{n})^{(0)}\right). \tag{2.16}$$

To avoid too many superscripts, the residual, R, superscript is dropped for the differentials of the entropy:

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\left(\frac{\partial S}{\partial T}\right)_P^{(r)} - \left(\frac{\partial S}{\partial T}\right)_P^{(0)}\right), \tag{2.17}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial S}{\partial P}\right)_T^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\left(\frac{\partial S}{\partial P}\right)_T^{(r)} - \left(\frac{\partial S}{\partial P}\right)_T^{(0)}\right), \tag{2.18}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,P} = \left(\frac{\partial S}{\partial n_i}\right)_{T,P}^{(0)} + \frac{\omega_M}{\omega^{(r)}}\left(\left(\frac{\partial S}{\partial n_i}\right)_{T,P}^{(r)} - \left(\frac{\partial S}{\partial n_i}\right)_{T,P}^{(0)}\right) + \frac{1}{\omega^{(r)}}\left(\frac{\partial \omega_M}{\partial n_i}\right)\left(S^{(r)} - S^{(0)}\right) \tag{2.19}$$

$$\tag{2.20}$$

3 Modifications to the Lee-Kesler reduced specific volume solver

Instead of solving directly for the reduced volume, $v_r(T_r, P_r)$, a solver for the compressibility factor, z, is used. In order to determine the compressibility factor, given T_r and P_r the following equation must be solved,

$$f(z) = z - \left[1 - \frac{v_r}{n}\left(\frac{\partial F}{\partial v_r}\right)_{T_r,\mathbf{n}}\right] = 0, \tag{3.1}$$

where $z = v_r P_r / T_r$.

To get good performance a third order method should be used. A third order method require $f(z), \partial f/\partial z, \partial^2 f/\partial z^2$:

$$\left(\frac{\partial f}{\partial z}\right) = 1 + \frac{T_r}{P_r n}\left[\left(\frac{\partial F}{\partial v_r}\right)_{T_r,\mathbf{n}} + v_r\left(\frac{\partial^2 F}{\partial v_r^2}\right)_{T_r,\mathbf{n}}\right], \tag{3.2}$$

$$\left(\frac{\partial^2 f}{\partial z^2}\right) = \frac{T_r^2}{P_r^2 n}\left[2\left(\frac{\partial^2 F}{\partial v_r^2}\right)_{T_r,\mathbf{n}} + v_r\left(\frac{\partial^3 F}{\partial v_r^3}\right)_{T_r,\mathbf{n}}\right]. \tag{3.3}$$

$$\tag{3.4}$$

In order to calculate these differentials, the third differential of F with respect to reduced specific volume, $\partial^3 F/\partial v_r^3$, is required:

$$\left(\frac{\partial^3 F}{\partial v_r^3}\right)_{T_r,\mathbf{n}} = n\left[-\frac{6B}{v_r^4} - \frac{12C}{v_r^5} - \frac{42D}{v_r^8}\right. \tag{3.5}$$

$$\left. -\frac{E}{v_r^5}\left(12\beta + \frac{(30 - 18\beta)\gamma}{v_r^2} + \frac{(4\beta - 26)\gamma^2}{v_r^4} + \frac{4\gamma^3}{v_r^6}\right)\exp\left(-\frac{\gamma}{v_r^2}\right)\right]. \tag{3.6}$$

$$\tag{3.7}$$

A Taylor expansion of f is used to calculate the next step, $\Delta z = z_{n+1} - z_n$, of the numerical procedure,

$$f(z) = f(z_n) + f'(z_n)\Delta z + \frac{1}{2}f''(z_n)\Delta z = 0. \tag{3.8}$$

The root giving the smallest change in z is selected, and the series approximation,

$$1 - \sqrt{1 - \alpha} = \frac{\alpha}{2} + \frac{\alpha^2}{8} + O(\alpha^3), \tag{3.9}$$

is used to simplify the expression, and to avoid taking the square root. We end up with the following step,

$$\Delta z = z_{n+1} - z_n = -\frac{f(z_n)}{f'(z_n)}\left(1 + \frac{f(z_n)f''(z_n)}{f'(z_n)^2}\right). \tag{3.10}$$

3.1 Selecting the correct roots of the simple and reference fluid

In order to get physical values for the fugacities, the roots from $f(z)$ for the simple and reference fluid must be selected carefully. The simple fluid and reference fluid either have 1 or two physical roots. If both the simple and reference fluid have a liquid root, this is used. If both the simple and reference fluid have a gas root, this is used. If the simple fluid have two roots, but the reference fluid only have a liquid root, then the liquid root is selected from both fluids, etc.

