Example bubble point calculation
for the system acetone - ethanol at 328.15 K

Peng-Robinson equation of state

$$P_{PR}\left(T, v_{PR}\right) := \frac{R \cdot T}{v_{PR} - b} - \frac{a(T)}{v_{PR} \cdot \left(v_{PR} + b\right) + b \cdot \left(v_{PR} - b\right)}$$

Volume Translated Peng-Robinson (VTPR) equation of state

$$P(T, v) := \frac{R \cdot T}{v + c - b} - \frac{a(T)}{(v + c) \cdot (v + c + b) + b \cdot (v + c - b)}$$

Data of pure components and constants for pure components, groups and etc.

General gas constant

$$R := 8.31433 \frac{J}{mol \cdot K}$$

Substance 0 : Acetone (C3H6O)

Main group 1: CH2
Sub group 1: CH3 x 1

Main group 9: CH2CO
Sub group 18:CH3CO x 1

Substance 1 : Ethanol (C2H6O)

Main group 1: CH2
Sub group 1: CH3 x 1
2: CH2 x 1

Main group 5: OH
Sub group 14: OH (p) x 1

Number of substances

$NS := 2$ $is := 0 .. NS - 1$ $js := 0 .. NS - 1$

Number of sub groups and main groups

$NG := 4$ $ki := 0 .. NG - 1$ $NM := 3$ $kmi := 0 .. NM - 1$

$kj := 0 .. NG - 1$ $kmj := 0 .. NM - 1$

$kk := 0 .. NG - 1$

Critical properties and acentric factors

$P_{c_0} := 4701480 \cdot Pa \quad T_{c_0} := 508.1 \cdot K \quad v_{c_0} := 209 \cdot 10^{-6} \cdot \frac{m^3}{mol} \quad \omega_0 := 0.309$

$P_{c_1} := 6383475 \cdot Pa \quad T_{c_1} := 516.2 \cdot K \quad v_{c_1} := 167 \cdot 10^{-6} \cdot \frac{m^3}{mol} \quad \omega_1 := 0.635$

Twu parameters

$L_0 := 1.15623 \quad M_0 := 1.05341 \quad N_0 := 0.690726$

$L_1 := 1.19559 \quad M_1 := 1.0148 \quad N_1 := 1.05841$

Volume translation parameters

$ci_0 := 10.24101 cm^3 \cdot mol^{-1}$

$ci_1 := 1.20878 cm^3 \cdot mol^{-1}$

Group parameters

k=0 : Subgroup 1, k=1 : Subgroup 2, k=2 : Subgroup 14, k=3 : Subgroup 18

km=0 : Main group 1, km=1 : Main group 5, km=2 : Main group 9

Relation between sub group and main group, mg_k=km

$mg_0 := 0 \quad mg_1 := 0 \quad mg_2 := 1 \quad mg_3 := 2$

Stoichiometric vector, $\nu_{i,k}$

$\nu_{is,ki} := 0$

$\nu := \begin{pmatrix} 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix}$

Surface areas of groups

1 : CH3 (sub group 1)	$Q_0 := 1.2958$
2 : CH2 (sub group 2)	$Q_1 := 0.9471$
3 : OH (p) (sub group 14)	$Q_2 := 1.0189$
4 : CH3CO (sub group 18)	$Q_3 := 1.4480$

Interaction parameters, $pa_{mi,mj}$, $pb_{mi,mj}$, $pc_{mi,mj}$

$pa_{kmi,kmi} := 0.0 \cdot K$ $\quad pb_{kmi,kmi} := 0.0$ $\quad pc_{kmi,kmi} := 0.0 \cdot \frac{1}{K}$

CH2 - OH

$pa_{0,1} := 1809.53 \cdot K$ $\quad pa_{1,0} := 725.658 \cdot K$

$pb_{0,1} := -0.485574$ $\quad pb_{1,0} := -0.905047$

$pc_{0,1} := -0.00232107 \cdot \frac{1}{K}$ $\quad pc_{1,0} := 0.00315378 \cdot \frac{1}{K}$

