Uncertainty analysis of the CPA and a quadrupolar CPA equation of state - With emphasis on CO₂

Bjørner, Martin G.; Sin, Gürkan; Kontogeorgis, Georgios M.

Published in:
Fluid Phase Equilibria

Link to article, DOI:
[10.1016/j.fluid.2015.12.037](https://doi.org/10.1016/j.fluid.2015.12.037)

Publication date:
2016

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Bjørner, M. G., Sin, G., & Kontogeorgis, G. M. (2016). Uncertainty analysis of the CPA and a quadrupolar CPA equation of state - With emphasis on CO₂. *Fluid Phase Equilibria*, 414, 29-47.
<https://doi.org/10.1016/j.fluid.2015.12.037>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Uncertainty analysis of the CPA and a quadrupolar CPA equation of state - with emphasis on CO₂

Martin G. Bjørner^{a,*}, Gürkan Sin^b, Georgios M. Kontogeorgis^a

^a*Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark.*

^b*CAPEC-PROCES Research Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 227, DK-2800 Kgs. Lyngby, Denmark.*

Abstract

The parameters of thermodynamic models, such as the cubic plus association (CPA) equation of state, are subject to uncertainties due to measurement errors in the experimental data that the models are correlated to. More importantly as the number of adjustable parameters increase, the parameter estimation problem becomes more complicated due to parameter identifiability issues. In this work the uncertainties in the pure compound parameters of CO₂ are investigated using several different CPA approaches, including a new quadrupolar CPA. The uncertainties are estimated using both least squares estimation and the bootstrap method for parameter estimation. The uncertainties in the parameters estimated from the bootstrap method are propagated to physical property and vapor liquid equilibrium predictions using Monte Carlo simulations.

The results indicate that both the pure compound parameter uncertainty and the propagated uncertainty is negligible for the modeling approaches which employ three adjustable parameters. For modeling approaches with more than three adjustable parameters, however, there may be significant uncertainties in the pure compound parameters, as well as a high degree of correlation between the adjustable parameters. This results in significant propagated errors

*Corresponding author

Email address: mgabj@kt.dtu.dk (Martin G. Bjørner)

for certain output properties. To reduce the uncertainty in the adjustable model parameters the heat of vaporization was included as additional correlation data. This resulted in parameter distributions which followed a normal distribution more closely, however, the correlation between the adjustable parameters remained high. Overall the results indicate, that it is important to report parameter uncertainties together with their correlation matrix when a model is developed, so that better informed decisions can be made, for instance about which model extension, or association scheme should be employed.

Keywords: equation of state, CPA, quadrupole, CO₂, Parameter Estimation, Propagation of uncertainty

1. Introduction

The pure compound parameters of advanced thermodynamic models such as the cubic plus association (CPA) equation of state (EoS) [1] and the Statistical Association Fluid Theory (SAFT) [2] are typically correlated to the saturated vapor pressure and saturated liquid densities using a least squares (LSQ) minimization approach in which, presumably, unique parameters are estimated. Even the most accurate experiments, however, are subject to measurement errors. Moreover the parameters may be correlated, so that a change in one parameter can be compensated by a change in another. Consequently the pure compound parameters will be associated with some degree of uncertainty, which is typically assumed insignificant in the majority of studies thus far. Even small errors in the parameters, however, may significantly affect the result of a simulation [3, 4]. While several researchers have drawn attention to this problem [4–10] surprisingly little work has been done on analysing and quantifying the uncertainty of parameters in thermodynamic models and their effect on physical property and equilibrium calculations.

The work of Whiting and co-workers [3, 11–16] is perhaps one of the most notable contributions to uncertainty estimates of thermodynamic models. Using a Monte Carlo approach the authors analysed the effect of uncertainties in ther-

20 thermodynamic data and their effect on process design. More recently Mathias and co-workers [17–19] also investigated the importance of uncertainty propagation for processes such as CO₂ capture. Hajipour and co-workers [20–22] estimated the critical properties for a large number of hydrocarbons. The authors took both the experimental uncertainty in the data as well as the correlation between
25 thermodynamic model parameters into account. Subsequently the uncertainties of the binary interaction parameters for 87 binary mixtures were estimated by use of the pure compound uncertainties.

Most research has focused on the propagated error from a thermodynamic model to various unit operations such as distillation columns (e.g. [5, 6, 17, 23]).
30 Uncertainty analysis, however, can also be used for model development and comparison; by comparing the uncertainties of selected physical properties and equilibria for different models, we can compare the models more objectively. For instance when models such as CPA and SAFT are compared, they often perform almost identically and what differences are present may, in many cases, be due
35 to statistical uncertainties in the pure compound parameters of the models, rather than due to one model being superior to the other.

In an effort to improve the performance of models such as SAFT and to obtain a physically more correct model, additional terms are often added to the base EoS. The addition of an extra term typically leads to an increase in
40 the number of adjustable parameters. This may make it difficult to estimate unique pure compound parameters due to high correlations between parameters as well as the possible presence of multiple local minima. One reason for this is that the data used for parameter estimation is too limited in relation to the model complexity, which must be able to predict a wide range of properties
45 besides those its parameters are fitted to. This may be particularly relevant for a molecule such as CO₂, for which the vapor pressure curve is very short. Both SAFT and CPA can for instance correlate the saturated vapor pressure and liquid density of CO₂ almost within experimental error, using only the three pure compound parameters commonly employed for non-associating molecules.

50 Unfortunately neither EoS can predict (i.e. $k_{ij} = 0$) the unusual phase be-

havior of mixtures containing CO_2 very well. The reason for this is believed to be, that CO_2 has a large quadrupole moment, which the traditional approaches do not account for. The large quadrupole moment is, for instance, believed to be the reason for the liquid-liquid equilibrium between CO_2 and heavy hydrocarbons. During the past decade several quadrupolar terms have been added to the SAFT framework [24–27]. Unfortunately the new terms are often parametrized by using an additional pure compound parameter (such as an ‘effective’ quadrupolar moment). Other more pragmatic approaches tend to treat CO_2 as a self-associating or solvating molecule. Tsivintzelis et al. [28], for instance, demonstrated that such an approach often works quite well, at the cost of two additional pure compound parameters. If the uncertainties in parameters are significant, however, it may be difficult to compare the performance of various modeling approaches, as their differences may be due to the parametrization, rather than the superiority of one model over the other.

In this work, the uncertainties in the pure compound parameters of CO_2 are systematically evaluated, when different modeling approaches are employed with CPA as the base model. The uncertainty estimates are obtained from either a linear approximation of the covariance matrix of estimated parameters from nonlinear regression (LSQ) or using the Bootstrap method [29]. A Monte Carlo procedure (with latin hypercube sampling (LHS) and Iman-Conover correlation control) is employed to quantify the effect of parameter uncertainty by propagating the uncertainties to various derivative properties and binary equilibrium calculations.

2. Methods

2.1. Parameter estimation - uncertainty and correlation

The pure compound parameters in CPA are typically fitted to saturated pressures and saturated liquid densities using a weighted LSQ objective function. Ideally experimental data should be used for such correlations, however, more often than not, pure compound correlations, such as that of Span and Wag-

ner [30], as implemented in the Reference Fluid Thermodynamic and Transport Properties (REFPROP) program [31] and as disseminated through the National Institute of Standards and Technology (NIST) Chemistry Webbook [32] are employed as pseudo-experimental data, since their correlations are accurate to within experimental error for many compounds. While such pseudo-experimental data are a convenient way of quickly obtaining quite accurate data for many compounds, the measurement errors present in the experimental data is lost. Moreover as the number of model parameters is increased and the closeness of fit improves, there is a clear risk of over-fitting.

In this work we investigate and compare the uncertainty when CO₂ is treated as either an inert (non-associating, non-quadrupolar) molecule, an associating molecule, and as a quadrupolar molecule. In the first two cases regular CPA is employed with and without association (with focus primarily on scheme 4C). In the latter case we employ the quadrupolar CPA (qCPA) which is a recent extension of CPA to quadrupolar fluids suggested by Bjørner and Kontogeorgis [33]. Equations for CPA and qCPA can be found in appendix Appendix A or in the literature [1, 33–36]. Two cases are evaluated when CO₂ is considered to be a quadrupolar molecule, one where no additional adjustable parameter is employed and one where an additional volumetric parameter is employed. Table 1 summarizes the various approaches and the adjustable parameters involved in each approach.

Table 1: Modeling approaches with CPA, including the number of adjustable pure compound parameters, investigated for CO₂.

Designation	Modeling approach	sites on each molecule	no. Adj	Adjustable parameters
A	inert	no sites	3	Γ^a, b_0, c_1
B	2B ^b	one positive, one negative	5	$\Gamma, b_0, c_1, \epsilon, \beta$
C	3B	one positive, two negative	5	$\Gamma, b_0, c_1, \epsilon, \beta$
D	4C	two positive, two negative	5	$\Gamma, b_0, c_1, \epsilon, \beta$
E	Quadrupolar	point quadrupole	3	Γ, b_0, c_1
F	Quadrupolar	point quadrupole	4	Γ, b_0, c_1, b_0^Q

^a $\Gamma = a_0/Rb_0$

^b Terminology from Huang and Radosz [37] .

