Summer Fellowship Report
on
Development and Extension of Thermodynamic Packages in OpenModelica

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1 Peng Robinson 1978 Thermodynamic Package

1.1 Introduction

The Peng Robinson 1978 is an improved version of the Peng Robinson Thermodynamic model. In this model the attraction term is modified according to the accentric factor of the pure component. There are two seperate equations for the attraction term for accentric factors less than 0.491 and more than 0.491 which improves the overall result of the compressibility factor which in turn improves the calculation of the fugacity coefficients in both liquid and vapour phases.

1.2 The Thermodynamic Model

The equation of state for a pure component in the Peng Robinson 78 model is

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

where the parameters are given by

$$a_i = 0.45724(\frac{R^2 T_{ci}^2}{P_{ci}})[1 + m_i(1 - \sqrt{(}T_{ri}))]^2 \tag{2}$$

where

$$T_{ri} = \frac{T}{T_{ci}}$$

$$b_i = 0.0778\frac{RT_{ci}}{P_{ci}} \tag{3}$$

if

$$\omega_i <= 0.491$$

$$m_i = 0.37464 + 1.5422\omega_i - 0.26992\omega_i^2 \tag{4}$$

if

$$\omega_i > 0.491$$

$$m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.01667\omega_i^3 \tag{5}$$

where ω is the accentric factor and Tc and Pc are the critical temperatures and critical pressure of the pure compounds

1.3 Calculations in the Thermodynamic Model

1)This is a fugacity coefficient based Thermodynamic model. So our end goal would be to calculate fugacity coefficients for the pure components in both liquid and vapour phases and consequently calculate the component activity coefficient. To approach this first we need to find the interaction parameters for different compounds which is stored in a function called **BIPPR** in OpenModelica.

2)The value of aij is determined for each component by using the mixing rules

$$a_{ij} = \sum_{j=1}^{N} \sum_{i=1}^{N} (\sqrt{((a_i)(a_j))})(1 - k_{ij}) \tag{6}$$

3)Now we can proceed to calculate parameters for vapour and liquid phases

$$aliq = \sum_{j=1}^{N} \sum_{i=1}^{N} ((x_i)(x_j))a_{ij} \tag{7}$$

$$bliq = \sum_{i=1}^{N} (b_i x_i) \tag{8}$$

$$avap = \sum_{j=1}^{N} \sum_{i=1}^{N} ((y_i)(y_j))a_{ij} \tag{9}$$

$$bvap = \sum_{i=1}^{N} (b_i y_i) \tag{10}$$

$$Aliq = \frac{aliqP}{R^2T^2} \tag{11}$$

$$Bliq = \frac{bliqP}{RT} \tag{12}$$

$$Avap = \frac{avapP}{R^2T^2} \tag{13}$$

$$Bvap = \frac{bvapP}{RT} \tag{14}$$

4)Now the value of compressibilty factor can be found out by finding the smallest root of the equation

$$Z^3 + (Bliq - 1)Z^2 + (Aliq - 2Bliq - 3Bliq^2)Z - (AliqBliq - Bliq^2 - Bliq^3) \tag{15}$$

5)Now the fugacity coefficient for liquid phase can be calculated by using the equation

$$ln\phi_i = \frac{b_i(Z-1)}{bliq} - ln(Z-1) + \frac{Aliq}{2\sqrt{(}2)Bliq}[\frac{b_i}{bliq} - 2(\frac{\sum_{i=1}^{N}\sum_{j=1}^{N}(x_j(a_{ij}))}{aliq})]ln[\frac{Z+(1+\sqrt{(}2))Bliq}{Z+(1-\sqrt{(}2))Bliq}] \quad (16)$$

6)This same routine can be applied to calculate vapour phase fugacity coefficient but this time the value of the compressibility factor is found by finding the largest root of the equation

$$Z^3 + (Bvap-1)Z^2 + (Avap - 2Bvap - 3Bvap^2)Z - (AvapBvap - Bvap^2 - Bvap^3) \quad (17)$$

7)Applying equation 16 while replacing the liquid terms with vapour terms and the liquid mole fraction with vapour mole fraction will give us the value for vapour phase fugacity coefficient for the compounds.

