

# Evaluation of SAFT and PC-SAFT models for the description of homo- and co-polymer solution phase equilibria

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## Abstract

Statistical associating fluid theory (SAFT) and perturbed-chain SAFT (PC-SAFT) are used to model the phase behavior of polymer–solvent mixtures over a wide temperature and pressure range. Homopolymers (polyolefins) as well as co-polymers are examined. Calculations were performed using various recently proposed robust algorithms for polydisperse polymers. Various polymer properties that affect substantially the phase behavior, such as molecular weight, polydispersity, and macromolecular architecture, were considered. For most of the systems examined, PC-SAFT correlation is marginally closer to experimental data than SAFT. Nevertheless, there are a number of mixtures where SAFT is the preferred model.

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## 1. Introduction

Accurate models for thermodynamic property and phase equilibrium predictions of pure polymers and mixtures over a wide range of temperature and pressure are of extreme importance for the optimization of existing and the design of new processes and/or materials in the chemical process industry [1]. Traditional approaches include empirical correlations for the calculation of single-phase properties and activity coefficient models or cubic equations of state (EoS) for the calculation of phase equilibria [2]. These models are usually accurate over a limited range of conditions and types of systems (pure compounds and mixtures). Polymer systems are more complex than systems of small molecules typically encountered in the petroleum and natural gas industry, due to

the large molecular size difference between polymers and solvents and to the polydispersity of polymers.

The development of novel processes at extreme conditions (as for example processes where one or more of the components is supercritical) and the design of new materials (as for example co-polymers with a specific molecular architecture) over the last two decades imposed the need for new models. At the same time, significant developments in the area of applied statistical mechanics resulted in a number of semi-empirical equations of state, such as the lattice fluid theory (LFT) [3], the perturbed-hard-chain-theory [4] and their modifications. These EoS are more complex than cubic EoS but significantly more accurate for various complex fluids, such as hydrogen bonding fluids, supercritical fluids, and polymers. Furthermore, the tremendous increase of computing power at affordable price made these new complex models attractive for process simulation calculations [5].

A semi-empirical EoS that was developed in the 1990s and has gained considerable popularity both in the academic and the industrial community is SAFT. SAFT was developed based on the thermodynamic perturbation theory (TPT) of Wertheim [6–8]. SAFT was parameterized for a wide range of fluids and shown to correlate accurately multi-component phase equilibria of polymer mixtures at low and high pressure [9]. Significant work was performed over the last 15 years towards the improvement of SAFT, in order to become more accurate for different types of fluid systems (as for example polar fluids,

*Abbreviations* HDPE, high density polyethylene; LDPE, low density polyethylene; PBA, poly(butyl acrylate); PEA, poly(ethyl acrylate); P(E-co-BA), poly(ethylene-co-butyl acrylate); P(E-co-EA), poly(ethylene-co-ethyl acrylate); P(E-co-MA), poly(ethylene-co-methyl acrylate); P(E-co-VAc), poly(ethylene-co-vinyl acetate); PMA, poly(methyl acrylate); PVAc, poly(vinyl acetate).

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co-polymers, electrolytes etc.). A critical review of these developments can be found in [10]. The most promising of these models for polymer mixtures is PC-SAFT [11]. In PC-SAFT, the reference fluid is the hard-chain term whereas in SAFT it is the hard sphere. Recently, Yelash et al. [12] presented some unrealistic phase equilibrium predictions by PC-SAFT for pure components at temperature and density values remote from experimental conditions.

In this work, a direct extensive comparison of the two models is performed for a number of polymer mixtures at different temperatures and pressures. In the majority of polymer processes, polymer(s) is(are) polydisperse. The effect of polydispersity is examined here explicitly. Homo-polymers and co-polymers of variable macromolecular architecture (block, alternating and random) are examined. Recently, developed robust algorithms for polydisperse polymers were implemented for this purpose [13,14].

## 2. The models

SAFT is a perturbation theory where the reference fluid is the hard sphere fluid and perturbation accounts explicitly for chain formation, dispersion interactions and association due to hydrogen bonding or other specific forces. In this work, non-associating fluids are considered and therefore the last term is ignored. Consequently, the compressibility factor,  $Z$ , and the chemical potential of species  $i$ ,  $\mu_i$ , in a mixture are written as

$$Z = \frac{P}{\rho RT} = 1 + Z^{\text{hs}} + Z^{\text{chain}} + Z^{\text{disp}} \quad (1)$$

and

$$\begin{aligned} \frac{\mu_i}{RT} &= \frac{\mu_i^{\text{ideal}}}{RT} + \frac{\mu_i^{\text{res}}}{RT} \\ &= \ln(\rho x_i) + f(T) + \frac{\mu_i^{\text{hs}}}{RT} + \frac{\mu_i^{\text{chain}}}{RT} + \frac{\mu_i^{\text{disp}}}{RT} \end{aligned} \quad (2)$$

where  $P$  is the pressure,  $T$  is the temperature,  $\rho$  is the molar density,  $x_i$  is the mole fraction of species  $i$ , and superscripts ideal, res, hs, chain and disp correspond to ideal gas, residual, hard sphere, chain formation and dispersion, respectively. In PC-SAFT, the reference fluid is the hard chain fluid and perturbation accounts for dispersion interactions. Eqs. (1) and (2) also hold for PC-SAFT, although the mathematical expression for the dispersion term is different.

The mathematical expressions for the pure fluid and mixtures for both models are given in the original publications [7,11,15] and are not repeated here. Both SAFT and PC-SAFT are three parameter EoS for non-associating fluids, that are the number of segments ( $m$ ), the segment dispersion energy ( $u^0/k$ ), and the volume of the spherical segment ( $v^{00}$ ). In PC-SAFT original publication [11], the diameter of the spherical segment,  $\sigma$ , is given which is correlated with  $v^{00}$  through the simple expression  $v^{00} = (\pi N_{A,i} / 6\tau) \sigma^3$ . In this work,  $v^{00}$  is reported for both SAFT and PC-SAFT so that a direct comparison of the parameter values is possible.

The focus of this work is on polydisperse polymer mixtures and co-polymers. For the general case of polydisperse polymers, we follow the formalism of Jog and Chapman [13] and we assume that the mixture consists of  $p$  polymer species and  $s$  solvents. In this way, the number average polymer molecular weight,  $\bar{M}_n$ , is calculated as

$$\bar{M}_n = \frac{\sum_{i=1}^p x_i M_i}{\sum_{i=1}^p x_i} \quad (3)$$

where  $M_i$  is the molecular weight of species  $i$ . Furthermore, parameter  $m_i$  for a polymer species of a given molecular weight is calculated from the expression:  $m_i = \alpha M_i$  where  $\alpha$  is a constant, characteristic for a given polymer. These assumptions result in simplified expressions for the various terms in compressibility factor (Eq. (1)) and chemical potential (Eq. (2)). The working equations for both EoS are given in Appendix A.