CH2 - CH3CO

$pa_{0,2} := 425.312 \cdot K$ $\quad pa_{2,0} := 284.25 \cdot K$

$pb_{0,2} := 0.68787$ $\quad pb_{2,0} := -1.77309$

$pc_{0,2} := -0.00030781 \cdot \frac{1}{K}$ $\quad pc_{2,0} := 0.00163576 \cdot \frac{1}{K}$

OH - CH3CO

$pa_{1,2} := -57.6638 \cdot K$ $\quad pa_{2,1} := 540.611 \cdot K$

$pb_{1,2} := 0.78748$ $\quad pb_{2,1} := -0.99216$

$pc_{1,2} := -0.00015955 \cdot \frac{1}{K}$ $\quad pc_{2,1} := 0.00035082 \cdot \frac{1}{K}$

The exponent for the combination rule of the b mixing rule

$$pow := \frac{3}{4}$$

Coefficients of equations of states for pure components

$$zc_{is} := \frac{Pc_{is} \cdot vc_{is}}{R \cdot Tc_{is}}$$

$$bi_{is} := 0.0778 \cdot \frac{R \cdot Tc_{is}}{P}$$

$P_{c_{is}}$

$$bi = \begin{pmatrix} 6.991 \times 10^{-5} \\ 5.231 \times 10^{-5} \end{pmatrix} m^3\,mol^{-1}$$

Twu alpha function

$$\alpha i(i,T) := \left| \begin{array}{l} T_r \leftarrow \dfrac{T}{T_{c_i}} \\ T_r^{N_i \cdot (M_i - 1)} \cdot e^{L_i \cdot \left(1 - T_r^{N_i \cdot M_i}\right)} \end{array} \right.$$

$$ai(i,T) := 0.45724 \cdot \frac{R^2 \cdot \left(T_{c_i}\right)^2}{P_{c_i}} \cdot \alpha i(i,T)$$

c - mixing rule

$$c_{mix}(zxy) := \sum_{is} zxy_{is} \cdot ci_{is}$$

b - mixing rule

$$b_{mix}(zxy) := \sum_{is} \left[\sum_{js} zxy_{is} \cdot zxy_{js} \left[\frac{\left(bi_{is}\right)^{pow} + \left(bi_{js}\right)^{pow}}{2} \right]^{\frac{1}{pow}} \right]$$

Excess Gibbs energy

$$gEres(zxy,T) := \left| \begin{array}{l} \text{for } mi \in 0 .. NM - 1 \\ \quad \text{for } mj \in 0 .. NM - 1 \\ \quad\quad \psi_{mi,mj} \leftarrow e^{\dfrac{-\left(pa_{mi,mj} + pb_{mi,mj} \cdot T + pc_{mi,mj} \cdot T^2\right)}{T}} \\ \text{for } i \in 0 .. NS - 1 \\ \quad \text{for } m \in 0 .. NG - 1 \\ \quad\quad Xi_{i,m} \leftarrow \dfrac{\nu_{i,m}}{\sum^{NG-1} \nu_{i,n}} \end{array} \right.$$

$$n = 0$$

for $i \in 0..NS-1$

for $m \in 0..NG-1$

$$\Theta i_{i,m} \leftarrow \frac{Q_m \cdot Xi_{i,m}}{\sum_{n=0}^{NG-1} Q_n \cdot Xi_{i,n}}$$

for $i \in 0..NS-1$

for $k \in 0..NG-1$

$$\Gamma i_{i,k} \leftarrow e^{Q_k \cdot \left[1 - \ln\left[\sum_{m=0}^{NG-1} \Theta i_{i,m} \cdot \Psi\left(mg_m, mg_k\right)\right] - \sum_{m=0}^{NG-1} \frac{\Theta i_{i,m} \cdot \Psi\left(mg_k, mg_m\right)}{\sum_{n=0}^{NG-1} \Theta i_{i,n} \cdot \Psi\left(mg_n, mg_m\right)}\right]}$$

