Equation of State (EoS) Peng Robinson (PR78) and Predictive Peng Robinson (PPR78)

L'CADAME Weekly Meetings

Gustavo E. O. Celis

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UFRJ
UNIVERSIDADE FEDERAL
DO RIO DE JANEIRO

CADAME

Laboratório de Computação de Alto Desempenho e Aprendizado de Máquina em Engenharia (L'CADAME)
Weekly Meetings

- PR78 and PPR78 EoS thermodynamic models
- Solving methodology of the EoS
- Ongoing
- Next steps

Peng Robinson (PR78) EoS [1]

For a pure component

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \tag{1}$$

with

$$
\begin{cases}
R = 8.314472 \, J.mol^{-1}.K^{-1} \\
b_i = 0.0777960739 \frac{RT_{c,i}}{P_{c,i}} \\
a_i = 0.457235529 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}}\right)\right]^2 \\
if \; w_i \leq 0.491...m_i = 0.37464 + 1.54226 w_i - 0.26992 w_i^2 \\
if \; w_i > 0.491...m_i = 0.374642 + 1.48503 w_i \\
\qquad\qquad\qquad - 0.164423 w_i^2 + 0.016666 w_i^3
\end{cases}
$$

Mixing rules

PR78

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j \sqrt{a_i a_j}(1 - k_{ij})$$

$$b = \sum_{i=1}^{N} z_i b_i$$

(2)

PPR78

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j \sqrt{a_i a_j}(1 - k_{ij}(T))$$

$$b = \sum_{i=1}^{N} z_i b_i$$

(3)

PPR78 model [2] is an extension of the PR78 [1] that taking into the account the addition of a Group Contribution Method (GCM) to estimate the binary interaction parameter (k_{ij}), whatever the temperature. Then, the k_{ij} for the PPR78 is a temperature dependent variable $k_{ij}(T)$.

Binary interaction parameter $k_{ij}(T)$

According to Jaubert, & Mutelet, 2004 [2] $k_{ij}(T)$ is given by the follow equation,

$$k_{ij}(T) = \frac{-\frac{1}{2}\sum_{i=1}^{N_g}\sum_{j=1}^{N_g}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}.\left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j}\right)}{2\frac{\sqrt{a_i(T).a_j(T)}}{b_i.b_j}}$$

(4)

N_g is the number of different groups defined by the Group Contribution Method (GCM).
A_{kl} and B_{kl} are constant parameters.
$A_{kl} = A_{lk}$, $B_{kl} = B_{lk}$ and $A_{kk} = B_{kk} = 0$ (where k and i are two different groups.
A_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i.

For any mixture

$$ln\phi_i = \int\limits_0^P \frac{Z-1}{P} dP \tag{5}$$

Equilibrium relations in a multicomponent mixture system are given from fugacity coefficients (ϕ_i), which are determinate after compressibility factor (Z) calculus. Then, we need to write EoS (Eq. 1) as a function of Z, F(Z).

Compressibility factor (Z)

Dimensionless relations

$$Z = \frac{Pv}{RT} \qquad A = \frac{aP}{R^2 T^2} \qquad B = \frac{bP}{RT} \tag{6}$$

Replacing constants of Equation 6 into Equation 1 we have:

For PR78 and PPR78 EoS

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \tag{7}$$

The problem is reduced to know the roots of the cubic equation (7).

Finally, fugacity coefficients for both PR78 and PPR78 are taking into account by the equation

$$ln\phi_i = \frac{b_i}{b}(Z-1) - ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum\limits_{k=1}^{nc} x_k a_{i,k}}{a} - \frac{b_i}{b}\right) ln\left(\frac{Z+2.41B}{Z-0.414B}\right)$$

(8)