2.1.1. The least squares method

The LSQ method is a frequentist approach, in which the underlying model parameters are assumed to have true fixed values. However, since experimental data are subject to measurement errors these values can only be estimated by probability distributions of the measurement errors with the aid of statistical estimators [38, 39]. That is, the model parameters are not random but the estimators are, since they depend on the measurements. If it is assumed that the experimental error can be described by a normal distribution with mean equal to the experimental measurement, then the LSQ method is equivalent to minimizing the weighted sum of squares of the difference between measurements (exp) and mathematical model (m):

$$\min \chi^2(\theta) = \sum_{i=1}^N \left(\frac{y_i^{exp} - y_i^m(\theta; T_i)}{\sigma_i^{exp}} \right)^2 \quad (1)$$

where N is the number of experiments, y_i^{exp} is the i th experimental value of an output property, such as the saturated density or saturated pressure, $y_i^m(\theta; T_i)$ represent the results from the model at temperature, T_i , where θ is a vector of adjustable parameters which depends on the modeling approach. The weight of the i th term is given as the inverse variance of the i th measurement, $(\sigma_{exp,i}^2)$. In principle σ is the total standard deviation including both the uncertainty in dependent and independent variables. In this work, however, we assume that the uncertainty in the independent variables is insignificant, which greatly simplifies the data fitting problem.

Under a linear approximation the covariance matrix of parameter estimators can be calculated from [40, 41]

$$Cov(\hat{\theta}) \approx \frac{\chi^2}{N-p} \left(\left(\frac{\partial \mathbf{y}}{\partial \theta} \right)^T \mathbf{V}^{-1} \left(\frac{\partial \mathbf{y}}{\partial \theta} \right) \right)^{-1} \quad (2)$$

where p is the number of estimators, $\mathbf{y}$ is a vector of outputs, and $\mathbf{V}$ is the diagonal variance matrix of measurement errors. The correlation matrix, a normalized symmetric matrix which approximates the correlation between parameters,

is calculated from the covariance matrix (Eq. (2)) as

$$cor(\theta_i, \theta_k) = \frac{Cov(\hat{\theta})}{\sqrt{\text{diag}(Cov(\hat{\theta}))\text{diag}(Cov(\hat{\theta}))}} \quad (3)$$

For large N the $100(1 - \alpha)\%$ confidence interval of the parameters can be approximated by

$$\hat{\theta} \pm t_{N-p}^{\alpha/2} \sqrt{\text{diag}(Cov(\hat{\theta}))} \quad (4)$$

where $t_{N-p}^{\alpha/2}$ is the student's t-distribution corresponding to the $\alpha/2$ percentile and with $N-p$ degrees of freedom. In Eq. (4) it is implicitly assumed that the various parameters are independent of each other. In reality the parameters are correlated resulting in confidence ellipsoids, or hyper-ellipsoids.

115 2.1.2. Bootstrap technique for uncertainty of parameter estimators

The LSQ method is by far the most well-known approach for parameter estimation. There are, however, several alternative parameter estimation methods. One of these is a method called bootstrap [29]. The basic idea of the bootstrap method is that it relies on random sampling with replacement of the residuals,
120 to generate a number of synthetic pseudo-experimental data sets. Since the development of the method by Efron [29] several bootstrapping schemes have been suggested. In this work we employ one of the variants used for regression problems, namely re-sampling of residuals. This scheme consists of four main steps;

125 **Step 1** Input parameters are correlated to the experimental data using Eq. (1) as the objective function.

Step 2 Residuals from the correlation are randomly sampled (with replacement) and added to the previously correlated output values.

Step 3 The parameters are refitted to the new synthetic data. Step 2 and 3 is
130 repeated a large number of times to simulate repeated experimental runs.

Step 4 The distribution of regressed mean estimators are evaluated to obtain confidence regions and parameter correlations.

If the underlying distribution of errors is close to the normal distribution, bootstrapping usually gives results similar to the LSQ approach. An advantage of
135 bootstrapping, however, is that it does not make any assumption with respect to the underlying distribution of errors [42].

2.2. Propagation of Parameter Uncertainty to Model Predictions

Uncertainty associated with the predictions from thermodynamic models can generally be classified as; (a) *input uncertainty* and (b) *structural uncertainty*
140 (or *model error*). The structural uncertainty deals with the mathematical form of the EoS, since all models, no matter their complexity, are only an approximation of the real physical system. The input uncertainty, on the other hand, represents the uncertainty in adjustable parameters mainly due to uncertainty in the experimental data, and the method employed to find these parameters
145 [13, 43]. The uncertainty in adjustable parameters will propagate through the model and will affect the accuracy of model outputs.

One popular method used for error propagation is Monte Carlo analysis. The Monte Carlo analysis is based on multiple model evaluations using inputs sampled from their corresponding uncertainty which is usually described by a
150 certain distribution function (uniform, normal, etc.). The main advantage of the Monte Carlo procedure is that uncertainty results can be obtained directly from the model in question without the need for calculation of the Jacobian matrix which is required by linear error propagation. It is thus conceptually easy to implement and, perhaps most importantly for this work, it can be used
155 to propagate uncertainties through a sequence of models without the need for modifications to the original model.

2.2.1. A Monte Carlo uncertainty analysis

For notational convenience assume that the desired output property from any of the equations of state under investigation can be represented by a function of the form

$$\mathbf{y} = \mathbf{f}(\theta, \mathbf{n}, P, T) \quad (5)$$

where $\mathbf{y}$ is a vector of output model predictions, θ is a vector of model inputs and $\mathbf{n}$, P and T are the composition vector, pressure and temperature respectively. The expression in Eq. (5) may represent not only the equation of state but a sequence of linked models or expressions needed to calculate a desired output property. For instance f may represent a dew or bubble point calculation.

Monte Carlo uncertainty analysis is based on performing multiple model evaluations of a function of the form in Eq. (5) with inputs sampled from a probabilistic distribution. The Monte Carlo uncertainty analysis involves four steps [43]:

Step 1 Specification of the range and underlying probability distribution of the input variables.

Step 2 Sampling from the input range and distribution specified in the first step, to simulate parameters obtained from repeated experimental runs.

Step 3 Evaluation of Eq. (5) for each input sample.

Step 4 Representation and interpretation of results.

In this work we employ the (kernel) probability density functions of the input variables as estimated from the bootstrapped subsamples. Commonly used methods to take samples from the input space in step 2 are; random sampling, shifted Hammersley sampling [44], equal probability sampling [13] and LHS [45]. In this work the samples are chosen using LHS sampling. Input parameter correlation is induced by applying the Iman-Conover correlation control method [46]. Additional introductions to Monte Carlo analysis are available elsewhere e.g. [47–50] and references herein.

3. Results and Discussion

3.1. Parameter estimation - uncertainty and correlation

The pure compound parameters of approaches A-F were correlated to the experimental saturated liquid density and saturated vapor pressures using Eq. (1)

185 as the objective function. The very accurate data from Duschek et al. [51] are used for the saturated liquid density (below 295 K the experimental uncertainty is estimated to less than $\pm 0.015\%$). For the saturated vapor pressure we employ data from [51–53] (experimental uncertainty estimated to $\pm 0.016–0.012\%$, ± 100 Pa and $\pm 0.1\%$ respectively). It is assumed that the standard deviation,
 190 σ_i^{exp} , of each experimental point can be approximated by the experimental uncertainties given in the references.

3.1.1. Least Squares estimation

Table 2 summarizes the estimated parameters for each modeling approach. We note that, as expected from the work of Tsivintzelis et al. [28] and Bjørner
 195 and Kontogeorgis [33], excellent agreement to saturated vapor pressures and saturated liquid densities are obtained for all approaches. With the exception of association scheme 2B the parameters for approach A-D are similar to those presented by Tsivintzelis et al. [28]. The small difference in parameters can probably be explained by the slightly different objective function and the use
 200 of experimental data for the correlation, rather than pseudo-experimental data. The deviations generally decrease when CO_2 is treated as either an associating or a quadrupolar compound. For approaches with four or five parameters the excellent correlations, however, may simply be due to the added flexibility of additional model terms and parameters. The good correlations which are already
 205 obtained for the approaches using only three adjustable parameters (A and E) suggest that models with more parameters are over-parameterized, which in turn reduces the reliability of the obtained parameters (see tables 4 and 5).

Tables 3-6 show the estimated parameter uncertainty, the correlation matrix between the parameters and the mean estimate for modeling approaches B, D,
 210 E and F. The confidence intervals are presented as a percentage of its mean estimator. Only the lower triangular part of the symmetric correlation matrix is shown.

It can be seen from table 3 that small confidence intervals are obtained as well as low correlations between b_0 and both Γ and c_1 for approach E. A

Table 2: Correlated pure compound parameters and %AADs in saturated liquid density and saturated pressure for CO₂ with the CPA EoS (Approaches A-D) and the qCPA (Approaches E-F). The parameters are correlated in the temperature range $T_r = 0.7 - 0.9$.