Extension of SAFT and PC-SAFT to co-polymers introduces two new variables that characterize the different types of segments [16]. More specifically, the fraction of segments of type  $\alpha$  in chain  $i$ ,  $z_{i\alpha}$ , is defined as

$$z_{i\alpha} = \frac{m_{i\alpha}}{\sum_a m_{i\alpha} (= m_i)} \quad (4)$$

and the bonding fraction  $B_{i\alpha i\beta}$  as

$$B_{i\alpha i\beta} = \frac{n_{i\alpha i\beta}}{m_i - 1} \quad (5)$$

where  $m_{i\alpha}$  is the number of segments  $\alpha$  in chain  $i$ , and  $n_{i\alpha i\beta}$  is the number of bonds between the segments of  $\alpha$  and  $\beta$  in chain  $i$ .  $B_{i\alpha i\beta}$  characterizes the macromolecular co-polymer chain architecture (i.e. alternating, random, block). These two new variables result in modified expressions for the compressibility factor and the chemical potential of the mixture. These expressions are given in Appendix A.

## 3. Phase equilibrium algorithm

An algorithm proposed recently by Jog and Chapman [13] was implemented here for the calculation of phase equilibria in systems containing polydisperse polymers. Solving the equilibrium problem for a polydisperse polymer is a cumbersome task since it involves simultaneous solution of a large number of non-linear equations of the form

$$\mu_i^I = \mu_i^{II} \quad i = 1, \dots, s + p \quad (6)$$

In this case, each fraction of the polydisperse polymer is treated as a separate component. Similar algorithms were proposed previously for cubic EoS [17] and the Sanchez–Lacombe EoS [18]. Some simplifications that are made to reduce the computational effort and are not expected to affect the accuracy of the calculations presented here are: the discrete polymer components have the same segment size  $v^{00}$  and segment interaction energy  $u^0/k$ , the chain length is proportional to molecular weight, and the binary interaction parameter  $k_{ij}$  between all polymer components is zero.

For the case of co-polymer mixtures, all co-polymers were treated as monodisperse polymers. The formalism of Gross et al. [16] was used in this case. The mathematical formalisms for polydisperse homopolymers and monodisperse co-polymers presented here can be combined in order to treat polydispersity in co-polymers explicitly.

## 4. Results and discussion

### 4.1. Polydisperse polymers

SAFT and PC-SAFT were used to correlate the ethylene-polydisperse PE high pressure phase equilibria data of de Loos et al. [19]. The polymer sample examined had  $M_n = 56,000$  and  $M_w = 99,000$ . In order to model such polydispersity, Jog and Chapman [13] proposed a 36-component distribution that was used also in this work. Model parameters for both ethylene and PE were taken from the literature and are shown in Table 1. Furthermore,  $k_{ij}$  assumed the value of 0.0392 for SAFT and of  $0.03464 + 1.9 \times 10^{-5} (T/K)$  for PC-SAFT, as proposed by Bokis and co-workers [20].

The liquid–liquid equilibria (LLE) of the system at 423 and 443 K are shown in Fig. 1(a) and (b). Experimental data together with cloud point (solid line) and shadow point (dashed line) predictions are presented. The molecular weight distribution of the polymer in the second liquid phase that is formed is different from that of the original phase. The total polymer concentration in the second phase determines the shadow point composition. In monodisperse polymers the critical point corresponds to the maximum coexistence pressure. However, for polydisperse polymers the cloud point curve continues to rise to higher pressures that correspond to polymer concentration values well below the critical concentration.

As can be seen in Fig. 1(a) and (b), both models capture reasonably well the experimental behavior. However, SAFT is in better agreement with the experimental data compared to PC-SAFT for both temperatures, and especially at subcritical pressures.

### 4.2. Co-polymers

The formalism for co-polymers presented in Appendix A for SAFT and PC-SAFT was applied to a number of co-polymer solutions. The following systems were examined:

Table 1  
SAFT [22] and PC-SAFT [20] parameters for the polydisperse PE-ethylene system

| EoS     | Component | $m$     | $v^{00}$ (cm <sup>3</sup> /mol) | $u^0/k$ (K) |
|---------|-----------|---------|---------------------------------|-------------|
| SAFT    | PE        | 0.0357M | 12.000                          | 228.36      |
| SAFT    | Ethylene  | 1.464   | 18.157                          | 212.06      |
| PC-SAFT | PE        | 0.0263M | 27.704                          | 252.00      |
| PC-SAFT | Ethylene  | 1.540   | 17.443                          | 180.68      |

$M$  is the molecular weight of the polymer.

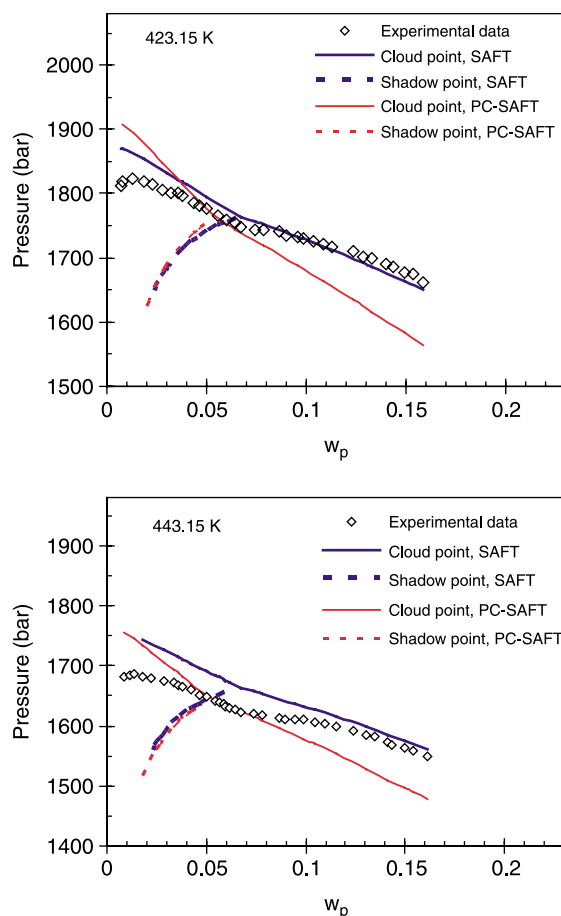


Fig. 1. Isothermal pressure-composition curves for the polydisperse PE-ethylene mixture at 423.15 K (top) and 443.15 K (bottom). Experimental data [19], and SAFT and PC-SAFT predictions.

ethylene-P(E-co-MA), propylene-P(E-co-MA), ethylene-P(E-co-EA), ethylene-P(E-co-BA) and ethylene-P(E-co-VAc). In Table 2, the pure component parameters for the solvents and polymers are given. Model parameters for ethylene and propylene were taken from the literature [7,11]. For polymers, SAFT parameters (with the exception of LDPE and HDPE) were evaluated in this work while for PC-SAFT they were taken from the literature [21]. Finally, a temperature-independent binary interaction parameter was fitted to experimental mixture data and is shown in Table 3.

Ethylene-P(E-co-MA) phase equilibria for different co-polymer compositions are shown in Fig. 2. As the MA content increases from 6 to 13 mol% the cloud point pressure decreases while further MA content increase to 44 mol% increases the pressure substantially. This behavior is captured quantitatively by both SAFT and PC-SAFT. Furthermore, PC-SAFT is more accurate for the 6 and 13 MA mol% while SAFT is more accurate for the high MA content.