8)Finally the component activity coefficient can be calculated by using the equation

$$K_i = \frac{\phi_{vapouri}}{\phi_{liquidi}} \quad (18)$$

1.4 Tables :Comparision of results from DWSIM and OpenModelica

1.4.1 Comparision of data in one phase regions

Compounds	Mol fraction	Temperature (K)	Pressure (Pa)	Vapour fugacity coefficient (OM)	Vapour fugacity coefficient (DWSIM)	Liquid fugacity coefficient (OM)	Liquid fugacity coefficient (DWSIM)
Methane	0.33	298	101325	0.999499	0.999499	-	-
Ethane	0.33	298	101325	0.991546	0.991546	-	-
Propane	0.34	298	101325	0.984968	0.984968	-	-
Isopentane	0.33	180	101325	-	-	0.000583	0.000582
Isobutane	0.33	180	101325	-	-	0.007557	0.00773
Propane	0.34	180	101325	-	-	0.0540567	0.05523
Benzene	0.25	300	101325	-	-	0.14974	0.14974
Toluene	0.3	300	101325	-	-	0.0472	0.0472
Phenol	0.2	300	101325	-	-	0.00142	0.00143
Cyclohexanol	0.25	300	101325	-	-	0.00432	0.00432

1.4.2 Comparision of data in VLE region

Compounds	Mol fraction (Mixture)	Vapour phase fraction	Vapour phase mole fraction (OM)	Vapour phase mole fraction (DWSIM)	Liquid phase mole fraction (OM)	Liquid phase mole fraction (DWSIM)	Temperature (K)	Pressure (Pa)	Vapour phase fugacity coefficient(OM)	Vapour phase fugacity coefficient(DWSIM)	Liquid phase fugacity coefficient(OM)	Liquid phase fugacity coefficient(DWSIM)
Methanol	0.5	0.5	0.708	0.709	0.288	0.29	298.15	10070	0.9975	0.9974	2.452	2.47
Toluene	0.5		0.291	0.2905	0.712	0.71	298.15	10070	0.994	0.994	0.407	0.4
Methane	0.33	0.2	0.495	0.491	0.288	0.288	300	6452180	1.717	1.719	1.0037	0.9998
Ethane	0.33		0.3	0.304	0.337	0.341	300	6452180	0.484	0.484	0.544	0.545
Propane	0.34		0.205	0.204	0.373	0.371	300	6452180	0.184	0.1837	0.3346	0.336
Methane	0.33	0.5	0.533	0.533	0.126	0.126	298.15	3441800	0.968	0.968	4.0909	4.0922
Ethane	0.33		0.345	0.345	0.314	0.314	298.15	3441800	0.739	0.739	0.8121	0.8123
Isobutane	0.34		0.1207	0.1207	0.559	0.559	298.15	3441800	0.499	0.499	0.1077	0.1077

2 Peng Robinson Stryjek-Vera 1 (PRSV-1) Thermodynamic Package

2.1 Introduction

The Peng Robinson Stryjek-Vera 1 is an improvement to the original Peng Robinson Thermodynamic Package. This model modifies the attraction factor by adding another parameter κ_1 which is a parameter that depends on the pure component. This helps to better estimate the attraction factor and in turn gives more accurate values for the vapour and liquid phase fugacity coefficients especially in the VLE regions. Stryjek and Vera defined the value of κ_1 for a number of compounds.

2.2 The Thermodynamic Model

The Peng Robinson Stryjek-Vera Thermodynamic Model is very similar to the original Peng Robinson Thermodynamic Model with the exception of the attraction factor.The compound parameters are

$$a_i = 0.45724\frac{\alpha R^2 T_{ci}^2}{P_{ci}}$$

$$b_i = 0.0778\frac{RT_{ci}}{P_{ci}}$$

where Tci and Pci are the critical temperatures and critical pressures of pure components. The value of α is given by

$$\alpha = (1 + \kappa(1 - \sqrt(T_r)))^2$$

where

$$\kappa = \kappa_0 + \kappa_1(1 + \sqrt(T_r))(0.7 - T_r)$$

$$T_r = \sqrt(\frac{T}{T_{ci}})$$

The value of κ_0 is given by

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.1713184\omega^2 + 0.0196554\omega^3$$

The values of κ_1 are defined for various compounds. A table containing the values of κ_1 for 65 different compounds used in OpenModelica is listed below.