Designation	Approach	b_0 mL/mol	$\Gamma(a_0/(Rb_0))$ K	c_1 -	$\beta \cdot 1000$ -	ϵ/R K	b_0^Q mL/mol	$\%AAD^a$ in P^{sat}	$\%AAD^a$ in ρ^{liq}
A	n.a.	27.3	1550	0.77	-	-	-	0.18	0.95
B	2B	26.9	1145	0.43	42.3	1089	-	0.07	0.11
C	3B	28.1	1310	0.64	34.7	671	-	0.06	0.10
D	4C	28.4	1329	0.66	25.7	513	-	0.07	0.10
E	Quad	27.9	1284	0.68	-	-	-	0.13	0.46
F	Quad	28.5	1027	0.60	-	-	20.2	0.12	0.07

$$^a\%AAD = \frac{100}{N^{exp}} \sum_i^{N^{exp}} \left| \frac{x_i^{calc} - x_i^{exp}}{x_i^{exp}} \right| \text{ where } x \text{ stands for } P^{sat} \text{ or } \rho^{liq} \text{ and } N^{exp} \text{ is the number of experimental data.}$$

Table 3: Estimated CO₂ parameters, uncertainty as a 95% confidence interval (CI) in percent of the parameter estimate, and parameter correlation matrix when modeling approach **E** is employed.

θ	Estimator	95% CI (%)	Correlation matrix		
			b_0	Γ	c_1
b_0	27.9	0.08	1		
Γ	1284	0.13	0.29	1	
c_1	0.68	0.77	-0.01	-0.95	1

215 higher correlation is observed between Γ and c_1 . This is probably the reason for the slightly larger confidence interval of the c_1 parameter. The correlation is unsurprising considering that these two parameters are closely related in the attractive Soave-Redlich-Kwong (SRK) term (see Eq. (A.5) in Appendix A). Similar results are obtained when CO_2 is modelled as an inert (approach A).

Table 4: Estimated CO_2 parameters, uncertainty as a 95% confidence interval (CI) in percent of the parameter estimate, and parameter correlation matrix when modeling approach **F** is employed.

θ	Mean estimator	95% CI (%)	Correlation matrix			
			b_0	Γ	c_1	b_0^Q
b_0	28.5	0.09	1			
Γ	1027	1.19	-0.98	1		
c_1	0.60	0.63	-0.91	0.91	1	
b_0^Q	20.2	1.15	-0.98	0.99	0.92	1

220 The results for approach F, shown in table 4, indicate that when one additional adjustable parameter is added to the model, all model parameters become highly correlated. That is, a small change in one parameter can be compensated by a change in another parameter. This suggests that the model is over-parametrized making it difficult, if not impossible, to uniquely identify its
 225 parameters. The large correlations, however, have not increased the estimated confidence intervals significantly, which may suggest that the parameters are also highly sensitive. This may indicate that such model extensions are undesirable, at least when it comes to parameter estimation, even if they have the potential to improve model predictions.

230 When CO_2 is modelled as an associating species (approaches B-D) there are even more adjustable parameters. Due to the added flexibility from the parameters, we would also expect the approaches with association to be highly correlated. It turns out, however, that the degree of correlation depends very much on the chosen association scheme. Tables 5 and 6 show the confidence

Table 5: Estimated CO₂ parameters, uncertainty as a 95% confidence interval (CI) in percent of the parameter estimate, and parameter correlation matrix when modeling approach **D** is employed.

θ	Mean estimator	95% CI (%)	Correlation matrix				
			b_0	Γ	c_1	β	ϵ
b_0	28.4	0.06	1				
Γ	1329	0.79	-0.47	1			
c_1	0.66	4.96	-0.24	-0.69	1		
β	25.7	22.65	-0.10	-0.80	0.97	1	
ϵ	512.7	9.63	0.26	0.68	-0.99	0.98	1

intervals and correlation matrices for the 4C and 2B association scheme respectively. When the 2B scheme is employed high correlations are obtained between all parameters. On the other hand, when the 4C scheme is employed only the association parameters (β and ϵ) and the c_1 parameter are highly correlated with each other. It is suspected that the correlation between these three parameters are due to the fact, that they all incorporate part of the models temperature dependence (see Eq. (A.5) and (A.8) in appendix Appendix A). As a consequence of the high correlations, relatively high confidence intervals are obtained for these parameters.

The high parameter correlations indicate that it is not possible to uniquely determine all the adjustable parameters with approaches B-D and F. That is, the parameters are not unique but depend on each other, this means that one should be careful about attaching too much physical meaning to the actual parameter values. Essentially the obtained mean estimators merely constitute a set of values, amongst many possible sets, which provide a good fit to the saturation data. This may be due to the model structure or because the data is too limited in relation to the model complexity [38, 41]. Since excellent correlations are obtained with only three adjustable parameters, we suspect that the latter possibility is predominant. However, the model structure clearly matters a

great deal, as the identifiability problems are much more significant when the
255 2B association scheme is employed rather than the 4C or 3B association schemes.
This indicates that the 2B scheme is less suited to model CO₂ than the 4C and
3B scheme. It is interesting to note that Tsivintzelis et al. [28] arrived at the
same conclusion by evaluating the phase equilibria of a large number of binary
mixtures.

Table 6: Estimated CO₂ parameters, uncertainty as a 95% confidence interval (CI) in percent
of the parameter estimate, and parameter correlation matrix when modeling approach **B** is
employed.

θ	Mean estimator	95% CI (%)	Correlation matrix					
			b_0	Γ	c_1	β	ϵ	
b_0	26.9	3.33	1					
Γ	1145	10.53	0.99	1				
c_1	0.43	38.27	0.99	0.99	1			
β	42.3	16.82	0.97	0.97	0.99	1		
ϵ	1089	19.53	-0.99	-0.99	0.99	0.99	1	

260 3.1.2. Parameters from the Bootstrap method

The bootstrap method for parameter estimation gives a distribution of pa-
rameter sets generated by the, slightly, different synthetic data sets. Figure 1
shows the obtained distribution of input parameters for approach E as a his-
togram, with the number of occurrences on the left y-axis, and as the estimated
265 probability density function (right y-axis). From figure 1 we see that the dis-
tributions of all input parameters follow a normal distribution quite accurately,
and we would expect the mean value of the input parameters to be similar to
those obtained from LSQ. Indeed by comparing figure 1 with table 3 we see that
the mean input parameters are almost identical to those obtained from the LSQ
270 estimation. The main difference is, that distributions from bootstrapping are
somewhat wider than the confidence intervals obtained from LSQ estimation.

Figure 1: Histograms approximating the distribution of each parameter (left y-axis), obtained from 500 re-sampled bootstraps, using modeling approach **E** for CO_2 . The full red lines show the estimated probability density function (right y-axis).

Figure 2: 95% confidence ellipsoids for the bootstrapped parameters of CO_2 when modeling approach **E** is employed. Each dot represents a realized parameter combination and each subfigure represents the dependency (if any) of one parameter on another.

Figure 2 visualizes the correlation between certain parameters by plotting each input parameter as a function of another input parameter. The ellipsoids in figure 2 represent 95% confidence intervals. The closer an ellipsoid is to a circle the more random is the parameter pair, and thus the weaker the correlation between the two. It is clear from the figure that there is almost no correlation between Γ and b_0 and c_1 and b_0 , while the value of Γ and c_1 depend on each other. This is consistent with the results in table 3 for LSQ estimation. Almost exactly the same conclusion can be made when approach A is employed. Both modeling approaches employ only three adjustable parameters.

Figures 3 and 4 show the bootstrapping results with approach F. It is clear from figure 3 that the input parameter distributions are no longer normal, rather it looks like the distribution of all input parameters are bimodal. That is, there

are two distinct peaks, or modes, in the distributions. This may suggest that
285 there are two different major minima in the objective function depending on
the generated synthetic data. Given the highly non-linear nature of equations of
state, and the fact that problems of multiple minima are not uncommon [54, 55],
it does not seem unlikely that multiple modes exist. If we compare these results
with table 4 it is obvious that the parameter set obtained with the LSQ method
290 does not correspond with any of the modes in figure 3. Moreover, the confidence
regions for the parameters are clearly much wider for the bootstrap than for
the LSQ method. That is, we are in a situation where both the parameters
and confidence regions are different between the two estimation methods. As
bootstrapping uses information in the data, rather than an assumption about
295 normality of the errors, we might expect this estimate to be more correct.

Figure 4 shows, unsurprisingly, that b_0^Q and b_0 are highly correlated. It is
more surprising that the energetic parameter, Γ , is highly correlated with b_0 as
well as b_0^Q . We suspect that this is due to the fact that the quadrupolar term is
an attractive energetic term, and since b_0^Q is the only adjustable parameter in
300 the quadrupolar term, Γ scales with this parameter as well, so as to balance the
two attractive terms. This in turn means that b_0 and Γ becomes intercorrelated.

Figure 5 shows the bootstrapping results with approach D. It is obvious from
the figure that the distribution of b_0 and Γ appears to follow a normal distribu-
tion, with relatively narrow parameter ranges. Both parameters and confidence
305 intervals are similar to the confidence intervals calculated with LSQ estimation.
The remaining parameter distributions, however, appear to follow bimodal dis-
tributions. Although not shown both LSQ estimation and bootstrapping tend
to agree about the degree of correlation between parameters.

Figure 3: Histograms approximating the distribution of each parameter (left y-axis), obtained from 500 re-sampled bootstraps, using modeling approach $\mathbf{F}$ for CO_2 . The full red lines show the estimated probability density function (right y-axis).

Figure 4: 95% confidence ellipsoids for the bootstrapped parameters of CO_2 when modeling approach **F** is employed. Each dot represents a realized parameter combination and each subfigure represents the dependency (if any) of one parameter on another.

Figure 5: Histograms approximating the distribution of each parameter (left y-axis), obtained from 500 re-sampled bootstraps, using modeling approach **D** for CO₂. The full red lines show the estimated probability density function (right y-axis).