The phase behavior changes significantly by shifting from ethylene to propylene (Fig. 3). At low and medium MA content, the cloud point pressure is below 1000 bar while for high MA content and for PMA the equilibrium pressure increases substantially up to close to 3000 bar at temperatures below

Table 2  
SAFT and PC-SAFT parameters for solvents [7,11] and polymers [21, and this work]

| Solvent   | SAFT     |                                 |             | PC-SAFT  |                                 |             |
|-----------|----------|---------------------------------|-------------|----------|---------------------------------|-------------|
|           | $m$      | $v^{00}$ (cm <sup>3</sup> /mol) | $u^0/k$ (K) | $m$      | $v^{00}$ (cm <sup>3</sup> /mol) | $u^0/k$ (K) |
| Ethylene  | 1.464    | 18.157                          | 212.06      | 1.593    | 17.412                          | 176.47      |
| Propylene | 2.223    | 15.648                          | 213.90      | 1.960    | 18.823                          | 207.19      |
| Polymer   |          |                                 |             |          |                                 |             |
| LDPE      | 0.05096M | 12                              | 216.15      | 0.02630M | 27.702                          | 249.50      |
| HDPE      | 0.05096M | 12                              | 216.15      | 0.02630M | 27.702                          | 252.00      |
| PVAc      | 0.05585M | 9.123                           | 225.00      | 0.03211M | 16.697                          | 204.65      |
| PMA       | 0.05100M | 13.192                          | 244.10      | 0.03090M | 18.260                          | 243.00      |
| PEA       | 0.05300M | 14.895                          | 222.12      | 0.02710M | 20.709                          | 229.00      |
| PBA       | 0.05288M | 12.95                           | 204.02      | 0.02590M | 26.247                          | 224.00      |

M is the molecular weight of the polymer.

470 K (Fig. 3 bottom). SAFT and PC-SAFT correlations are reasonably accurate for propylene-PMA but significantly less accurate for propylene-P(E-co-MA).

In Fig. 4, cloud point curves for ethylene-P(E-co-EA) are shown. PC-SAFT correlation is in very good agreement with experimental data. Nevertheless, for the P(E<sub>71</sub>-co-EA<sub>29</sub>) mixture, PC-SAFT predicts a change in the curvature of the phase boundary from convex to concave that is not supported by experimental data. SAFT correlation is less accurate, especially for the ethylene-PEA mixture. In Fig. 5, cloud point curves for ethylene-P(E-co-BA) are shown for two different co-polymer contents. Both models are in good agreement with experimental data, although SAFT is overall closer to the data than PC-SAFT.

The last mixture examined was ethylene-P(E-co-VAc) mixture for 18 wt% VAc in the co-polymer. Experimental data and model correlations are shown in Fig. 6. Both models are in good agreement with the data, with SAFT being more accurate at low polymer composition and PC-SAFT at higher polymer composition.

#### 4.3. Effect of co-polymer macromolecular architecture, co-polymer molecular weight, and concentration on the phase diagram

Both SAFT and PC-SAFT account explicitly for the macromolecular chain architecture and the polymer molecular weight. As a result, an attempt was made to predict the effect of these parameters on the phase diagram of a given co-polymer–

Table 3  
Binary interaction parameter,  $k_{ij}$ , for SAFT and PC-SAFT

| Pair             | SAFT   | PC-SAFT                    |
|------------------|--------|----------------------------|
| Ethylene–LDPE    | 0.054  | 0.04                       |
| Ethylene–HDPE    | 0.0565 | 0.0404                     |
| Ethylene–PMA     | 0.046  | 0.02                       |
| Ethylene–PEA     | 0.044  | 0.0135                     |
| Ethylene–PBA     | 0.047  | 0.03                       |
| Ethylene–PVAc    | 0.09   | 0.04                       |
| Propylene–PMA    | 0.0315 | 0.0127                     |
| Propylene–PE     | 0.028  | 0.0257                     |
| PE seg.–PMA seg. | 0.055  | 0.01161 $x_{MA}$ + 0.04006 |
| PE seg.–PEA seg. | 0.037  | 0.02                       |
| PE seg.–PBA seg. | 0.01   | 0.0                        |
| PE seg.–PVAc     | 0.06   | 0.05                       |

solvent mixture. The mixture chosen was ethylene-P(E-co-MA). In Fig. 7, SAFT and PC-SAFT predictions are shown for 5 wt% of di-block (50 mol% MA) co-polymer in ethylene. Both models predict that as the polymer molecular weight increases the cloud point pressure increases, especially at lower temperatures. The molecular weight effect is considerably

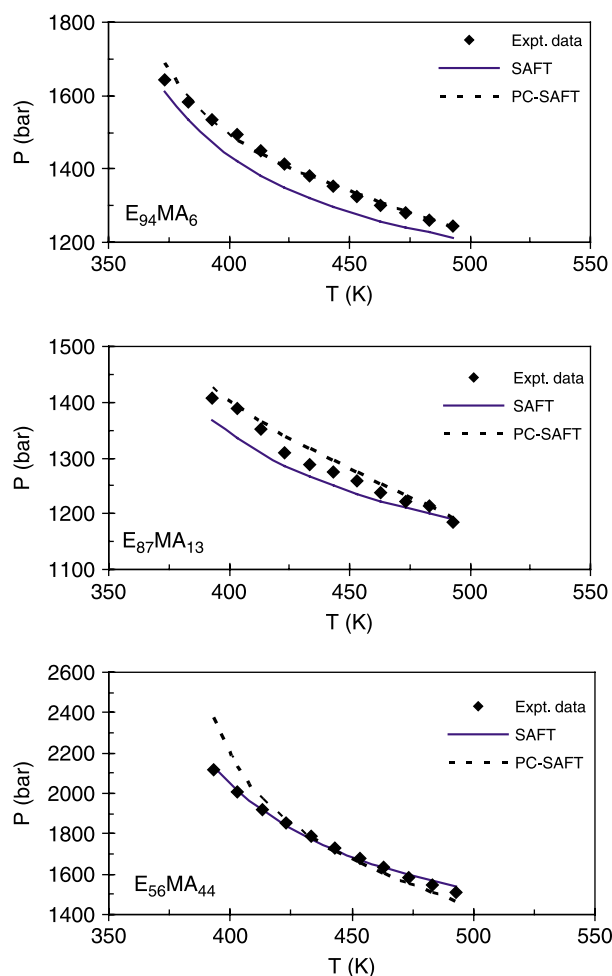


Fig. 2. Cloud point curves for ethylene-P(E-co-MA) mixture for various co-polymer compositions (6, 13, 44 mol% MA from top to bottom). The polymer concentration is 5 wt% and the molecular weights are 128.48, 109.96, 112.54 kg/mol, respectively. Experimental data [21], and SAFT and PC-SAFT predictions.