for $m \in 0..NG-1$

$$X_m \leftarrow \frac{\sum_{j=0}^{NS-1} \nu_{j,m} \cdot zxy_j}{\sum_{j=0}^{NS-1} \sum_{n=0}^{NG-1} \left(\nu_{j,n} \cdot zxy_j\right)}$$

for $m \in 0..NG-1$

$$\Theta_m \leftarrow \frac{Q_m \cdot X_m}{\sum_{n=0}^{NG-1} Q_n \cdot X_n}$$

for $k \in 0..NG-1$

$$\Gamma_k \leftarrow e^{Q_k \cdot \left[1 - \ln\left[\sum_{m=0}^{NG-1} \Theta_m \cdot \Psi\left(mg_m, mg_k\right)\right] - \sum_{m=0}^{NG-1} \frac{\Theta_m \cdot \Psi\left(mg_k, mg_m\right)}{\sum_{n=0}^{NG-1} \Theta_n \cdot \Psi\left(mg_n, mg_m\right)}\right]}$$

for $i \in 0..NS-1$

$$\gamma RES_i \leftarrow e^{\sum_{k=0}^{NG-1} \nu_{i,k} \cdot \left(\ln\left(\Gamma_k\right) - \ln\left(\Gamma i_{i,k}\right)\right)}$$

$$\sum_{i=0}^{NS-1} zxy_i \cdot R \cdot T \cdot \ln\left(\gamma RES_i\right)$$

a - mixing rule

$$a_{mix}(zxy, T) := \quad b \leftarrow b_{mix}(zxy)$$

$$u \leftarrow 1.22498$$

$$A \leftarrow \frac{1}{2 \cdot \sqrt{2}} \cdot \ln\left[\frac{u + \left(1 - \sqrt{2}\right)}{u + \left(1 + \sqrt{2}\right)}\right]$$

$$b \cdot \left(\sum_{i=0}^{NS-1} zxy_i \cdot \frac{ai(i,T)}{bi_i} + \frac{gEres(zxy,T)}{A} \right)$$

VTPR equation of state

$$P_{VTPR}(zxy,T,v) := \left| \begin{array}{l} a \leftarrow a_{mix}(zxy,T) \\ b \leftarrow b_{mix}(zxy) \\ c \leftarrow c_{mix}(zxy) \\ \dfrac{R \cdot T}{v+c-b} - \dfrac{a}{(v+c)\cdot(v+c+b) + b\cdot(v+c-b)} \end{array} \right.$$

Peng-Robinson equation of state

$$P_{PR}(zxy,T,v) := \left| \begin{array}{l} a \leftarrow a_{mix}(zxy,T) \\ b \leftarrow b_{mix}(zxy) \\ \dfrac{R \cdot T}{v-b} - \dfrac{a}{v\cdot(v+b) + b\cdot(v-b)} \end{array} \right.$$

Partial molar excess Gibbs energy

$$gEresi(i,zxy,T) := \left| \begin{array}{l} \text{for } mi \in 0..NM-1 \\ \quad \text{for } mj \in 0..NM-1 \\ \quad\quad \Psi_{mi,mj} \leftarrow e^{\frac{-\left(pa_{mi,mj}+pb_{mi,mj}\cdot T+pc_{mi,mj}\cdot T^2\right)}{T}} \\ \text{for } m \in 0..NG-1 \\ \quad Xi_{i,m} \leftarrow \dfrac{\nu_{i,m}}{\sum_{n=0}^{NG-1} \nu_{i,n}} \\ \text{for } m \in 0..NG-1 \\ \quad \Theta i_{i,m} \leftarrow \dfrac{Q_m \cdot Xi_{i,m}}{\sum_{n=0}^{NG-1} Q_n \cdot Xi_{i,n}} \\ \text{for } k \in 0..NG-1 \\ \quad Q_k \cdot \left[1 - \ln\left[\sum_{m=0}^{NG-1} \Theta i_{i,m} \cdot \Psi\left(mg_m, mg_k\right) \right] - \sum_{m=0}^{NG-1} \dfrac{\Theta i_{i,m} \cdot \Psi\left(mg_k, mg_m\right)}{\sum_{n=0}^{NG-1} \Theta i_{i,n} \cdot \Psi(mg \ldots, mg \ldots)} \right. \end{array} \right.$$