3.2. Propagation of parameter estimation errors to property prediction

310 To estimate the effect of the input parameter uncertainty on output properties for the various modelling approaches, 500 Monte Carlo input parameter samples are generated using the LHS and Iman-Conover correlation control method [43]. Each subsample is subsequently used to calculate output properties of interest. It is assumed that the error distribution of the input parameters follow the kernel distribution obtained from bootstrapping, although
315 a normal distribution with mean and standard deviation from the bootstrapped results would have been sufficient for approach A and E. All pure compound pseudo-experimental data is obtained from the Span and Wagner EoS [30] as implemented in REFPROP [31].

320 Figure 6 shows the propagated uncertainty of the saturated liquid density (one of the fitted properties) for approaches A, D, E and F. Very low propagated uncertainties are predicted especially by approaches D, E and F. In fact, the largest uncertainty is observed when CO_2 is treated as an inert (Figure 6a). It may initially seem counter intuitive that the model with the largest uncertainty
325 in the saturated density, is in fact the simplest of the approaches. The reason for this is, that when CPA is considered an inert the correlation is not quite as good, resulting in a range of realizations which favour either the high or low density region. This effect is reflected in the propagated uncertainty. That almost no uncertainty is observed for the output properties which the model
330 parameters are correlated to, however, does not mean that the range of input parameter sets does not incur uncertainty in other outputs, which may depend on the inputs in a different way.

It is well-known that the isochoric heat capacity is a challenging property to predict even with modern equations of state [33, 56]. It is believed that this
335 is primarily due to structural issues with the temperature dependence of the equations of state. It is possible, however, that at least part of the problem can be explained by uncertainties in the parameters. Figures 7 and 8 map the input uncertainty onto the residual isochoric and isobaric heat capacity at saturation respectively. From both plots we see that the uncertainty is significant

(a) Approach A.

(b) Approach D.

(c) Approach E.

(d) Approach F.

Figure 6: Propagated uncertainty in the model predictions for the liquid density at saturation. Approach A (a), D (b), E (c) and F (d) is employed. Grey lines represent the simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. As the simulations, and their mean are almost identical the lines are difficult to see. Blue circles are pseudo-experimental data from Span and Wagner [30].

340 for approach D, smaller, but still present, for approaches E and F and almost
 non-existent for approach A. This illustrates how larger uncertainty in input
 parameters, e.g. for the approaches using more adjustable parameters, result in
 higher uncertainties in the non-fitted derivative properties. The large uncertain-
 ties for the isochoric heat capacity in figure 7b suggest that the uncertainty in
 345 pure compound parameters lead to significant uncertainties in the temperature
 derivatives of the equation of state. This should be non-surprising as the three
 most uncertain parameters in approach D are parameters responsible for the
 temperature dependence (c_1, ε, β) (Eq. (A.5) and (A.8)). This may, in part,
 explain why C_V^{res} is such a difficult property to calculate for many equations
 350 of state [33, 56]. However, the deviation from the pseudo-experimental data is
 so large, that at least part of the deviation is expected to be due to structural
 uncertainty rather than input uncertainty. It is somewhat surprising that CPA
 with CO₂ as an inert molecule, models C_V^{res} so well, while none of the more
 sophisticated equations of state yield particularly good results.

355 Due to the relation between C_V^{res} and C_P^{res} (see Appendix B) uncertainties in
 C_V^{res} should lead to, at least, similar sized uncertainties in C_P^{res} . The uncertainty
 in figure 8 is of the same magnitude as that in figure 7, which suggests that the
 input uncertainty does not lead to significant additional uncertainties in the
 ratio between the $(\partial P/\partial T)^2$ and $\partial P/\partial V$ derivatives. As opposed to the results
 360 for C_V^{res} we see that the more advanced approaches all estimate C_P^{res} rather well
 within the input uncertainty, while the calculations when CO₂ is treated as an
 inert compound fail to follow the trend of the pseudo-experimental data. We
 may note, however, that while approaches D, E and F capture the right trend of
 C_P^{res} as a function of temperature, the only reason that the predictions represent
 365 the experimental data so well, is the off-set cause by the poor representation
 of C_V^{res} , thus some cancellation of error must occur between C_V^{res} and the ratio
 $(\partial P/\partial T)^2/\partial P/\partial V$.

One of the primary objectives of most equations of state is the accurate
 description of phase equilibria [56, 57]. It is therefore of particular interest
 370 to investigate how the input uncertainty affects the prediction of vapour liq-

(a) Approach **A**.

(b) Approach **D**.

(c) Approach **E**.

(d) Approach **F**.

Figure 7: Propagated uncertainty in the model predictions for the residual isochoric heat capacity of CO_2 at saturation, employing approach **A** (a), **D** (b), **E** (c) and **F** (d). Grey lines represent the simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. Pseudo-experimental data from Span and Wagner [30].

(a) Approach **A**.

(b) Approach **D**.

(c) Approach **E**.

(d) Approach **F**.

Figure 8: Propagated uncertainty in the model predictions for the residual isobaric heat capacity of CO_2 at saturation, employing approach **A** (a), **D** (b), **E** (c) and **F** (d). Grey lines represent the simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. Pseudo-experimental data from Span and Wagner [30].

uid equilibrium (VLE). In this work we only take the input uncertainty in the CO_2 parameters into account, and ignore the input uncertainty of the other component. The mixtures investigated are two CO_2 +hydrocarbon mixtures.

Hydrocarbons are modelled with only three parameters (approach A) and the
 375 predictions of binary hydrocarbon+hydrocarbon mixtures, are generally quite accurate. It is thus expected, that the error in their parameters are negligible, and that almost all sources of error in mixtures of CO_2 and hydrocarbons are due to the quadrupolar CO_2 molecule.

Figures 9-10 show the propagated input uncertainty on the CO_2 +ethane and
 380 CO_2 +propane VLEs at 250K and 230K respectively. The small quadrupolar moment of ethane is ignored. All VLE plots are predictions ($k_{ij} = 0$). The uncertainty with approaches A and E, both of which have three input parameters, is negligible. The model error with approach A, however, is significant, illustrating the need for improved modeling approaches. All other model approaches
 385 qualitatively predict the azeotrope in figure 9 and improve the representation of the CO_2 +propane VLE.

The output uncertainty with approach D for the VLE is quite small, which is in contrast to the uncertainties in the pure compound heat capacities. On the other hand, while uncertainties in the pure compound derivative properties
 390 were small to moderate for approach F, they are clearly significant for the liquid phase of the VLE systems. The uncertainty depends on the mole fraction of CO_2 , with the largest uncertainty in model output being around $x_{\text{CO}_2} = 0.5$. It is noteworthy that while the uncertainties in the VLE systems are significant for approach F, it is the only model which could accurately predict the data
 395 within its 95% percentile.

In any case, the results show that for models such as the qCPA and CPA with association a simple LSQ estimation may not give the optimal parameters in terms of phase equilibrium predictions, as the input uncertainty results in significant output uncertainties. It is worth noting that it is the same parameter
 400 set which generate the best (closest to the the experimental data) prediction in figures 9-10. It is thus possible to find a parameter set, which generates

excellent predictions for the VLE of CO₂+alkanes, based only on uncertainties in the input parameters.

Figure 9: Propagated uncertainty in the model predictions for the CO_2 +ethane VLE at $T=250\text{K}$. Employing approach **A** (a), **D** (b), **E** (c) and **F** (d). Grey lines represent the simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. Experimental data from [58].

Figure 10: Propagated uncertainty in the model predictions for the CO_2 +propane VLE at $T=230\text{K}$. Employing approach **A** (a), **D** (b), **E** (c) and **F** (d). Grey lines represent the Monte Carlo simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. Experimental data from [59].

3.3. The effect of adding additional output properties

405 The high degree of correlation, and the complex distributions obtained from bootstrapping may suggest that the data used for parameter estimation is too limited in relation to the model complexity.

One way to address this problem is to add more pure compound or binary data to the LSQ regression. Several authors have proposed extended fitting
410 procedures [56, 60–62], where for instance properties such as the heat of vaporization or the speed of sound has been used in the objective function.

In order to investigate how the addition of another property in the objective function affects the parameter distribution, we re-estimate the input parameters of CO₂ to the heat of vaporization, in addition to the saturated vapor pressures
415 and liquid densities. Here we investigate approaches D and F only, as the parameters with approaches A and E were well-defined, and any change in these parameters will probably be at the cost of the density and/or vapor pressure description.

It is clear from figure 11 that the distribution of the new input parameters
420 is nearly normal, which is in clear contrast to the parameter distribution in figure 3 which showed evidence of bimodality. Clearly the addition of the heat of vaporization has moved the parameters towards what was the minor mode in figure 3, although the center of the old mode is not quite the same as the new. From figure 12 it can be seen the distribution of parameter estimates also
425 looks much smoother for approach D, especially considering the very complex distributions previously observed for especially c_1 , β , and ε . Unfortunately the parameter distribution is quite wide (i.e. large standard deviation), and, although not shown here, the parameters are still rather correlated.