Since Z has three solutions (roots), it is necessary to define a criteria for the right Z values to guarantee equilibrium solutions. A simple test criteria is to assign the lowest real positive value of $Z = Z_{min}$ for the liquid phase (bubble point), and the highest, real, positive value of $Z = Z_{max}$ for the vapor phase (dew point).
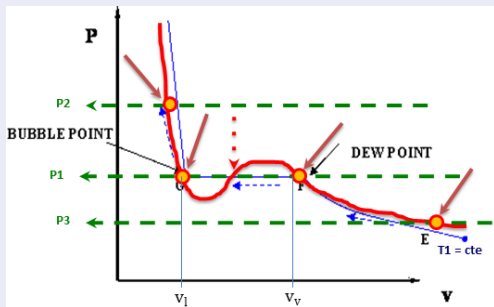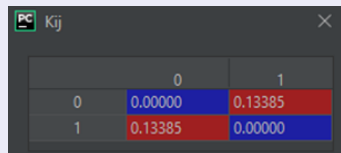
$$v_i = \frac{Z_i RT}{P} \qquad (9)$$

$$Z_i = \begin{cases} Z_{min} , & v_l \\ Z_{max} , & v_v \end{cases}$$

The development of the fugacity coefficients from the PPR78 EoS is already implemented (programming) in Python.

k_{ij} validation tests

For a binary mixture, CO_2 + heptane at $T = 394.15K$
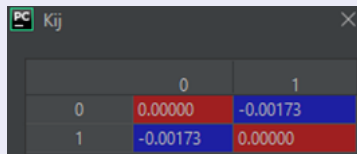
Table 1: *Al Ghafri, et. al., 2014* [3]

kij	0	1
0	0	0.1156
1	0.1156	0

2,4-dimethyl pentane + n-octane at $T = 313.15K$

Table 2: *Jaubert, & Mutelet, 2004* [2]

kij	0	1
0	0	-0.0017
1	-0.0017	0

For a multicomponent mixture, live oil + CO2 at $T = 394.15K$ [3]