Compound	κ1
Nitrogen	0.01996
Oxygen	0.01512
Carbon Dioxide	0.04285
Ammonia	0.001
Water	-0.06635
Hydrogen Chloride	0.01989
Methane	-0.00159
Ethane	0.02669
Propane	0.03136
Butane	0.03443
Pentane	0.03946
Neopentane	0.04303
Hexane	0.05104
Heptane	0.04648
Octane	0.04464
Nonane	0.04104
Decane	0.0451
Undecane	0.02919
Dodecane	0.05426
Tridecane	0.04157
Tetradecane	0.02686
Pentadecane	0.01892

Hexadecane	0.02665
Heptadecane	0.04048
Octadecane	0.08291
Cyclohexane	0.07023
Benzene	0.07019
Toluene	0.03849
Ethyl Benzene	0.03994
Para Xylene	0.01277
Indane	0.01173
N-Propyl benzene	0.02715
1,2,3-Trimethylbenzene	-0.01384
Naphthalene	0.03297
Di Isopropyl ether	0.03751
Nitromethane	-0.10299
Acetonitrile	-0.13991
Acetic Acid	-0.19724
Tetrahydrofuran	0.03961
Pyridine	0.06946
Furfural	-0.03471
M-Cresol	0.24705

1-Methyl Naphthalene	-0.01842
2-Methyl Naphthalene	-0.01639
Biphenyl	0.11487
Acetone	-0.00888
2-Pentanone	0.01681
3-Pentanone	0.03558
2-Hexanone	0.00984
3-Hexanone	0.02321
2-Heptanone	0.02731
Methanol	-0.16816
Ethanol	-0.03374
1-Propanol	0.21419
1-Butanol	0.33431
2-Butanol	0.39045
2-Methyl 1-Propanol	0.372
2-Methyl 2-Propanol	0.43099
1-Pentanol	0.36781
1-Hexanol	-0.00237
Dimethylether	0.05717
MethylEthyl Ether	0.16948
Methyl N Propyl Ether	0.023
Methyl iso Propyl Ether	0.04123
Methyl-t-butyl-ether	0.05129

Since the attraction term is now affected by the term κ_1 which is unique to each compound. The fugacity coefficient for systems can be calculated more accurately

2.3 Calculations in the Thermodynamic model

The calculation routine for Peng Robinson Stryjek-Vera 1 thermodynamic model is the same as the Peng Robinson thermodynamic model with the exception of calculation of the attraction factor as mentioned above.

3 Peng Robinson Stryjek-Vera 2 (PRSV-2) Thermodynamic Package

3.1 Introduction

Stryjek and J.H. Vera further developed their thermodynamic model in 1986 by introducing more compound specific factors in their equations and modifying the equations used to calculate the fugacity coefficients. This model adds two more parameters κ_2 and κ_3 which also depend on the pure component similar to κ_1. With all these very specific components and modified equations this model better predicts the properties of liquids and gases in the VLE region.

3.2 The Thermodynamic Model

The constants for this thermodynamic model are the same as the original Peng Robinson's model.

$$a_i = 0.45724\frac{\alpha R^2 T_{ci}^2}{P_{ci}}$$

$$b_i = 0.0778\frac{RT_{ci}}{P_{ci}}$$

where Tci and Pci are the critical temperatures and critical pressures of pure components. The value of α is given by

$$\alpha = (1 + \kappa(1 - \sqrt(T_r)))^2$$

where

$$\kappa = \kappa_0 + [\kappa_1 + \kappa_2(\kappa_3 - T_r)(1 - \sqrt(T_r)](1 + \sqrt(T_r))(0.7 - T_r)$$

$$T_r = \sqrt(\frac{T}{T_{ci}})$$

The value of κ_0 is given by

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.1713184\omega^2 + 0.0196554\omega^3$$

The values of κ_2 and κ_3 are defined for various compounds. A table containing the values of κ_2 and κ_3 used in OpenModelica is listed.