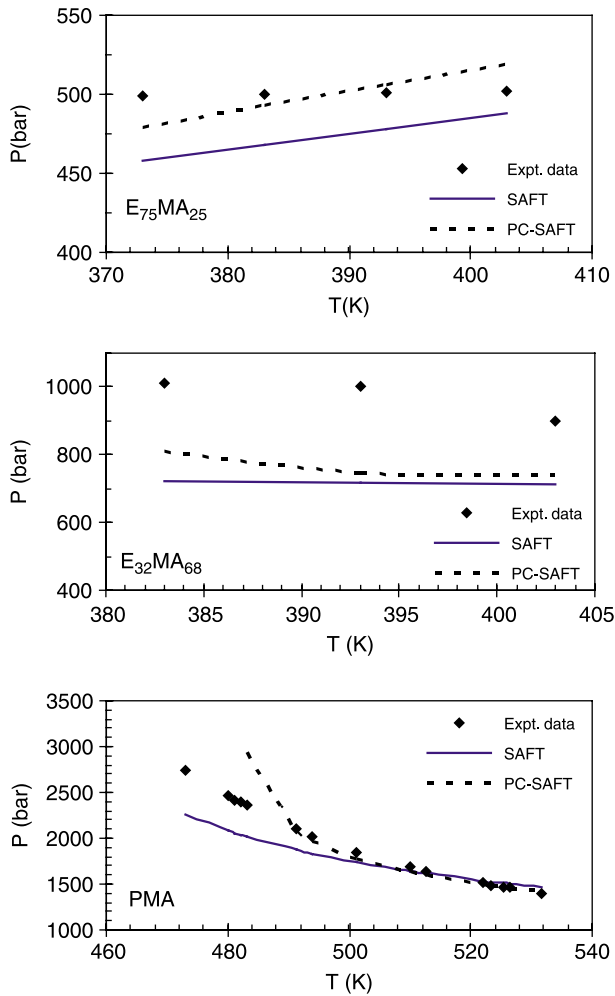


Fig. 3. Cloud point curves for propylene-P(E-co-MA) mixture for various copolymer compositions (25, 68, 100 mol% MA from top to bottom). The polymer concentration is 5 wt% and the molecular weights are 75, 110, 186.94 kg/mol, respectively. Experimental data [21,23] and SAFT and PC-SAFT predictions.

more pronounced in PC-SAFT predictions. Additional calculations were performed for the same mixture by assuming a statistical co-polymer (with 50 mol% MA). Predictions in this case are almost indistinguishable compared to the di-block copolymer and are not shown here. In all cases, the difference in cloud point pressure is less than 0.5% between the two systems.

The final parameter examined was the co-polymer composition of the mixture. In Fig. 8, model predictions are shown for the statistical P(E-co-MA) co-polymer in ethylene at different concentrations. As the polymer weight fraction increases the cloud point pressure decreases. The effect is more pronounced for the case of SAFT. In PC-SAFT, the effect of concentration is marginal, for the weight fraction range examined. Similar results were obtained for the other co-polymers examined in this work, too.

## 5. Conclusions

In this work, SAFT and PC-SAFT were evaluated for the correlation of high pressure polydisperse polymer and

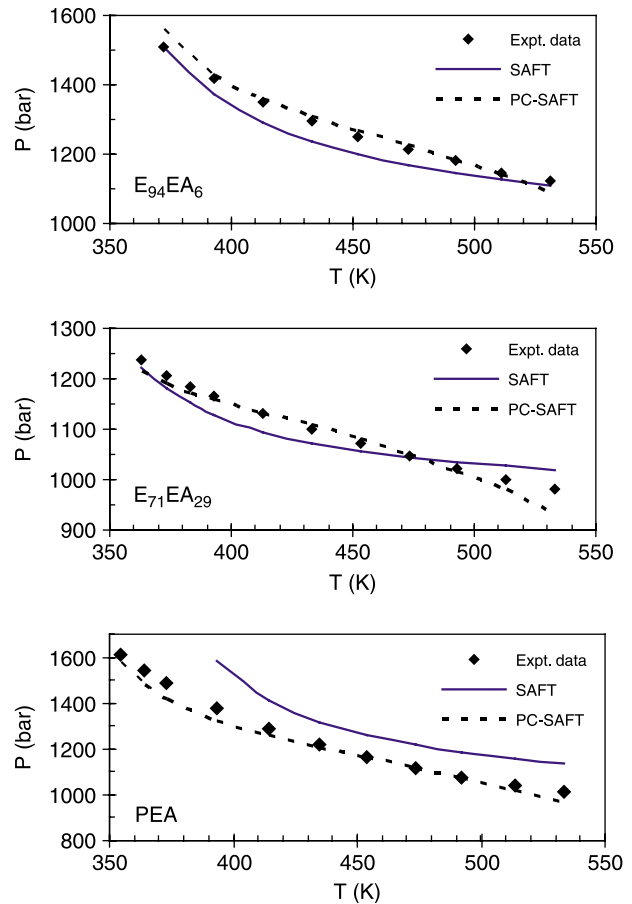


Fig. 4. Cloud point curves for ethylene-P(E-co-EA) mixture for various copolymer compositions (6, 29, 100 mol% EA from top to bottom). The polymer concentration is 5 wt% and the molecular weights are 112.6, 116.7, 153.7 kg/mol, respectively. Experimental data [21] and SAFT and PC-SAFT predictions.

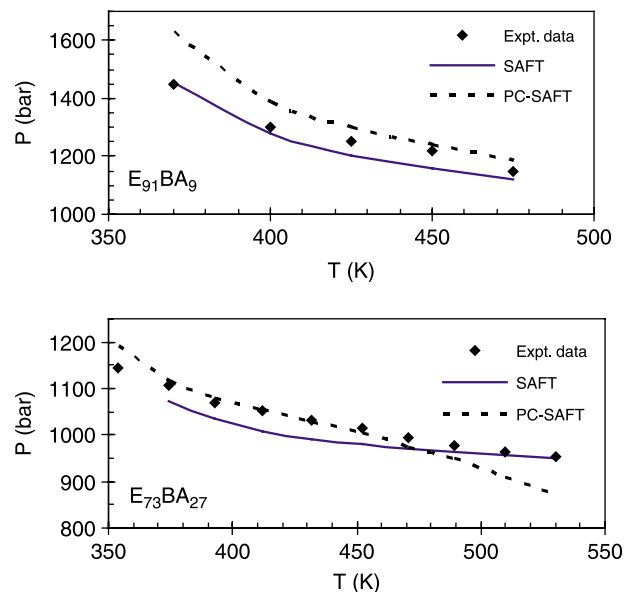


Fig. 5. Cloud point curves for ethylene-P(E-co-BA) mixture for two copolymer compositions (9, 27 mol% BA from top to bottom). The polymer concentration is 5 wt% and the molecular weights are 154.6, 159.5 kg/mol, respectively. Experimental data [21] and SAFT and PC-SAFT predictions.