$$\Gamma i_{i,k} \leftarrow e^{\left[\ldots \sum_{n=0} \ldots (mg_n, mg_m) \right]}$$

$$\text{for } m \in 0..NG-1$$

$$X_m \leftarrow \frac{\sum_{j=0}^{NS-1} \nu_{j,m} \cdot zxy_j}{\sum_{j=0}^{NS-1} \sum_{n=0}^{NG-1} (\nu_{j,n} \cdot zxy_j)}$$

$$\text{for } m \in 0..NG-1$$

$$\Theta_m \leftarrow \frac{Q_m \cdot X_m}{\sum_{n=0}^{NG-1} Q_n \cdot X_n}$$

$$\text{for } k \in 0..NG-1$$

$$\Gamma_k \leftarrow e^{Q_k \cdot \left[1 - \ln\left[\sum_{m=0}^{NG-1} \Theta_m \cdot \Psi(mg_m, mg_k) \right] - \sum_{m=0}^{NG-1} \frac{\Theta_m \cdot \Psi(mg_k, mg_m)}{\sum_{n=0}^{NG-1} \Theta_n \cdot \Psi(mg_n, mg_m)} \right]}$$

$$\gamma RES_i \leftarrow e^{\sum_{k=0}^{NG-1} \nu_{i,k} \cdot (\ln(\Gamma_k) - \ln(\Gamma i_{i,k}))}$$

$$R \cdot T \cdot \ln(\gamma RES_i)$$

<u>logarithmic fugacity coefficient of component i using PR equation of state</u>

$$L\phi_{PR}(i, zxy, T, v) := $$

$$P \leftarrow P_{PR}(zxy, T, v)$$

$$B \leftarrow \frac{b_{mix}(zxy) \cdot P}{R \cdot T}$$

$$u \leftarrow 1.22498$$

$$A \leftarrow \frac{1}{2 \cdot \sqrt{2}} \cdot \ln\left[\frac{u + (1 - \sqrt{2})}{u + (1 + \sqrt{2})} \right]$$

$$z \leftarrow \frac{P \cdot v}{R \cdot T}$$

$$phi0 \leftarrow \left[\frac{2 \cdot \sum_{j=0}^{NS-1} zxy_j \cdot \left[\frac{(bi_i)^{pow} + (bi_j)^{pow}}{2} \right]^{\frac{1}{pow}}}{b_{mix}(zxy)} - 1 \right] \cdot (z - 1)$$

$$phi1 \leftarrow \ln(z - B)$$

$$phi2 \leftarrow \frac{1}{2 \cdot \sqrt{2} \cdot R \cdot T} \cdot \left(\frac{ai(i, T)}{bi_i} + \frac{gEresi(i, zxy, T)}{A} \right)$$

$$phi3 \leftarrow \ln\left[\frac{z + (1 + \sqrt{2}) \cdot B}{z + (1 - \sqrt{2}) \cdot B} \right]$$