Figure 13b shows the uncertainty in the new input parameters propagated to
430 the CO₂+ethane VLE, it can be seen from the figure that although the parameter distributions are close to the expected normal distribution, the uncertainty in the VLE estimation is still high for approach F. It is furthermore noteworthy that approach F is, again, the only model which can predict the data within its 95th percentile. The uncertainty range has, however, changed so that the vari-

Figure 11: Histograms approximating the distribution of each parameter (left y-axis), obtained from 500 re-sampled bootstraps, using modeling approach **F** for CO_2 . The parameters have been fitted to ΔH^{vap} in addition to ρ_{sat}^{liq} and P^{sat} . The full red line shows the estimated probability density function (right y-axis).

Figure 12: Histograms approximating the distribution of each parameter (left y-axis), obtained from 500 re-sampled bootstraps, using modeling approach **D** for CO_2 . The parameters have been fitted to ΔH^{vap} in addition to ρ_{sat}^{liq} and P^{sat} . The full red line shows the estimated probability density function (right y-axis).

Figure 13: Propagated uncertainty in the model predictions for the CO_2 +ethane VLE at $T=250$ K. Approach **F** (a) and **D** (b) fitted to ΔH^{vap} in addition to ρ_{sat}^{liq} and P^{sat} . Grey lines represent the simulations, red dashed lines are the 5th and 95th percentile of the simulations and black full lines are the mean of the simulations. Blue circles are experimental data from [58].

ous realizations generally under-predict the VLE data, whereas they previously over-predicted the data. This suggests a quite large total area of uncertainty, and a very flexible model. For approach D we see from figure 13b that the uncertainty in the VLE is larger now, than it was with the bimodal distribution, however, the VLE predictions are almost identical to those in figure 9b. The reason for the wide parameter distributions may be because the obtained parameter sets constitute a compromise between correlating either of the fitted properties better than the other. Figure 13b, for instance, suggests that the pure compound vapour pressure is not captured very well for some parameter sets.

4. Concluding remarks

In this work the uncertainty in the pure compound parameters of CO_2 was investigated for various modeling approaches. The models employ between three and five adjustable pure compound parameters. The uncertainties are estimated

using either LSQ estimation or the bootstrap method. The pure compound
450 uncertainty from the bootstrap method is propagated to selected derivative
properties and CO₂+hydrocarbon VLE systems using a Monte Carlo approach.

The results indicate that modeling approaches which use only three ad-
justable parameters have relatively low parameter uncertainties. However, when
the models contained four or five parameters the uncertainties and parameter
455 correlations were significant. The association volume, β , for instance is highly
correlated with the association strength, ε , and its value may vary about 100%
from its mean value, without loss of accuracy in the properties the parameters
are correlated to (saturated pressure and liquid density). The main reason for
the large parameters uncertainties appears to be the high correlation between
460 parameters.

It was shown that when CO₂ is treated as an associating species with five
parameters, the propagated uncertainty appear to be significant for highly tem-
perature dependent properties such as the heat capacities. On the other hand
the uncertainty is relatively small for the VLE systems. When qCPA was em-
465 ployed with four adjustable parameters, however, the uncertainties were rela-
tively small in the temperature dependent properties, whereas the uncertainty
in VLE was significant. Of the evaluated models qCPA (with approach F) is
the only model which can predict the VLEs within the propagated uncertainty.
That is partly due to the larger uncertainty range, but also better model predic-
470 tions. This suggests that one or more parameter sets can be found, within the
uncertainty of the adjustable parameters, which accurately predicts the VLE.
Alternatively qCPA with three parameters gives excellent qualitative results
with low uncertainties.

Although similar parameter correlations are typically obtained, the param-
475 eter uncertainties from LSQ estimation are generally significantly smaller than
those obtained from the bootstrap method. This may be because the bootstrap
method accounts for the high degree of correlation between parameters, by using
the experimental data itself rather than indirectly using the linear approxima-
tion of the covariance matrix for estimators. It is thus clear that one might not

480 obtain the 'best' parameter set, e.g for modeling VLE systems, by a standard
LSQ estimation procedure. In any case, one should be aware that an obtained
parameter set may be quite uncertain, which may incur significant uncertainties
in physical property predictions.

The effect of adding the heat of vaporization to the parameter estimation
485 was investigated. This resulted in parameter distributions, which were signifi-
cantly closer to a normal distribution. Unfortunately the standard deviations
for the parameters were still high and the propagated error is significant. qCPA
with four parameters is still the only model which can, within the propagated
uncertainty, predict the VLEs. The propagated uncertainty, however, differs
490 from the previously estimated one, so that the model tend to under-predict,
rather than over-predict, the VLE data.

The uncertainty results for qCPA are strictly valid only for CO₂ and the
quadrupolar term which we have employed in this work. However, most other
quadrupolar and polar terms are structurally similar, and we suspect that these
495 terms may have similar uncertainty properties. Indicating that published pa-
rameters should be treated with caution. On the other hand, it is clear from
the VLE examples that the quadrupolar models may offer significantly improved
predictions, even if the cost of this may be a higher uncertainty in the param-
eters. In either case the results indicate that it is important that researchers
500 report the parameter uncertainties when a new model is developed or parame-
ters are estimated for a new compound. In this way better informed decisions
and comparisons can be made.

Finally we note that while we have assumed good data coverage in our analy-
sis, it would be very informative to also analyze the effect of especially sparse or
505 limited data on the CPA type models as well as which types of data/properties
are employed to correlate the parameters.

Appendix A. The CPA and qCPA Equations of State

This appendix summarizes the necessary equations for the CPA and qCPA equations of state, as presented by Kontogeorgis et al. [1] and Bjørner and
510 Kontogeorgis [33].

In terms of the reduced residual Helmholtz free energy qCPA can be expressed as:

$$\frac{A_{CPA}^r(T, V, \mathbf{n})}{RT} = \frac{A_{SRK}^r(T, V, \mathbf{n})}{RT} + \frac{A_{Assoc}^r(T, V, \mathbf{n})}{RT} + \frac{A_{Quad}^r(T, V, \mathbf{n})}{RT} \quad (\text{A.1})$$

where T is the temperature, V is the volume, $\mathbf{n}$ the molar composition vector and R the ideal gas constant.

The SRK term. The reduced residual Helmholtz energy of the SRK EoS for n moles of a mixture is expressed as [63]:

$$\frac{A_{SRK}^r(T, V, \mathbf{n})}{RT} = -n \ln \left(1 - \frac{B}{V} \right) - \frac{D(T)}{RTB} \ln \left(1 + \frac{B}{V} \right) \quad (\text{A.2})$$

where, using the van der Waals one-fluid mixing rules

$$D(T) = \sum_i n_i \sum_j n_j a_{ij}(T) \quad (\text{A.3a})$$

$$B = \sum_i n_i b_{ii} \quad (\text{A.3b})$$

b_{ii} or b_0 is the pure compound co-volume parameter for component i . The cross energetic parameter, a_{ij} , is calculated as

$$a_{ij} = \sqrt{a_{ii}(T)a_{jj}(T)}(1 - k_{ij}) \quad (\text{A.4})$$

where k_{ij} is a binary interaction parameter, typically correlated to experimental data. In this work the k_{ij} is always equal to zero. The temperature dependent energetic parameter, $a_{ii}(T)$, is given as

$$a_{ii}(T) = a_0 \left(1 + c_1 \left(1 - \sqrt{T_r} \right) \right)^2 \quad (\text{A.5})$$

where a_0 and c_1 are pure compound parameters and T_r is the reduced temperature ($= T/T_c$). To avoid ambiguity it is common practice to tabulate the a_0
515 parameter as $\Gamma = a_0/(Rb_0)$.

Association contribution. The reduced residual Helmholtz energy of the association term is given by [63–65]:

$$\frac{A_{Assoc}^r(T, V, \mathbf{n})}{RT} = \sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \quad (\text{A.6})$$

where A_i indicates bonding sites on molecule i and X_{A_i} denotes the fraction of A-sites on molecule i not bonded to another association site. X_{A_i} is given by

$$X_{A_i} = \frac{1}{1 + \frac{1}{V} \sum_j n_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (\text{A.7})$$

where the association strength, $\Delta^{A_i B_j}$, is calculated as

$$\Delta^{A_i B_j} = g(n, V) \left(\exp \left(\frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right) b_{ij} \beta^{A_i B_j} \quad (\text{A.8})$$

where $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are the association energy and volume between site A of molecule i and site B of molecule j respectively. b_{ij} is the cross-covolume calculated from as $b_{ij} = (b_{ii} + b_{jj})/2$, and g is the RDF. In CPA the RDF is approximated as

$$g(n, V) = \frac{1}{1 - 1.9\eta} \quad (\text{A.9})$$

where $\eta (= B/4V)$ is the reduced fluid density.

If more than one associating compound is present the CR-1 combining rule is employed for $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$.

$$\epsilon^{A_i B_j} = \frac{1}{2} (\epsilon^{A_i B_i} + \epsilon^{A_j B_j}) \quad (\text{A.10a})$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \quad (\text{A.10b})$$

The association term is dependent on the association scheme (see Eq. (A.7)). To denote the different association schemes the notation of Huang and Radosz [37] is adopted.