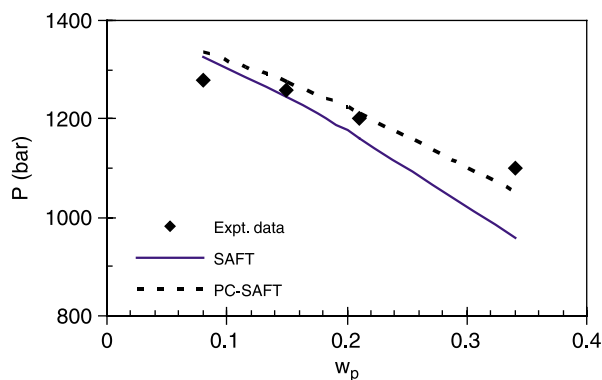


Fig. 6. Cloud point pressure as a function of polymer concentration for ethylene-P(E-co-VAc) mixture at 433 K. The co-polymer composition is 18 wt% VAc and the MW is 126 kg/mol. Experimental data [24] and SAFT and PC-SAFT predictions.

co-polymer mixtures phase behavior. For the majority of the systems examined, both models were in good agreement with experimental data. Based on the systems examined, one cannot make a general argument that one model is preferable over the other. If model parameters are selected carefully, then both models can be used reliably for the prediction of fairly complex macromolecular phase diagrams at extreme conditions.

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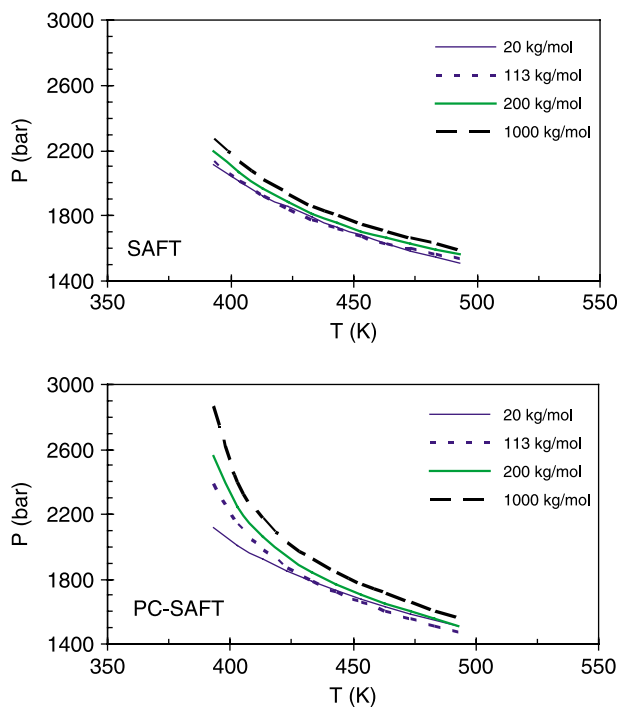


Fig. 7. SAFT (top) and PC-SAFT (bottom) prediction of the effect of MW on the  $P$ - $T$  diagram of ethylene-P(E-co-MA) for diblock macromolecular architecture (50 mol% MA). The polymer concentration is 5 wt%.

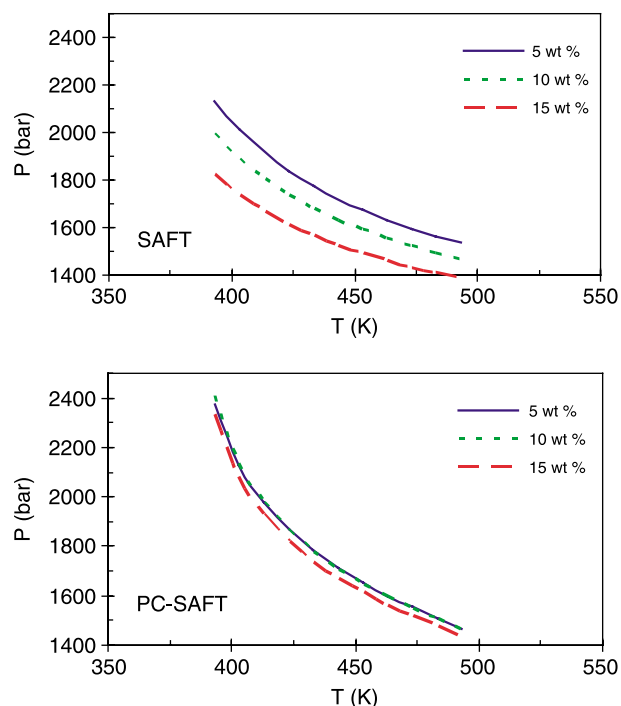


Fig. 8. SAFT (top) and PC-SAFT (bottom) prediction of the effect of polymer concentration on the  $P$ - $T$  diagram of ethylene-P(E-co-MA) for statistical macromolecular architecture (with 50 mol% MA). The polymer MW is 113 kg/mol.

### Appendix A

The working equations are presented here for the compressibility factor,  $Z$ , (Eq. (1)) and the chemical potential,  $\mu$ , (Eq. (2)) for SAFT and PC-SAFT for polydisperse polymer systems and co-polymer systems.

#### A.1. Polydisperse polymers

All of the expressions presented here were taken from [13]. The system consists of  $s$  solvents and  $p$  polymer species, so the total number of components in the system is  $p + s$ .

##### A.1.1. Hard sphere term

The expressions in SAFT and PC-SAFT are identical.

$$\begin{aligned}
 Z^{\text{hs}} &= \frac{P^{\text{hs}}}{\rho RT} = \sum_{i=1}^{p+s} x_i m_i + \frac{2}{3} \pi \rho \sum_{i=1}^{p+s} \sum_{j=1}^{p+s} x_i m_i x_j m_j d_{ij}^3 g_{ij}^{\text{hs}}(d_{ij}) \\
 &= \sum_{i=1}^{p+s} x_i m_i + \frac{2}{3} \pi \rho \left\{ d_{pp}^3 x_p^2 (a \bar{M}_n)^2 g_{pp}^{\text{hs}}(d_{pp}) \right. \\
 &\quad \left. + 2 x_p a \bar{M}_n \sum_{k=1}^s x_k m_k d_{pk}^3 g_{pk}^{\text{hs}}(d_{pk}) \right. \\
 &\quad \left. + \sum_{i=p+1}^{p+s} \sum_{j=p+1}^{p+s} x_i m_i x_j m_j d_{ij}^3 g_{ij}^{\text{hs}}(d_{ij}) \right\} \quad (\text{A1})
 \end{aligned}$$

where

$$x_p = \sum_{i=1}^p x_i \quad (\text{A2})$$

$$g_{ij}^{\text{hs}}(d_{ij}) = \frac{1}{1-\zeta_3} + \left( \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right) \frac{\zeta_2}{(1-\zeta_3)^2} + 2 \left( \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right)^2 \frac{\zeta_2^2}{(1-\zeta_3)^2} \quad (\text{A3})$$

$$\zeta_n = \frac{\pi}{6} \rho \sum_{i=1}^{p+s} x_i m_i d_{ii}^n = \frac{\pi}{6} \rho \left( x_p a \bar{M}_n d_{pp}^n + \sum_{i=p+1}^{p+s} x_i m_i d_{ii}^n \right) \quad n = 0, \dots, 3 \quad (\text{A4})$$