$$\text{phi0} - \text{phi1} - \text{phi2} \cdot \text{phi3}$$

Fugacity of component i using PR equation of state, is=0:liquid, is=2:vapor

$$fug_{PR}(zxy, T, P, is) := \begin{array}{|l} A \leftarrow \dfrac{a_{mix}(zxy, T) \cdot P}{(R \cdot T)^2} \\ B \leftarrow \dfrac{b_{mix}(zxy) \cdot P}{R \cdot T} \\ v_{min} \leftarrow b_{mix}(zxy) \\ cf \leftarrow \begin{bmatrix} -\left(A \cdot B - B^2 - B^3\right) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix} \\ Z \leftarrow \text{polyroots}(cf) \\ \text{for } i \in 0..2 \\ \quad \left(Z_i \leftarrow -1\right) \text{ if } \left(\text{Im}\left(Z_i\right) \neq 0\right) \\ Z \leftarrow \text{sort}(Z) \\ v \leftarrow \dfrac{R \cdot T \cdot Z}{P} \\ v_2 \leftarrow \text{if}\left[\left(v_2 < v_{min}\right), v_{min} + 10^{-4} \cdot \dfrac{m^3}{mol}, v_2\right] \\ v_0 \leftarrow \text{if}\left[(is = 0), \text{if}\left[\left(v_0 < v_{min}\right), v_2, v_0\right], v_0\right] \\ \text{for } i \in 0..NS - 1 \\ \quad f_{PR_i} \leftarrow P \cdot zxy_i \cdot e^{L\phi_{PR}\left(i, zxy, T, v_{is}\right)} \\ f_{PR} \end{array}$$

Guess of y and summation of y

$$sum(y, zxy, T, P) := \begin{array}{|l} \varepsilon \leftarrow 0.001 \\ fugl \leftarrow fug_{PR}(zxy, T, P, 0) \\ it \leftarrow 1 \\ y_{sum} \leftarrow \displaystyle\sum_{i=0}^{NS-1} y_i \\ \text{for } i \in 0..NS - 1 \\ \quad y_i \leftarrow \dfrac{y_i}{y_{sum}} \\ \text{for } k \in 0..15 \\ \quad \begin{array}{|l} fugv \leftarrow fug_{PR}(y, T, P, 2) \\ \text{for } i \in 0..NS - 1 \\ \qquad\qquad fugl_i \end{array} \end{array}$$

$$
\begin{array}{l}
\quad y_{new_i} \leftarrow y_i \cdot \frac{}{fugv_i} \\
\quad y_{sum} \leftarrow \sum_{i=0}^{NS-1} y_{new_i} \\
\quad it \leftarrow 0 \\
\quad \text{for } i \in 0..NS-1 \\
\quad\quad it \leftarrow \text{if}\left[\left(\left|y_{new_i} - y_i\right| > \varepsilon\right), it+1, it\right] \\
\quad\quad y_i \leftarrow \frac{y_{new_i}}{y_{sum}} \\
\quad yy_{NS} \leftarrow y_{sum} \\
\quad \text{for } i \in 0..NS-1 \\
\quad\quad yy_i \leftarrow y_i \\
\quad \text{break if } it < 1 \\
yy
\end{array}
$$

Iteration for the bubble point pressure, Pb

$$
P_b(y, zxy, T, P) :=
\begin{array}{l}
\varepsilon_p \leftarrow 1 \cdot Pa \\
dlp \leftarrow 500 \cdot Pa \\
\text{while } |dlp| > \varepsilon_p \\
\quad s_1 \leftarrow sum(y, zxy, T, P)_{NS} \\
\quad P \leftarrow P - \varepsilon_p \\
\quad s_2 \leftarrow sum(y, zxy, T, P)_{NS} \\
\quad dsdp \leftarrow \frac{s_2 - s_1}{\varepsilon_p} \\
\quad dlp \leftarrow \frac{s_2 - 1}{dsdp} \\
\quad P \leftarrow P + dlp + \frac{\varepsilon_p}{2} \\
\quad P \\
P
\end{array}
$$