Quadrupole contribution. The reduced residual Helmholtz energy for the quadrupolar term is based on a Padé approximation for a perturbation series

$$\frac{A_{Quad}^r(T, V, \mathbf{n})}{RT} = \frac{A_{2,Quad}^r(T, V, \mathbf{n})/RT}{1 - A_{3,Quad}^r(T, V, \mathbf{n})/A_{2,Quad}^r(T, V, \mathbf{n})} \quad (\text{A.11})$$

The third-order term is the sum of both a two-body and a three-body contribution, so that

$$\frac{A_{3,Quad}^r(T, V, \mathbf{n})}{RT} = \frac{A_{3,2,Quad}^r(T, V, \mathbf{n})}{RT} + \frac{A_{3,3,Quad}^r(T, V, \mathbf{n})}{RT} \quad (\text{A.12})$$

The expressions for the second- and third-order pure compound terms developed by Larsen et al. [66] were extended to mixtures by Bjørner and Kontogeorgis [33]. The expressions are

$$\frac{A_{2,Quad}^r}{RT} = -\frac{7}{10} \frac{N_A}{V (k_b T)^2} \sum_i^{nc} n_i \sum_j^{nc} n_j \frac{Q_{ij}^4}{\sigma_{ij}^7} I_{10}^{HS} \quad (\text{A.13})$$

$$\frac{A_{3,2,Quad}^r}{RT} = \frac{36}{245} \frac{N_A}{V k_b^2 T^3} \sum_i^{nc} n_i \sum_j^{nc} n_j \frac{Q_{ij}^6}{\sigma_{ij}^{12}} I_{15}^{HS} \quad (\text{A.14})$$

$$\frac{A_{3,3,Quad}^r}{RT} = -\frac{1}{6400} \frac{N_A^2}{V^2 (k_b T)^3} \sum_i^{nc} n_i \sum_j^{nc} n_j \sum_k^{nc} n_k \frac{Q_{ijk}^6}{\sigma_{ij}^3 \sigma_{ik}^3 \sigma_{jk}^3} I_{TQ}^{HS} \quad (\text{A.15})$$

520 where N_A is the Avogadro constant, k_b is Boltzmann's constant, Q the quadrupolar moment, σ the hard sphere diameter and I_n and I_{TQ} are correlation integrals.

It is presumed that the correlation integrals can be truncated at the zeroth order term of the density expansion in [66]. The coefficients are given as:

$$I_n^{HS} \approx J_{0,n} = \frac{4\pi}{n-3} \quad (\text{A.16a})$$

$$I_{triple}^{HS} \approx J_{0,TQ} = 54\pi^2 \quad (\text{A.16b})$$

For mixtures, the two- and three body cross-quadrupolar moments are calculated using from

$$Q_{ij} = \sqrt{Q_{ii} Q_{jj}} \quad (\text{A.17})$$

$$Q_{ijk} = \sqrt[3]{Q_{ii} Q_{jj} Q_{kk}} \quad (\text{A.18})$$

The co-volume parameter in CPA is approximated based on the molecular diameter of a hard-sphere molecule as

$$b_0^Q = N_A \pi \sigma^3 / 3 \quad (\text{A.19})$$

where b_0^Q is the co-volume parameter in the quadrupolar term. Note that the original definition of the co-volume is twice that shown in Eq. (A.19).

Two variations of qCPA are considered in this work; one where the quadrupolar co-volume in Eq. (A.19) is considered identical to the regular co-volume, i.e. $b_0 = b_0^Q$, and one where b_0^Q was used as an adjustable parameter.

Appendix B. Equations for the employed derivative properties

This appendix list expressions for the employed derivative properties; residual isochoric- and isobaric heat capacities and the residual enthalpy. The properties are given in terms of the reduced residual Helmholtz energy ($F = A^r/RT$).

Residual isochoric heat capacity.

$$C_V^{res}(T, V, \mathbf{n}) = -RT^2 \left(\frac{\partial^2 F}{\partial T^2} \right)_{V, \mathbf{n}} - 2RT \left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{n}} \quad (\text{B.1})$$

Residual isobaric heat capacity.

$$C_P^{res}(T, V, \mathbf{n}) = C_V^{res} - T \frac{\left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}}^2}{\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}}} - nR \quad (\text{B.2})$$

Residual enthalpy.

$$\frac{H^{res}}{nRT} = Z - \frac{T}{n} \left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{n}} - 1 \quad (\text{B.3})$$

where

$$\left(\frac{\partial P}{\partial V} \right)_{T, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial V^2} \right)_{T, \mathbf{n}} - \frac{nRT}{V^2} \quad (\text{B.4})$$

$$\left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{n}} = -RT \left(\frac{\partial^2 F}{\partial V \partial T} \right)_{\mathbf{n}} - \frac{P}{T} \quad (\text{B.5})$$

Acknowledgements

The authors gratefully acknowledge the Danish Research Council for Independent Research for funding this work as part of the project "CO₂ Hydrates - Challenges and Possibilities".

535 References

- [1] G. M. Kontogeorgis, E. C. Voutsas, I. V. Yakoumis, D. P. Tassios, An equation of state for associating fluids, *Industrial & Engineering Chemistry Research* 35 (1996) 4310–4318. doi:10.1021/ie9600203.
URL <http://pubs.acs.org/doi/abs/10.1021/ie9600203>
- 540 [2] W. G. Chapman, K. E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, In *Industrial & Engineering Chemistry Research* 29 (8) (1990) 1709–1721. arXiv:<http://dx.doi.org/10.1021/ie00104a021>, doi:10.1021/ie00104a021.
URL <http://dx.doi.org/10.1021/ie00104a021>
- 545 [3] M. E. Reed, W. Whiting, Sensitivity and uncertainty of process design to thermodynamic model parameters: a monte carlo approach, *Chemical Engineering Communications* 124 (1) (1993) 39–48. arXiv:<http://dx.doi.org/10.1080/00986449308936176>, doi:10.1080/00986449308936176.
550 URL <http://dx.doi.org/10.1080/00986449308936176>
- [4] R. Dohrn, O. Pfohl, Thermophysical properties - industrial directions, *Fluid Phase Equilibria* 194-197 (2002) 15–29.
- [5] R. S. Mah, Effects of thermophysical property estimation on process design, *Computers & Chemical Engineering* 1 (3) (1977) 183 – 189.
555 doi:[http://dx.doi.org/10.1016/0098-1354\(77\)85003-5](http://dx.doi.org/10.1016/0098-1354(77)85003-5).
URL <http://www.sciencedirect.com/science/article/pii/0098135477850035>
- [6] A. R. Nelson, J. H. Olson, S. I. Sandler, Sensitivity of distillation process design and operation to vle data, *Industrial & Engineering Chemistry Process Design and Development* 22 (3) (1983) 547–552.
560 arXiv:<http://dx.doi.org/10.1021/i200022a034>, doi:10.1021/i200022a034.
URL <http://dx.doi.org/10.1021/i200022a034>

- [7] A. H. Larsen, Data quality for process design, *Fluid Phase Equilibria* 29 (0) (1986) 47–58. doi:[http://dx.doi.org/10.1016/0378-3812\(86\)85010-5](http://dx.doi.org/10.1016/0378-3812(86)85010-5).
URL <http://www.sciencedirect.com/science/article/pii/0378381286850105>
- 565 [8] S. Zeck, Thermodynamics in process development in the chemical industry - importance, benefits, current state and future development, *Fluid Phase Equilibria* 70 (1991) 125–140.
- [9] S. Gupta, J. D. Olson, Industrial needs in physical properties, *Ind. Eng. Chem. Res* 42 (2003) 6359–6374.
- 570 [10] A. Hukkerikar, S. Kalakul, B. Sarup, D. Young, G. Sin, R. Gani, Estimation of environment-related properties of chemicals for design of sustainable processes: Development of group-contribution+ (gc+) models and uncertainty analysis, *Journal of Chemical Information and Modeling* 52 (11) (2012) 2823–2839, 2012 American Chemical Society. doi:10.1021/ci300350r.
- 575 [11] W. B. Whiting, T. M. Tong, M. E. Reed, Effect of uncertainties in thermodynamic data and model parameters on calculated process performance, *Industrial & Engineering Chemistry Research* 32 (7) (1993) 1367–1371. arXiv:<http://dx.doi.org/10.1021/ie00019a011>, doi:10.1021/ie00019a011.
URL <http://dx.doi.org/10.1021/ie00019a011>
- 580 [12] W. B. Whiting, Effects of uncertainties in thermodynamic data and models on process calculations, *Journal of Chemical & Engineering Data* 41 (5) (1996) 935–941. arXiv:<http://dx.doi.org/10.1021/je9600764>, doi:10.1021/je9600764.
URL <http://dx.doi.org/10.1021/je9600764>
- 585 [13] W. B. Whiting, V. R. Vasquez, M. M. Meerschaert, Techniques for assessing the effects of uncertainties in thermodynamic models and data, *Fluid Phase Equilibria*, *Fluid Phase Equilib* 158-160 (1999) 627–641. doi:10.1016/S0378-3812(99)00054-0.