The chemical potential,  $\mu_i$ , for each pseudocomponent can be written as a linear function of the molecular weight

$$\frac{\mu_{i,p}^{\text{hs}}}{RT} = \frac{\mu_A^{\text{hs}}}{RT} + m_i \frac{\mu_B^{\text{hs}}}{RT} \quad (\text{A5})$$

The two terms  $\mu_A$  and  $\mu_B$  are the same for all pseudocomponents. For the hard sphere,  $(\mu_A^{\text{hs}}/RT) = 0$ , and

$$\begin{aligned} \frac{\mu_B^{\text{hs}}}{RT} &= \frac{P^{\text{hs}} d_{pp}^3 \pi N_{Av}}{6RT} - \ln(1-\zeta_3) + \frac{3\zeta_2 d_{pp}}{1-\zeta_3} + \frac{3\zeta_1 d_{pp}^2}{1-\zeta_3} \\ &+ \frac{9}{2} \left( \frac{\zeta_2 d_{pp}}{1-\zeta_3} \right)^2 + 3 \left( \frac{\zeta_2 d_{pp}}{\zeta_3} \right)^2 \left( \ln(1-\zeta_3) \right. \\ &+ \left. \frac{\zeta_3}{1-\zeta_3} - \frac{\zeta_3^2}{2(1-\zeta_3)^2} \right) - \left( \frac{\zeta_2 d_{pp}}{\zeta_3} \right)^3 \\ &\times \left( 2 \ln(1-\zeta_3) + \frac{\zeta_3(2-\zeta_3)}{1-\zeta_3} \right) \end{aligned} \quad (\text{A6})$$

$$\frac{u}{kT} = \frac{\sum_{i=1}^{p+s} \sum_{j=1}^{p+s} x_i m_i x_j m_j v_{ij}^0(u_{ij}/kT)}{\sum_{i=1}^{p+s} \sum_{j=1}^{p+s} x_i m_i x_j m_j v_{ij}^0} = \frac{(x_p a \bar{M}_n)^2 v_p^0(u_p/kT) + 2x_p a \bar{M}_n \sum_{j=p+1}^{p+s} x_j m_j v_{pj}^0(u_{pj}/kT) + \sum_{i=p+1}^{p+s} \sum_{j=p+1}^{p+s} x_i m_i x_j m_j v_{ij}^0(u_{ij}/kT)}{(x_p a \bar{M}_n)^2 v_p^0 + 2x_p a \bar{M}_n \sum_{j=p+1}^{p+s} x_j m_j v_{pj}^0 + \sum_{i=p+1}^{p+s} \sum_{j=p+1}^{p+s} x_i m_i x_j m_j v_{ij}^0} \quad (\text{A14})$$

### A.1.2. Chain term

The expressions in SAFT and PC-SAFT are identical.

$$\begin{aligned} Z_{\text{chain}} &= \frac{P_{\text{chain}}}{\rho RT} = \sum_{i=1}^{p+s} x_i (1-m_i) \rho \frac{\partial \ln g_{ii}^{\text{hs}}(d_{ii})}{\partial \rho} \\ &= x_p (1-a \bar{M}_n) \rho \frac{\partial \ln g_{pp}^{\text{hs}}(d_{pp})}{\partial \rho} \\ &+ \sum_{i=p+1}^{p+s} x_i (1-m_i) \rho \frac{\partial \ln g_{ii}^{\text{hs}}(d_{ii})}{\partial \rho} \end{aligned} \quad (\text{A7})$$

$$\frac{\mu_p^{\text{chain}}}{RT} = \frac{\mu_A^{\text{chain}}}{RT} + m_i \frac{\mu_B^{\text{chain}}}{RT} \quad (\text{A8})$$

where

$$\frac{\mu_A^{\text{chain}}}{RT} = \ln g_{pp}^{\text{hs}}(d_{pp}) \quad (\text{A9})$$

$$\begin{aligned} \frac{\mu_B^{\text{chain}}}{RT} &= x_p (1-a \bar{M}_n) \rho \frac{\partial \ln g_{pp}^{\text{hs}}(d_{pp})}{\partial \rho} \\ &+ \sum_{i=p+1}^{p+s} x_i (1-m_i) \rho \frac{\partial \ln g_{ii}^{\text{hs}}(d_{ii})}{\partial \rho} - \ln g_{pp}^{\text{hs}}(d_{pp}) \end{aligned} \quad (\text{A10})$$

$$\begin{aligned} \frac{\partial g_{ii}^{\text{hs}}(d_{ii})}{\partial \rho_p} &= \frac{\pi N_{Av}}{6} \left( \frac{d_{pp}^3}{(1-\zeta_3)^2} + 3C_{ii} \left( \frac{d_{pp}^2}{(1-\zeta_3)^2} + \frac{2d_{pp}^3 \zeta_2}{(1-\zeta_3)^3} \right) \right. \\ &+ \left. 2C_{ii}^2 \left( \frac{2d_{pp}^2 \zeta_2}{(1-\zeta_3)^3} + \frac{3d_{pp}^3 \zeta_2^2}{(1-\zeta_3)^4} \right) \right) \end{aligned} \quad (\text{A11})$$

and

$$C_{ij} = \frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}} \quad (\text{A12})$$

### A.1.3. Dispersion term

For SAFT, it is

$$Z_{\text{disp}} = \frac{P^{\text{disp}}}{\rho RT} = m \sum_i \sum_j D_{ij} \left( \frac{u}{kT} \right)^i j \left( \frac{\zeta_3}{\tau} \right)^j \quad (\text{A13})$$

where

where

$$u_{ij} = (1-k_{ij})(u_{ii} u_{jj})^{1/2} \quad (\text{A15})$$

$$m = \sum_{i=1}^{p+s} x_i m_i = x_p a \bar{M}_n + \sum_{j=p+1}^{p+s} x_j m_j \quad (\text{A16})$$

For the chemical potential

$$\frac{\mu_{i,p}^{\text{disp}}}{RT} = \frac{\mu_A^{\text{disp}}}{RT} + m_i \frac{\mu_B^{\text{disp}}}{RT} \quad (\text{A17})$$

where

$$\frac{\mu_A^{\text{disp}}}{RT} = 0 \quad (\text{A18})$$

$$\begin{aligned} \frac{\mu_B^{\text{disp}}}{RT} = & \sum_l \sum_j D_{lj} \left(\frac{u}{kT}\right)^l \left(\frac{\zeta_3}{\tau}\right)^j \\ & + \rho m \sum_l \sum_j D_{lj} \left(l \left(\frac{u}{kT}\right)^{l-1} \left(\frac{\zeta_3}{\tau}\right)^j \left(\frac{\partial(u/kT)}{\partial \rho_i}\right)_{T, \rho_{m \neq i}} \right. \\ & \left. + j \left(\frac{u}{kT}\right)^l \left(\frac{\zeta_3^{j-1}}{\tau^j}\right) \left(\frac{\pi N_{Av}}{6} d_{pp}^3\right)\right) \end{aligned} \quad (\text{A19})$$

and  $(\partial(u/kT)/\partial \rho_i)_{T, \rho_{m \neq i}}$  is given by Jog and Chapman [13].