In some situations, the simple fluid only have a gas root, and the reference fluid only have a liquid root, see Figure 1. In this situation, these roots are combined.
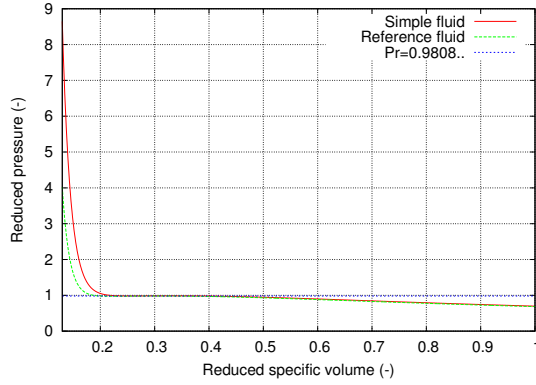
(a) Reduced pressure vs. reduced specific volume
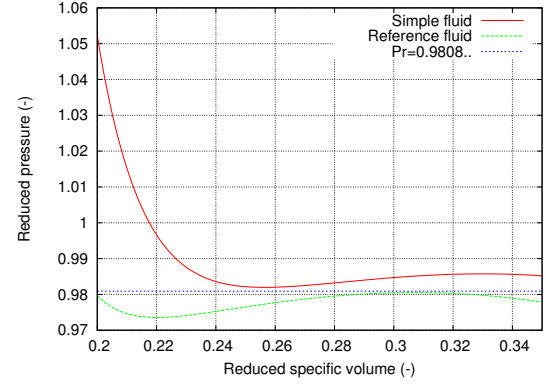
(b) Reduced pressure vs. reduced specific volume. Zoomed version of Figure 1a

Figure 1: Reduced pressure P_r as a function of reduced specific volume, for $T_r = 0.9973...$ For $P_r = 0.9808..$ it is seen that the simple fluid has a gas root, while the reference fluid has a liquid root.

4 Testing

The entropies and enthalpies are tested for consistency, by comparing G^R with $H^R - TS^R$. The ideal contribution is calculated using the Cp polinomials already implemented in ThermoPack.

4.1 TP-flash using the Lee-Kesler EoS

To test the Lee-Kesler implementation, a mixture of CO_2 and N_2 is used. The phase diagram, as calculated by the TP-flash, is shown in Figure 2.

5 Further work

The Lee-Kesler implementation need more testing, and it is also interesting to see how the models performes for densities of high pressure CO_2-mixtures. Some further work is listed below.

- Further testing to ensure robustness of the TP-flash

- Test HP, SP and UV flash using Lee-Kesler EoS

- Add a function to solve the EoS, returning the minimum Gibbs single phase solution. Test how close the solutions, z_1 and z_2, are. Use,

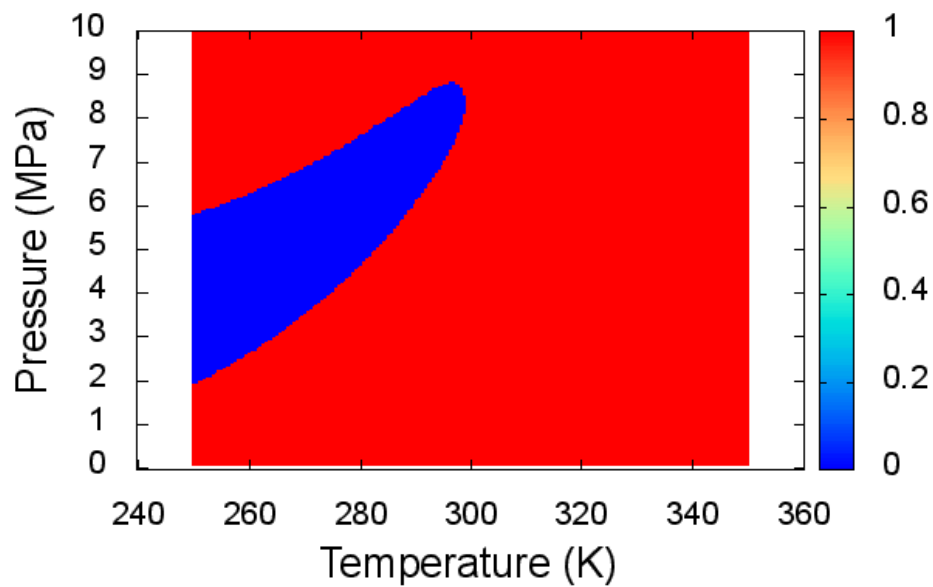$$\frac{|z_1 - z_2|}{\max(z_1, z_2)} < \epsilon, \tag{5.1}$$

Figure 2: Phase diagram of CO_2-N_2 mixture, as calculated by the TP-flash, with 95 mass % CO_2. The blue area is the two-phase gas-liquid area.

where ϵ is the tolerance for the compressibillity solver.

References

[1] Lee, B.I., Kesler, M.G., *A Generalized thermodynamic correlation based on a three-parameter corresponding states*, AlChE Journal, 21 (3), 510 (1975)

[2] Plöcker, U., Knapp, H., Prausnitz, J., *Calculations of High-Pressure Vapor-Liquid Equilibria from a Corresponding-States Correlation with Emphasis on Asymmetric Mixtures*, Ind. Eng. Chem. Process Des. Dev, 17 (3) 324 (1978)