- [14] V. R. Vasquez, W. B. Whiting, Effect of systematic and random errors in thermodynamic models on chemical process design and simulation: A monte carlo approach, *Industrial & Engineering Chemistry Research* 38 (8) (1999) 3036–3045. arXiv:<http://dx.doi.org/10.1021/ie980748e>, doi:10.1021/ie980748e.
URL <http://dx.doi.org/10.1021/ie980748e>
- [15] V. R. Vasquez, W. B. Whiting, Uncertainty and sensitivity analysis of thermodynamic models using equal probability sampling (eps), *Computers & Chemical Engineering* 23 (1112) (2000) 1825 – 1838. doi:[http://dx.doi.org/10.1016/S0098-1354\(00\)00297-0](http://dx.doi.org/10.1016/S0098-1354(00)00297-0).
URL <http://www.sciencedirect.com/science/article/pii/S0098135400002970>
- [16] Y. Xin, W. B. Whiting, Case studies of computer-aided design sensitivity to thermodynamic data and models, *Industrial & Engineering Chemistry Research* 39 (8) (2000) 2998–3006. arXiv:<http://dx.doi.org/10.1021/ie990617t>, doi:10.1021/ie990617t.
URL <http://dx.doi.org/10.1021/ie990617t>
- [17] P. M. Mathias, J. P. Gilmartin, Quantitative evaluation of the effect of uncertainty in property models on the simulated performance of solvent-based co₂-capture, *Energy Procedia* 63 (2014) 1171 – 1185, 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12. doi:<http://dx.doi.org/10.1016/j.egypro.2014.11.127>.
URL <http://www.sciencedirect.com/science/article/pii/S1876610214019420>
- [18] P. M. Mathias, Sensitivity of process design to phase equilibrium - a new perturbation method based upon the margules equation, *Journal of Chemical & Engineering Data* 59 (4) (2014) 1006–1015. arXiv:<http://dx.doi.org/10.1021/je400748p>, doi:10.1021/je400748p.
URL <http://dx.doi.org/10.1021/je400748p>
- [19] P. M. Mathias, Effect of {VLE} uncertainties on the design of separation sequences by distillation - study of the benzene-chloroform-

acetone system, Fluid Phase Equilibria 408 (2016) 265 – 272.
doi:<http://dx.doi.org/10.1016/j.fluid.2015.09.004>.

620 URL <http://www.sciencedirect.com/science/article/pii/S0378381215301096>

- [20] S. Hajipour, M. A. Satyro, Uncertainty analysis applied to thermodynamic models and process design - 1. pure components, Fluid Phase Equilibria 307 (1) (2011) 78 – 94. doi:<http://dx.doi.org/10.1016/j.fluid.2011.05.014>.
URL <http://www.sciencedirect.com/science/article/pii/S037838121100255X>

- 625 [21] S. Hajipour, M. A. Satyro, M. W. Foley, Uncertainty analysis applied to thermodynamic models and process design - 2. binary mixtures, Fluid Phase Equilibria 364 (0) (2014) 15 – 30.
doi:<http://dx.doi.org/10.1016/j.fluid.2013.12.004>.
URL <http://www.sciencedirect.com/science/article/pii/S0378381213007097>

- 630 [22] S. Hajipour, M. A. Satyro, M. W. Foley, Uncertainty analysis applied to thermodynamic models and fuel properties -natural gas dew points and gasoline reid vapor pressures, Energy & Fuels 28 (2) (2014) 1569–1578.
arXiv:<http://dx.doi.org/10.1021/ef4019838>, doi:10.1021/ef4019838.
URL <http://dx.doi.org/10.1021/ef4019838>

- 635 [23] W. A. Wakeham, G. S. Cholakov, R. P. Stateva, Consequences of property errors on the design of distillation columns, Fluid Phase Equilibria 185 (1 - 2) (2001) 1 – 12, proceedings of the 14th symposium on thermophysical properties. doi:[http://dx.doi.org/10.1016/S0378-3812\(01\)00490-3](http://dx.doi.org/10.1016/S0378-3812(01)00490-3).
URL <http://www.sciencedirect.com/science/article/pii/S0378381201004903>

- 640 [24] J. Gross, An equation-of-state contribution for polar components: Quadrupolar molecules, AIChE Journal 51 (9) (2005) 2556–2568.
doi:10.1002/aic.10502.
URL <http://dx.doi.org/10.1002/aic.10502>

- 645 [25] E. K. Karakatsani, I. G. Economou, Perturbed chain-statistical associating fluid theory extended to dipolar and quadrupolar molecular fluids, The Journal of Physical Chemistry B 110 (18) (2006)

9252–9261. arXiv:<http://pubs.acs.org/doi/pdf/10.1021/jp056957b>,
doi:10.1021/jp056957b.

URL <http://pubs.acs.org/doi/abs/10.1021/jp056957b>

- 650 [26] E. Karakatsani, G. Kontogeorgis, I. Economou, Evaluation of the truncated
perturbed chain-polar statistical associating fluid theory for complex mix-
ture fluid phase equilibria, *Industrial & Engineering Chemistry Research*
45 (17) (2006) 6063–6074.
- [27] D. NguyenHuynh, J.-P. Passarello, P. Tobaly, J.-C. de Hemptinne,
655 Application of GC-SAFT EOS to polar systems using a seg-
ment approach, *Fluid Phase Equilibria* 264 (1-2) (2008) 62–75.
doi:<http://dx.doi.org/10.1016/j.fluid.2007.10.019>.
URL <http://www.sciencedirect.com/science/article/pii/S0378381207006838>
- [28] I. Tsivintzelis, G. M. Kontogeorgis, M. L. Michelsen, E. H. Stenby, Model-
660 ing phase equilibria for acid gas mixtures using the {CPA} equation of state.
part ii: Binary mixtures with {CO₂}, *Fluid Phase Equilibria* 306 (1) (2011)
38 – 56, 20 years of the {SAFT} equation of state Recent advances and
challenges Symposium. doi:<http://dx.doi.org/10.1016/j.fluid.2011.02.006>.
URL <http://www.sciencedirect.com/science/article/pii/S0378381211000641>
- 665 [29] B. Efron, Bootstrap methods: Another look at the jackknife, *Ann. Statist.*
7 (1) (1979) 1–26. doi:10.1214/aos/1176344552.
URL <http://dx.doi.org/10.1214/aos/1176344552>
- [30] R. Span, W. Wagner, A new equation of state for carbon dioxide covering
the fluid region from the triplepoint temperature to 1100 k at pressures
670 up to 800 mpa, *Journal of Physical and Chemical Reference Data* 25 (6)
(1996) 1509–1596. doi:<http://dx.doi.org/10.1063/1.555991>.
URL <http://scitation.aip.org/content/aip/journal/jpcrd/25/6/10.1063/1.555991>
- [31] E. W. Lemmon, M. O. McLinden, M. L. Huber, NIST Standard Reference
Database 23: Reference Fluid Thermodynamic and Transport Properties-

- 675 REFPROP, Version 7, National Institute of Standards and Technology,
Gaithersburg, standard Reference Data Program (2002).
- [32] M. M. E.W. Lemmon, D. Friend, NIST Chemistry WebBook, NIST Stan-
dard Reference Database Number 69, National Institute of Standards and
Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, 2014, Ch.
680 Thermophysical Properties of Fluid Systems.
URL <http://webbook.nist.gov>
- [33] M. G. Bjørner, G. M. Kontogeorgis, Modeling derivative properties and
binary mixtures with {CO₂} using the {CPA} and the quadrupolar
{CPA} equations of state, Fluid Phase Equilibria 408 (2016) 151 – 169.
685 doi:<http://dx.doi.org/10.1016/j.fluid.2015.08.011>.
URL <http://www.sciencedirect.com/science/article/pii/S0378381215300819>
- [34] G. M. Kontogeorgis, M. L. Michelsen, G. K. Folas, S. Derawi, N. von Solms,
E. H. Stenby, Ten years with the cpa (cubic-plus-association) equation of
state. part 1. pure compounds and self-associating systems, Industrial &
690 Engineering Chemistry Research 45 (14) (2006) 4855–4868.
- [35] G. M. Kontogeorgis, M. L. Michelsen, G. K. Folas, S. Derawi, N. von
Solms, E. H. Stenby, Ten years with the cpa (cubic-plus-association) equa-
tion of state. part 2. cross-associating and multicomponent systems, In-
dustrial & Engineering Chemistry Research 45 (14) (2006) 4869–4878.
695 arXiv:<http://dx.doi.org/10.1021/ie051306n>, doi:10.1021/ie051306n.
URL <http://dx.doi.org/10.1021/ie051306n>
- [36] G. Kontogeorgis, G. Folas, Thermodynamic Models for Industrial Applica-
tions - From classical and advanced mixing rules to association theories, 1st
Edition, John Wiley and Sons, 2010, Ch. 9-12 The Cubic Plus Association
700 Equation of State.
- [37] S. H. Huang, M. Radosz, Equation of state for small, large, polydisperse,
and associating molecules, Industrial & Engineering Chemistry Research