For PC-SAFT, it is

$$\begin{aligned} Z_{\text{disp}} = \frac{P^{\text{disp}}}{\rho RT} = & -2\pi\rho \frac{\partial(\eta I_1)}{\partial \eta} \overline{m^2 u \sigma^3} \\ & - \pi\rho \bar{m} \left(C_1 \frac{\partial(\eta I_2)}{\partial \eta} + C_2 \eta I_2\right) \overline{m^2 u^2 \sigma^3} \end{aligned} \quad (\text{A20})$$

where  $\eta \equiv \zeta_3$ . Furthermore,  $I_1$  and  $I_2$  are power series of  $\eta$  with coefficients that are functions of the chain length [11], and  $C_1$  and  $C_2$  are functions of  $\eta$  and are also given in [11]. Finally

$$\begin{aligned} \overline{m^2 u \sigma^3} = & (x_p a \bar{M}_n)^2 \left(\frac{u_p}{kT}\right) \sigma_{pp}^3 + 2x_p a \bar{M}_n \sum_{j=p+1}^{p+s} x_j m_j \left(\frac{u_{pj}}{kT}\right) \sigma_{pj}^3 \\ & + \sum_{j=p+1}^{p+s} \sum_{k=p+1}^{p+s} x_j m_j x_k m_k \left(\frac{u_{jk}}{kT}\right) \sigma_{jk}^3 \end{aligned} \quad (\text{A21})$$

and

$$\begin{aligned} \overline{m^2 u^2 \sigma^3} = & (x_p a \bar{M}_n)^2 \left(\frac{u_p}{kT}\right)^2 \sigma_{pp}^3 + 2x_p a \bar{M}_n \sum_{j=p+1}^{p+s} x_j m_j \left(\frac{u_{pj}}{kT}\right)^2 \sigma_{pj}^3 \\ & + \sum_{j=p+1}^{p+s} \sum_{k=p+1}^{p+s} x_j m_j x_k m_k \left(\frac{u_{jk}}{kT}\right)^2 \sigma_{jk}^3 \end{aligned} \quad (\text{A22})$$

The chemical potential is expressed as in Eq. (A17) where  $(\mu_A^{\text{disp}}/RT) = 0$  and

$$\begin{aligned} \frac{\mu_B^{\text{disp}}}{RT} = & \pi\rho \left(-2 \left(\frac{\partial I_1}{\partial x_i} \overline{m^2 u \sigma^3} + I_1 \frac{\partial}{\partial x_i} (\overline{m^2 u \sigma^3})\right) \right. \\ & - \overline{m^2 u^2 \sigma^3} \left(C_1 I_2 + \bar{m} I_2 \frac{\partial C_1}{\partial x_i} + \bar{m} C_1 \frac{\partial I_2}{\partial x_i}\right) \\ & \left. - \frac{\partial}{\partial x_i} (\overline{m^2 u^2 \sigma^3}) \bar{m} C_1 I_2\right) \end{aligned} \quad (\text{A23})$$

## A.2. Co-polymers

The expressions for SAFT are based in the work of Banaszak et al. [22] while for PC-SAFT are based in the work of Gross et al. [16].

### A.2.1. Hard sphere term

The expressions in SAFT and PC-SAFT are identical. In the following expressions, subscripts  $i$  and  $j$  denote components and subscripts  $\alpha$  and  $\beta$  denote segment types of the co-polymer.

$$\begin{aligned} Z^{\text{hs}} = & \frac{P^{\text{hs}}}{\rho RT} \\ = & \sum_i x_i m_i + \frac{2}{3} \pi \rho \sum_i \sum_j x_i m_i x_j m_j \sum_{\alpha} \sum_{\beta} z_{i\alpha} z_{j\beta} d_{i\alpha j\beta}^3 g_{i\alpha j\beta}^{\text{hs}}(d_{i\alpha j\beta}) \end{aligned} \quad (\text{A24})$$

$$\begin{aligned} g_{i\alpha j\beta}^{\text{hs}}(d_{i\alpha j\beta}) = & \frac{1}{1-\zeta_3} + \left(\frac{d_{i\alpha} d_{j\beta}}{d_{i\alpha} + d_{j\beta}}\right) \frac{3\zeta_2}{(1-\zeta_3)^2} \\ & + \left(\frac{d_{i\alpha} d_{j\beta}}{d_{i\alpha} + d_{j\beta}}\right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3} \end{aligned} \quad (\text{A25})$$

$$\zeta_n = \frac{\pi N_{Av}}{6} \rho \sum_i x_i m_i \sum_{\alpha} z_{i\alpha} d_{i\alpha}^n, \quad n=0, \dots, 3 \quad (\text{A26})$$

The expression for the chemical potential is identical to the expression in Huang and Radosz [15] where

$$d_{ii}^n = \sum_{\alpha} z_{i\alpha} d_{i\alpha}^n \quad (n=1, 2, 3) \quad (\text{A27})$$

and is not repeated here.

### A.2.2. Chain term

The expressions in SAFT and PC-SAFT are identical. It is

$$\begin{aligned} Z^{\text{chain}} = & \frac{P^{\text{chain}}}{\rho RT} \\ = & \sum_i x_i (1-m_i) \rho \sum_{\alpha} \sum_{\beta} B_{i\alpha i\beta} \left(\frac{\partial \ln g_{i\alpha i\beta}^{\text{hs}}(d_{i\alpha i\beta})}{\partial \rho}\right)_{T,x} \end{aligned} \quad (\text{A28})$$

For the chemical potential of co-polymer  $i$  in a mixture it is

$$\begin{aligned} \frac{\mu_i^{\text{chain}}}{RT} = & (1-m_i) \sum_{\alpha} \sum_{\beta} B_{i\alpha i\beta} \ln g_{i\alpha i\beta}^{\text{hs}}(d_{i\alpha i\beta}) \\ & + \sum_j x_j (1-m_j) \rho \sum_{\alpha} \sum_{\beta} B_{j\alpha j\beta} \left(\frac{\partial \ln g_{j\alpha j\beta}^{\text{hs}}(d_{j\alpha j\beta})}{\partial \rho_i}\right)_{T,V, n_{k \neq i}} \end{aligned} \quad (\text{A29})$$



where

$$\frac{\partial g_{j\omega\beta}^{\text{hs}}(d_{j\omega\beta})}{\partial \rho_i} = \frac{\pi N_{Av}}{6} m_i \left\{ \frac{d_{ii}^3}{(1-\zeta_3)^2} + 3C_{j\omega\beta} \left( \frac{d_{ii}^2}{(1-\zeta_3)^2} + \frac{2d_{ii}^3\zeta_2}{(1-\zeta_3)^3} \right) + 2C_{j\omega\beta}^2 \left( \frac{2d_{ii}^2\zeta_2}{(1-\zeta_3)^3} + \frac{3d_{ii}^3\zeta_2^2}{(1-\zeta_3)^4} \right) \right\} \quad (\text{A30})$$

$$C_{j\omega\beta} = \frac{d_{j\alpha} d_{j\beta}}{d_{j\alpha} + d_{j\beta}} \quad (\text{A31})$$

### A.2.3. Dispersion term

Every repeat unit is characterised by an energetic parameter  $u_{i\alpha}$  while interaction parameters  $k_{i\omega\beta}$  are introduced for pairs of different units  $\alpha$  and  $\beta$  in the same or different chains.