	κ_2	κ_3
	Inorganics	
Nitrogen	0.3162	0.535
Oxygen	−0.0090	0.490
Carbon dioxide	0.0000	0.000
Ammonia	−0.1265	0.510
Water	0.0199	0.443
Hydrogen chloride	−0.0036	0.310
	Organics	
Hydrocarbons		
Methane	0.1521	0.517
Ethane	0.1358	0.424
Propene	0.2610	0.424
Propane	0.2757	0.447
Butane	0.6767	0.461
Pentane	0.3940	0.457
Neopentane	0.8697	0.615
Hexane	0.8634	0.460
Heptane	0.9331	0.496
Octane	0.6214	0.509
Nonane	0.6621	0.519
Decane	0.8549	0.527
Undecane	1.3288	0.568
Dodecane	0.8744	0.505
Tridecane	0.9387	0.528
Tetradecane	0.9408	0.528
Pentadecane	1.0908	0.559
Hexadecane	0.0334	0.767
Heptadecane	2.9805	0.571
Octadecane	4.1441	0.577
Cyclohexane	0.6146	0.530
Bicyclohexyl	3.0438	0.606
Benzene	0.7939	0.523
Toluene	0.5261	0.510

Ethylbenzene	0.5342	0.519
p-Xylene	0.5963	0.524
Indane	0.9246	0.548
n-Propylbenzne	0.7310	0.530
1,2,3-Trimethylbenzene	0.4777	0.538
Naphthalene	0.6634	0.510
1-Methyl-naphthalene	−0.8140	0.577
2-Methyl-naphthalene	−0.0750	0.597
Biphenyl	0.1077	0.407
Diphenylmethane	0.3703	0.579
9,10-Dihydrophenanthrene	−5.8256	0.587
Ketones		
Acetone	0.2871	0.537
Butanone	0.6847	0.613
2-Pentanone	0.7787	0.620
3-Pentanone	0.6180	0.610
Methylbutanone	0.5138	0.615
2-Hexanone	0.8448	0.550
3-Hexanone	0.8891	0.619
Dimethylbutanone	0.7451	0.535
3-Heptanone	0.9236	0.561
5-Nonanone	0.9649	0.579
Alcohols		
Methanol	−1.3400	0.588
Ethanol	−2.6846	0.592
1-Propanol	−3.6816	0.640
2-Propanol	−3.5578	0.652
1-Butanol	−1.1748	0.642
2-Butanol	0.0026	0.676
2-Methyl-1-propanol	−1.2792	0.642
2-Methyl-2-propanol	−0.0480	0.658

	κ_2	κ_3
1-Pentanol	0.2918	0.621
1-Hexanol	−3.3938	0.551
1-Octanol	2.7372	0.543
1-Decanol	1.4978	0.470
Ethers		
Dimethyl ether	−0.1211	0.481
Methyl ethyl ether	0.0515	0.768
Methyl *n*-propyl ether	0.9179	0.558
Methyl *i*-propyl ether	0.3833	0.562
Methyl *n*-butyl ether	0.6140	0.548
Methyl *t*-butyl ether	−0.2022	0.585
Ethyl *n*-propyl ether	1.1679	0.553
Di-*n*-propyl ether	1.4094	0.577
Di-*i*-propyl ether	0.8810	0.590
Methyl phenyl ether	1.0478	0.616
Various		
Nitromethane	0.5905	0.463
Acetonitrile	−0.3777	0.522
Acetic acid	0.8136	0.541
Dimethyl formamide	−0.1857	0.470
2-Methoxyethanol	0.0020	0.407
1-Propylamine	1.1002	0.614
2-Propylamine	2.2851	0.603
2-Methoxypropionitrile	0.0033	0.931
2-Methyl-2-propylamine	0.9308	0.635
Tetrahydrofuran	0.5029	0.573
Pyridine	0.4241	0.575
Furfural	4.5512	0.539
N-Methylpyrrolidine	−0.7871	0.537
Hexafluorobenzene	0.8172	0.565
Nitrotoluene	0.5425	0.582
m-Cresol	5.6910	0.597
Thianaphthene	−0.1210	0.592

3.3 Calculations in the Thermodynamic model

The calculations for the PRSV-2 model can be done in two major ways. The first method is by using Margulues equations which leads to the PRSV2-M model. The second method is by using Van-Laars equations which leads to the PRSV2-VL model.