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0	0.0000	0.1303	0.1339	0.1103	0.1095	0.1093	0.1653	0.1493	0.1127	0.1299	0.1068	0.0926	0.0895	0.0863	0.0773	0.0910	0.0930	0.0382	0.1346	0.1286	0.1363
1	0.1303	0.0000	0.0054	-0.0059	-0.0076	-0.0011	0.0917	0.0753	0.0619	0.0113	0.0517	-0.0134	-0.0150	-0.0164	-0.0223	0.0261	-0.0110	-0.0337	0.0682	0.0728	-0.0003
2	0.1339	0.0054	0.0000	0.0420	0.0247	0.0493	0.1806	0.1490	0.1632	-0.0040	0.1488	0.0305	0.0303	0.0309	0.0274	0.1135	0.0373	0.0365	0.0728	0.0228	-0.0031
3	0.1103	-0.0059	0.0420	0.0000	-0.0075	-0.0014	0.0458	0.0106	0.0230	0.0502	0.0125	-0.0289	-0.0325	-0.0365	-0.0463	-0.0144	-0.0309	-0.0497	0.0291	0.0335	0.0387
4	0.1095	-0.0076	0.0247	-0.0075	0.0000	-0.0001	0.0680	0.0527	0.0615	0.0435	0.0529	-0.0030	-0.0041	-0.0052	-0.0093	0.0314	-0.0019	-0.0106	0.0423	0.0131	0.0117
5	0.1093	-0.0011	0.0493	-0.0014	-0.0001	0.0000	0.0422	0.0156	0.0280	0.0648	0.0191	-0.0168	-0.0197	-0.0230	-0.0310	-0.0037	-0.0187	-0.0343	0.0384	0.0346	0.0411
6	0.1653	0.0917	0.1806	0.0458	0.0680	0.0422	0.0000	-0.0128	-0.0162	0.2130	-0.0183	0.0325	0.0274	0.0210	0.0096	-0.0249	0.0228	-0.0124	0.1334	0.1991	0.1683
7	0.1493	0.0753	0.1490	0.0106	0.0527	0.0156	-0.0128	0.0000	-0.0169	0.1948	-0.0160	0.0335	0.0306	0.0267	0.0206	-0.0144	0.0261	-0.0061	0.1420	0.1928	0.1260
8	0.1127	0.0619	0.1632	0.0230	0.0615	0.0280	-0.0162	-0.0169	0.0000	0.2127	-0.0000	0.0422	0.0394	0.0355	0.0296	-0.0008	0.0341	0.0195	0.1239	0.1428	0.1382
9	0.1299	0.0113	-0.0040	0.0502	0.0435	0.0648	0.2130	0.1948	0.2127	0.0000	0.1996	0.0652	0.0673	0.0703	0.0718	0.1681	0.0748	0.0861	0.1003	0.0196	-0.0150
10	0.1068	0.0517	0.1488	0.0125	0.0529	0.0191	-0.0183	-0.0160	-0.0000	0.1996	0.0000	0.0370	0.0347	0.0313	0.0264	-0.0005	0.0297	0.0167	0.1139	0.1248	0.1224
11	0.0926	-0.0134	0.0305	-0.0289	-0.0030	-0.0168	0.0325	0.0335	0.0422	0.0652	0.0370	0.0000	-0.0001	-0.0003	-0.0017	0.0244	0.0003	-0.0043	0.0423	0.0032	0.0078
12	0.0895	-0.0150	0.0303	-0.0325	-0.0041	-0.0197	0.0274	0.0306	0.0394	0.0673	0.0347	-0.0001	0.0000	-0.0001	-0.0010	0.0232	0.0002	-0.0038	0.0418	-0.0010	0.0063
13	0.0863	-0.0164	0.0309	-0.0365	-0.0052	-0.0230	0.0210	0.0267	0.0355	0.0703	0.0313	-0.0003	-0.0001	0.0000	-0.0005	0.0213	-0.0002	-0.0036	0.0412	-0.0011	0.0053
14	0.0773	-0.0223	0.0274	-0.0463	-0.0093	-0.0310	0.0096	0.0206	0.0296	0.0718	0.0264	-0.0017	-0.0010	-0.0005	0.0000	0.0189	-0.0016	-0.0030	0.0387	-0.0086	-0.0014
15	0.0910	0.0261	0.1135	-0.0144	0.0314	-0.0037	-0.0249	-0.0144	-0.0008	0.1681	-0.0005	0.0244	0.0232	0.0213	0.0189	0.0000	0.0189	0.0105	0.0893	0.0799	0.0831
16	0.0930	-0.0110	0.0373	-0.0309	-0.0019	-0.0187	0.0228	0.0261	0.0341	0.0748	0.0297	0.0003	0.0002	-0.0002	-0.0016	0.0189	0.0000	-0.0054	0.0428	0.0058	0.0134
17	0.0382	-0.0337	0.0365	-0.0497	-0.0106	-0.0343	-0.0124	-0.0061	0.0195	0.0861	0.0167	-0.0043	-0.0038	-0.0036	-0.0030	0.0105	-0.0054	0.0000	0.0472	-0.0010	0.0052
18	0.1346	0.0682	0.0728	0.0291	0.0423	0.0384	0.1334	0.1420	0.1239	0.1003	0.1139	0.0423	0.0418	0.0412	0.0387	0.0893	0.0428	0.0472	0.0000	0.0167	0.0547
19	0.1286	0.0728	0.0228	0.0335	0.0131	0.0346	0.1991	0.1928	0.1428	0.0196	0.1248	0.0032	-0.0010	-0.0011	-0.0086	0.0799	0.0058	-0.0010	0.0167	0.0000	0.0228
20	0.1363	-0.0003	-0.0031	0.0387	0.0117	0.0411	0.1683	0.1260	0.1382	-0.0150	0.1224	0.0078	0.0063	0.0053	-0.0014	0.0831	0.0134	0.0052	0.0547	0.0228	0.0000

Binary mixture (CO_2 + heptane) at $T = 394.15$ K
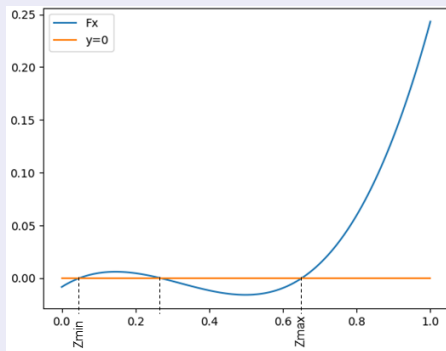
$$v_i = \frac{Z_i R T}{P} \tag{10}$$

$$Z_i \begin{cases} Z_{min} , & v_l \\ Z_{max} , & v_v \end{cases}$$

📄 D.B. Robinson and D.Y. Peng.
The Characterization of the Heptanes and Heavier Fractions for the GPA Peng-Robinson Programs.
Research report (Gas Processors Association). Gas Processors Association, 1978.

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Fluid Phase Equilibria, 224(2):285–304, oct 2004.

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Experimental and modeling study of the phase behavior of synthetic crude oil+CO2.
Fluid Phase Equilibria, 365:20–40, mar 2014.