For SAFT, it is

$$Z_{\text{disp}} = \frac{P^{\text{disp}}}{\rho RT} = m \sum_i \sum_j D_{ij} \left( \frac{u}{kT} \right)^i j \left( \frac{\zeta_3}{\tau} \right)^j \quad (\text{A32})$$

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i m_i x_j m_j v_{ij}^0 \sum_{\alpha} \sum_{\beta} (u_{i\omega\beta}/kT)}{\sum_i \sum_j x_i m_i x_j m_j v_{ij}^0} \quad (\text{A33})$$

$$u_{i\omega\beta} = (1 - k_{i\omega\beta})(u_{i\alpha} u_{j\beta})^{1/2} \quad (\text{A34})$$

For PC-SAFT, it is

$$Z_{\text{disp}} = \frac{P^{\text{disp}}}{\rho RT} = -2\pi\rho \frac{\partial(\eta I_1)}{\partial \eta} \overline{m^2 u \sigma^3} - \pi\rho \bar{m} \left( C_1 \frac{\partial(\eta I_2)}{\partial \eta} + C_2 \eta I_2 \right) \overline{m^2 u^2 \sigma^3} \quad (\text{A35})$$

$$\overline{m^2 u \sigma^3} = \sum_i \sum_j x_i m_i x_j m_j \sum_{\alpha} \sum_{\beta} z_{i\alpha} z_{j\beta} \left( \frac{u_{i\omega\beta}}{kT} \right) \sigma_{i\omega\beta}^3 \quad (\text{A36})$$

$$\overline{m^2 u^2 \sigma^3} = \sum_i \sum_j x_i m_i x_j m_j \sum_{\alpha} \sum_{\beta} z_{i\alpha} z_{j\beta} \left( \frac{u_{i\omega\beta}}{kT} \right)^2 \sigma_{i\omega\beta}^3 \quad (\text{A37})$$

For the chemical potential of co-polymer  $i$  in a mixture, it is for the case of SAFT

$$\begin{aligned} \frac{\mu_i^{\text{disp}}}{RT} &= m_i \sum_l \sum_j D_{lj} \left( \frac{u}{kT} \right)^l \left( \frac{\zeta_3}{\tau} \right)^j \\ &+ \rho m \sum_l \sum_j D_{lj} \left( l \left( \frac{u}{kT} \right)^{l-1} \left( \frac{\zeta_3}{\tau} \right)^j \left( \frac{\partial(u/kT)}{\partial \rho_i} \right)_{T,V,\rho_{m \neq i}} \right. \\ &\left. + \left( \frac{u}{kT} \right)^l j \left( \frac{\zeta_3}{\tau} \right)^{j-1} \left( \frac{\pi N_{Av}}{6} m_i d_{ii}^3 \right) \right) \end{aligned} \quad (\text{A38})$$

where

$$\begin{aligned} \left( \frac{\partial(u/kT)}{\partial \rho_i} \right)_{T,V,\rho_{m \neq i}} &= \frac{2 \sum_j m_i x_j m_j v_{ij}^0 \sum_{\alpha} \sum_{\beta} (u_{i\omega\beta}/kT)}{\rho \sum_l \sum_j x_l m_l x_j m_j v_{lj}^0} \\ &- \frac{\sum_l \sum_j x_l m_l x_j m_j v_{lj}^0 \sum_{\alpha} \sum_{\beta} (u_{l\omega\beta}/kT)}{\rho \left( \sum_l \sum_j x_l m_l x_j m_j v_{lj}^0 \right)^2} \left( 2 \sum_j m_i x_j m_j v_{ij}^0 \right) \end{aligned} \quad (\text{A39})$$

For the chemical potential of co-polymer  $i$  in a mixture, it is for the case of PC-SAFT

$$\begin{aligned} \frac{\mu_i^{\text{disp}}}{RT} &= \pi\rho \left\{ -2 \left[ \frac{\partial I_1}{\partial x_i} \overline{m^2 u \sigma^3} + I_1 \frac{\partial}{\partial x_i} (\overline{m^2 u \sigma^3}) \right] \right. \\ &\quad \left. - \overline{m^2 u^2 \sigma^3} \left[ m_i C_1 I_2 + \bar{m} I_2 \frac{\partial C_1}{\partial x_i} + \bar{m} C_1 \frac{\partial I_2}{\partial x_i} \right] \right. \\ &\quad \left. - \frac{\partial}{\partial x_i} (\overline{m^2 u^2 \sigma^3}) \bar{m} C_1 I_2 \right\} \end{aligned} \quad (\text{A40})$$

where all partial derivatives are based on Gross and Sadowski for PC-SAFT [11]

$$\frac{\partial I_1}{\partial x_i} = \sum_{k=0}^6 \left( a_k(\bar{m}) k \frac{\partial \eta}{\partial x_i} \eta^{k-1} + \frac{\partial a_k}{\partial x_i} \eta^k \right) \quad (\text{A41})$$

$$\frac{\partial I_2}{\partial x_i} = \sum_{k=0}^6 \left( b_k(\bar{m}) k \frac{\partial \eta}{\partial x_i} \eta^{k-1} + \frac{\partial b_k}{\partial x_i} \eta^k \right) \quad (\text{A42})$$

$$\frac{\partial a_k}{\partial x_i} = \frac{m_i}{\bar{m}^2} a_{1k} + \frac{m_i}{\bar{m}^2} \left( 3 - \frac{4}{\bar{m}} \right) a_{2k} \quad (\text{A43})$$

$$\frac{\partial b_k}{\partial x_i} = \frac{m_i}{\bar{m}^2} b_{1k} + \frac{m_i}{\bar{m}^2} \left( 3 - \frac{4}{\bar{m}} \right) b_{2k} \quad (\text{A44})$$

$$\frac{\partial}{\partial x_i} (\overline{m^2 u \sigma^3}) = 2m_i \sum_j x_j m_j \sum_{\alpha} \sum_{\beta} z_{i\alpha} z_{j\beta} \left( \frac{u_{i\omega\beta}}{kT} \right) \sigma_{i\omega\beta}^3 \quad (\text{A45})$$

$$\frac{\partial}{\partial x_i} (\overline{m^2 u^2 \sigma^3}) = 2m_i \sum_j x_j m_j \sum_{\alpha} \sum_{\beta} z_{i\alpha} z_{j\beta} \left( \frac{u_{i\omega\beta}}{kT} \right)^2 \sigma_{i\omega\beta}^3 \quad (\text{A46})$$

$$\frac{\partial C_1}{\partial x_i} = C_2 \frac{\partial \eta}{\partial x_i} - C_2^2 \left\{ m_i \frac{8\eta - 2\eta^2}{(1-\eta)^4} - m_i \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \right\} \quad (\text{A47})$$

$$\frac{\partial \eta}{\partial x_i} = \frac{\pi}{6} \rho m_i d_{ii}^3 \quad (\text{A48})$$

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