Iteration for the mole fraction in the vapor phase, y, (algorithm is as same as Pb calculation)

$$
yy(y, zxy, T, P) :=
\begin{array}{l}
\varepsilon_p \leftarrow 1 \cdot Pa \\
dlp \leftarrow 500 \cdot Pa \\
\text{while } |dlp| > \varepsilon_p \\
\quad s_1 \leftarrow sum(y, zxy, T, P)_{NS} \\
\quad P \leftarrow P - \varepsilon_p
\end{array}
$$

$$s0_2 \leftarrow \mathrm{sum}(y, zxy, T, P)$$
$$s_2 \leftarrow s0_{2_{NS}}$$
$$dsdp \leftarrow \frac{s_2 - s_1}{\varepsilon_p}$$
$$dlp \leftarrow \frac{s_2 - 1}{dsdp}$$
$$P \leftarrow P + dlp + \frac{\varepsilon_p}{2}$$
$$y_{d_0} \leftarrow s0_{2_0}$$
$$y_{d_1} \leftarrow s0_{2_1}$$
$$y_d$$

Translated volume

$$v_{VTPR}(y, zxy, T, P) :=$$
$$A \leftarrow \frac{a_{mix}(zxy, T) \cdot P}{(R \cdot T)^2}$$
$$B \leftarrow \frac{b_{mix}(zxy) \cdot P}{R \cdot T}$$
$$v_{min} \leftarrow b_{mix}(zxy)$$
$$cf \leftarrow \begin{bmatrix} -\left(A \cdot B - B^2 - B^3\right) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix}$$
$$Z \leftarrow \mathrm{polyroots}(cf)$$
$$\text{for } i \in 0..2$$
$$\left(Z_i \leftarrow -1\right) \text{ if } \left(\mathrm{Im}\left(Z_i\right) \neq 0\right)$$
$$Z \leftarrow \mathrm{sort}(Z)$$
$$v_0 \leftarrow \frac{R \cdot T \cdot Z_0}{P} - c_{mix}(zxy)$$
$$v_2 \leftarrow \frac{R \cdot T \cdot Z_2}{P} - c_{mix}(y)$$
$$v$$

Guess of saturation pressure for the pure component

$$P_s(i, T) := \quad Tr \leftarrow \frac{T}{T_c}$$

$$\begin{aligned}
&\text{LPsr} \leftarrow 5.373 \cdot (\omega_i + 1) \cdot \left(1 - \frac{1}{\text{Tr}}\right)\\
&P \leftarrow P_{c_i} \cdot e^{\text{LPsr}}\\
&P
\end{aligned}$$

Bubble point calculation

$$\text{xTyP}(xx, T) := \begin{aligned}
&x \leftarrow \begin{pmatrix} xx \\ 1 - xx \end{pmatrix}\\
&P \leftarrow \sum_{i=0}^{NS-1} x_i \cdot P_s(i, T)\\
&\text{for } i \in 0..1\\
&\quad K_{i_i} \leftarrow \frac{P_s(i, T)}{P}\\
&\quad y_i \leftarrow K_{i_i} \cdot x_i\\
&P \leftarrow P_b(y, x, T, P)\\
&y \leftarrow yy(y, x, T, P)\\
&\text{xTyP}_0 \leftarrow \frac{P}{Pa}\\
&\text{xTyP}_1 \leftarrow y_0\\
&\text{xTyP}
\end{aligned}$$

Isothermal VLE of acetone(1) - ethanol (2) at 328.15 K

$T := 328.15 \cdot K$

$i := 1..101$ Number of data points to calculate.

$\text{res}_{0,i} := \frac{i}{101}$ x – values

$\text{res}_{1,i} := \text{xTyP}\left(\frac{i}{101}, T\right)_0$ P – values

$\text{res}_{2,i} := \text{xTyP}\left(\frac{i}{101}, T\right)_1$ y – values

Experimental data (circles and squares): Vinichenko I.G., Susarev M.P., J.Appl.Chem.USSR, 39(7), 1475-1478, 1966

P_exp :=	x_exp :=	y_exp :=
37316.9	0	0
46022.9	0.062	0.217
52489	0.125	0.339
62354.9	0.25	0.504
71727.4	0.375	0.619
77460.3	0.5	0.712
84179.7	0.625	0.791
89206	0.75	0.853
93685.6	0.875	0.928
97392	1	1