- 29 (11) (1990) 2284–2294. arXiv:<http://dx.doi.org/10.1021/ie00107a014>,
doi:10.1021/ie00107a014.
- 705 URL <http://dx.doi.org/10.1021/ie00107a014>
- [38] M. Omlin, P. Reichert, A comparison of techniques for the estimation of model prediction uncertainty, *Ecological Modelling* 115 (1) (1999) 45 – 59.
- [39] M. J. Bayarri, J. O. Berger, The interplay of bayesian and frequentist analysis, *Statistical Science* 19 (1) (2004) 58–80.
- 710 [40] G. A. F. Seber, C. Wild, *Nonlinear Regression*, John Wiley & Sons, 1989.
- [41] G. Sin, A. S. Meyer, K. V. Gernaey, Assessing reliability of cellulose hydrolysis models to support biofuel process design - identifiability and uncertainty analysis, *Computers & Chemical Engineering* 34 (9) (2010) 1385 – 1392, selected papers from the 7th
715 International Conference on the Foundations of Computer-Aided Process Design (FOCAPD), 2009, Breckenridge, Colorado, USA.
doi:<http://dx.doi.org/10.1016/j.compchemeng.2010.02.012>.
URL <http://www.sciencedirect.com/science/article/pii/S0098135410000554>
- [42] T. J. DiCiccio, B. Efron, Bootstrap confidence intervals, *Statist. Sci.* 11 (3)
720 (1996) 189–228. doi:10.1214/ss/1032280214.
URL <http://dx.doi.org/10.1214/ss/1032280214>
- [43] G. Sin, K. V. Gernaey, A. E. Lantz, Good modeling practice for pat applications: Propagation of input uncertainty and sensitivity analysis, *Biotechnology Progress* 25 (4).
- 725 [44] U. M. Diwekar, J. R. Kalagnanam, Efficient sampling technique for optimization under uncertainty, *AIChE Journal* 43 (2) (1997) 440–447.
doi:10.1002/aic.690430217.
URL <http://dx.doi.org/10.1002/aic.690430217>

- [45] M. McKay, R. Beckman, W. Conover, A comparison of three methods for
 730 selecting values of input variables in the analysis of output from a computer
 code, *TECHNOMETRICS* 21 (2) (1979) 239–245.
- [46] R. L. Iman, W. J. Conover, A distribution-free approach to
 inducing rank correlation among input variables, *Communications in Statistics - Simulation and Computation* 11 (3) (1982)
 735 311–334. arXiv:<http://dx.doi.org/10.1080/03610918208812265>,
 doi:10.1080/03610918208812265.
 URL <http://dx.doi.org/10.1080/03610918208812265>
- [47] J. C. Helton, Uncertainty and sensitivity analysis techniques for
 use in performance assessment for radioactive waste disposal, *Reliability Engineering & System Safety* 42 (2-3) (1993) 327 – 367.
 740 doi:[http://dx.doi.org/10.1016/0951-8320\(93\)90097-I](http://dx.doi.org/10.1016/0951-8320(93)90097-I).
 URL <http://www.sciencedirect.com/science/article/pii/095183209390097I>
- [48] N. Metropolis, S. Ulam, The monte carlo method, *Journal of the American Statistical Association* 44 (247) (1949) pp. 335–341.
 745 URL <http://www.jstor.org/stable/2280232>
- [49] J. H. Halton, A retrospective and prospective survey of the monte carlo
 method, *SIAM Review* 12 (1) (1970) pp. 1–63.
 URL <http://www.jstor.org/stable/2029039>
- [50] J. Helton, F. Davis, Latin hypercube sampling and the propagation of
 750 uncertainty in analyses of complex systems, *Reliability Engineering & System Safety* 81 (1) (2003) 23 – 69. doi:[http://dx.doi.org/10.1016/S0951-8320\(03\)00058-9](http://dx.doi.org/10.1016/S0951-8320(03)00058-9).
 URL <http://www.sciencedirect.com/science/article/pii/S0951832003000589>
- [51] W. Duschek, R. Kleinrahm, W. Wagner, Measurement and correlation of
 755 the (pressure, density, temperature) relation of carbon dioxide ii. saturated-
 liquid and saturated-vapour densities and the vapour pressure along the

entire coexistence curve, The Journal of Chemical Thermodynamics 22 (9) (1990) 841 – 864. doi:[http://dx.doi.org/10.1016/0021-9614\(90\)90173-N](http://dx.doi.org/10.1016/0021-9614(90)90173-N).
URL <http://www.sciencedirect.com/science/article/pii/002196149090173N>

760 [52] E. Fernández-Fassnacht, F. D. Río, The vapour pressure of CO_2 from 194 to 243 K, The Journal of Chemical Thermodynamics 16 (5) (1984) 469 – 474. doi:[http://dx.doi.org/10.1016/0021-9614\(84\)90204-0](http://dx.doi.org/10.1016/0021-9614(84)90204-0).
URL <http://www.sciencedirect.com/science/article/pii/0021961484902040>

[53] J. R. Roebuck, T. A. Murrell, E. E. Miller, The joule-thomson effect in carbon dioxide, Journal of the American Chemical Society 64 (2) (1942) 400–411. arXiv:<http://dx.doi.org/10.1021/ja01254a048>, doi:10.1021/ja01254a048.
URL <http://dx.doi.org/10.1021/ja01254a048>

770 [54] S. G. Sauer, W. G. Chapman, A parametric study of dipolar chain theory with applications to ketone mixtures, Industrial & Engineering Chemistry Research 42 (22) (2003) 5687–5696. arXiv:<http://dx.doi.org/10.1021/ie034035u>, doi:10.1021/ie034035u.
URL <http://dx.doi.org/10.1021/ie034035u>

775 [55] S. Korden, N. Van Nhu, J. Vrabec, J. Gross, K. Leonhard, On the treatment of electrostatic interactions of non-spherical molecules in equation of state models, Soft Materials 10 (1-3) (2012) 81–105. arXiv:<http://dx.doi.org/10.1080/1539445X.2011.599701>, doi:10.1080/1539445X.2011.599701.
URL <http://dx.doi.org/10.1080/1539445X.2011.599701>

780 [56] A. de Villiers, C. Schwarz, A. Burger, G. Kontogeorgis, Evaluation of the PC-SAFT, SAFT and CPA equations of state in predicting derivative properties of selected non-polar and hydrogen-bonding compounds, Fluid Phase Equilibria 338 (0) (2013) 1–15. doi:<http://dx.doi.org/10.1016/j.fluid.2012.09.035>.
785 URL <http://www.sciencedirect.com/science/article/pii/S0378381212004839>

- [57] U. K. Deiters, K. M. D. Reuck, Guidelines for publication of equations of state i. pure fluids: Technical report, Chemical Engineering Journal 69 (1) (1998) 69 – 81. doi:[http://dx.doi.org/10.1016/S1385-8947\(97\)00070-3](http://dx.doi.org/10.1016/S1385-8947(97)00070-3). URL <http://www.sciencedirect.com/science/article/pii/S1385894797000703>
- 790 [58] M. S.-W. Wei, T. S. Brown, A. J. Kidnay, E. D. Sloan, Vapor + liquid equilibria for the ternary system methane + ethane + carbon dioxide at 230 k and its constituent binaries at temperatures from 207 to 270 k, Journal of Chemical & Engineering Data 40 (4) (1995) 726–731. arXiv:<http://dx.doi.org/10.1021/je00020a002>, doi:10.1021/je00020a002. URL <http://dx.doi.org/10.1021/je00020a002>
- 795 [59] L. A. Webster, A. J. Kidnay, Vapor-liquid equilibria for the methan-propane-carbon dioxide systems at 230 k and 270 k, Journal of Chemical & Engineering Data 46 (3) (2001) 759–764. arXiv:<http://dx.doi.org/10.1021/je000307d>, doi:10.1021/je000307d. URL <http://dx.doi.org/10.1021/je000307d>
- 800 [60] T. Lafitte, D. Bessieres, M. M. Pieiro, J.-L. Daridon, Simultaneous estimation of phase behavior and second-derivative properties using the statistical associating fluid theory with variable range approach, The Journal of Chemical Physics 124 (2) (2006) –. doi:<http://dx.doi.org/10.1063/1.2140276>. URL <http://scitation.aip.org/content/aip/journal/jcp/124/2/10.1063/1.2140276>
- [61] G. M. Kontogeorgis, I. Tsivintzelis, N. von Solms, A. Grenner, D. Bøgh, M. Frost, A. Knage-Rasmussen, I. G. Economou, Use of monomer fraction data in the parametrization of association theories, Fluid Phase Equilibria 296 (2) (2010) 219 – 229, {VIII} Ibero-American Conference on Phase Equilibria and Fluid Properties for Process Design. doi:<http://dx.doi.org/10.1016/j.fluid.2010.05.028>. URL <http://www.sciencedirect.com/science/article/pii/S03783881210002840>
- 810 [62] P. C. Tybjerg, G. M. Kontogeorgis, M. L. Michelsen, E. H. Stenby, Phase

- 815 equilibria modeling of methanol-containing systems with the {CPA} and
 spc-saft equations of state, *Fluid Phase Equilibria* 288 (12) (2010) 128 –
 138. doi:<http://dx.doi.org/10.1016/j.fluid.2009.10.021>.
 URL <http://www.sciencedirect.com/science/article/pii/S0378381209004312>
- [63] M. L. Michelsen, J. M. Mollerup, *Thermodynamic Models: Fundamentals*
 820 & Computational aspects, 2nd Edition, Tie-Line Publications, 2007.
- [64] G. Jackson, W. G. Chapman, K. E. Gubbins, Phase equilibria of associating
 fluids, *Molecular Physics* 65 (1) (1988) 1–31.
- [65] W. G. Chapman, G. Jackson, K. E. Gubbins, Phase equilibria of associating
 fluids, *Molecular Physics* 65 (5) (1988) 1057–1079.
- 825 [66] B. Larsen, J. Rasaiah, G. Stell, Thermodynamic perturbation theory for
 multipolar and ionic liquids, *Molecular Physics* 33 (4) (1977) 987–1027.
 arXiv:<http://www.tandfonline.com/doi/pdf/10.1080/00268977700100901>,
 doi:10.1080/00268977700100901.
 URL <http://www.tandfonline.com/doi/abs/10.1080/00268977700100901>