3.3.1 PRSV2-M

In the Margules equations the factor aij is defined as

$$a_{ij} = \sqrt{(a_i * a_j)}(1 - k_{ij}) \tag{19}$$

The conventional mixing rules are applied to get

$$a = \sum_{j=1}^{N} \sum_{i=1}^{N} (x_i * x_j * a_{ij})$$

$$b = \sum_{i=1}^{N}(x_i * b_i)$$

The values of the compressibility factor and the dimensionless parameters are calculated as follows.

$$aliq = \sum_{j=1}^{N}\sum_{i=1}^{N}((x_i)(x_j))a_{ij} \tag{20}$$

$$bliq = \sum_{i=1}^{N}(b_i x_i) \tag{21}$$

$$avap = \sum_{j=1}^{N}\sum_{i=1}^{N}((y_i)(y_j))a_{ij} \tag{22}$$

$$bvap = \sum_{i=1}^{N}(b_i y_i) \tag{23}$$

$$Aliq = \frac{aliqP}{R^2T^2} \tag{24}$$

$$Bliq = \frac{bliqP}{RT} \tag{25}$$

$$Avap = \frac{avapP}{R^2T^2} \tag{26}$$

$$Bvap = \frac{bvapP}{RT} \tag{27}$$

$$Z^3 + (B-1)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) \tag{28}$$

The highest root is taken as the correct compressibility factor for vapour phase and the lowest root for the liquid phase. Now the fugacity coefficient is calculated with the following equation

$$ln\phi_i = \frac{b_i(Z-1)}{b} - ln(Z-B) - (\frac{A}{2\sqrt{(}2)B}(\frac{\bar{a_i}}{a} + 1 - \frac{b_i}{b})ln[\frac{Z + (1+\sqrt{(}2))B}{Z + (1-\sqrt{(}2))B}]) \tag{29}$$

where the terms are given by

$$\frac{\bar{a_i}}{a} + 1 = \frac{2}{a}(\sum_k x_k a_{ik} + \sum_{j\neq i} x_i x_j [n\frac{\partial a_{ij}}{\partial n_i}_{j\neq i}] + \sum_{j\neq i}\sum_{m>j}^{m\neq i} x_j x_m [n\frac{\partial a_{jm}}{\partial n_i}_{j\neq i_{m>j_{m\neq i}}}]) \tag{30}$$

For PRSV2-M the variables are given by

$$n\frac{\partial a_{ij}}{\partial n_i}_{j\neq i} = (a_{ii}a_{jj})^{0.5}[x_j k_{ji} - (1-x_i)k_{ij}]$$

$$n\frac{\partial a_{jm}}{\partial n_i}_{j\neq i_{m>j_{m\neq i}}} = (a_{jj}a_{mm})^{0.5}(x_j k_{jm} + x_m k_{mj})$$

With (19) and the above mentioned equations the PRSV2-M model is completely defined.

3.3.2 PRSV2-VL

For the PRSV2-VL model the term aij is given by

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - \frac{k_{ij}k_{ji}}{x_i k_{ij} + x_j k_{ji}})$$

The rest of the calculations until the calculation of the fugacity coefficient are the same. The equation (29) is used to calculate the fugacity coefficient. The variables for the calculation are given by

$$n\frac{\partial a_{ij}}{\partial n_i}_{j\neq i} = (a_{ii}a_{jj})^{0.5}k_{ij}k_{ji}(\frac{(1-x_i)k_{ij} - x_j k_{ji}}{(x_i k_{ij} + x_j k_{ji})^2}$$

$$n\frac{\partial a_{jm}}{\partial n_i}_{j\neq i_{m>j_{m\neq i}}} = -(a_{jj}a_{mm})^{0.5}\frac{k_{jm}k_{mj}}{x_j k_{jm} + x_m k_{mj}} \tag{31}$$

The equation (30) is used again for the calculations. This completes the PRSV2-VL thermodynamic model. Note: The last term in (30) vanishes for binary systems in both the models.