Implementation and performance evaluation of different cubic equations of state for the estimation of properties of organic mixtures

Auteur : Welliquet, Jonathan
Promoteur(s) : Quoilin, Sylvain
Faculté : Faculté des Sciences appliquées
Diplôme : Master en ingénieur civil électromécanicien, à finalité approfondie
Année académique : 2015-2016
URI/URL : https://github.com/CoolProp/CoolProp; http://hdl.handle.net/2268.2/2013

Implementation and performance evaluation of different cubic equations of state for the estimation of properties of organic mixtures.

Jonathan Welliquet

University of Liège, Faculty of Applied Sciences
Aerospace and mechanical engineering department
Thermodynamic Laboratory

Abstract

The thermodynamic properties of organic mixtures is a really important aspect for the development of the new thermodynamic cycles. However, mixtures are not all yet well known and a model that could give a good approximation of the properties in a fast way could help.

The cubic equations of states provide a simple way requiring minimal information to approximate the state of a fluid. This provide an interesting tool with enough flexibility to improve the accuracy as more experimental data become available. The results for vapour-liquid equilibrium of mixtures are particularly good.

Keywords: CoolProp, Cubic, EOS, Mixtures

Contents

1. Introduction

The improvements in thermodynamic cycles relies on the possibility to chose the most suitable fluid and to model it accurately.

Thermodynamic libraries likes RefProp, FluidProp and CoolProp provides efficient models for sufficiently well known fluids (mainly through Helmholtz equation of state or interpolation from experimental data). However, there are still a lack of data for less studied fluids, particularly mixtures, which usually need experimental data to evaluate the interaction parameters required for the models. These interaction parameter are often approximated or not used at all.

Accurate models like the Helmholtz equations of state (HEOS) usually require a consequent number of experimental data, whereas the cubic equations of state are simpler model that can already gives good results with very few experimental data (critical pressure and temperature p_{crit}, T_{crit} and acentric factor ω). Being simpler models, they also have the benefit from being faster. Of course these advantages comes at the cost of a lower accuracy. These cubic models can be enhanced by some parameters (approximated or fitted to experimental data) to increase their accuracy.

The cubic equations of state, are thus a good candidate to have a fast model to approximate the behaviour of non yet well studied fluids. This is extremely helpful in the research field where this allows to quickly evaluate a lot of potentials fluids and select the one worthy of interest before running expensive experimental setup to evaluate more accurately their behaviour.

The scope of this work is to evaluate what can be expected from these Cubic equations of state. A focus will be set on organic mixtures relevant for refrigeration and heat pump applications. The implementation a simple volume translation model has also been proceed and is explained in this report.

2. State of the art

2.1. Cubic Equations of State

The thermodynamic state of a fluid can be defined by two independent state variables. An equations of state (EOS) is a relation between state variables, generally aiming to compute a third variable from two other known ones.

Cubic equations of state have of cubic that they can be expressed as a cubic equation of the molar volume v.

The first cubic equation of state was the so called Van der Waals equation of state and of the form:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{1}$$

With the a and b parameters depending on the critical pressure and critical molar volume.

This equation 1 is linking the pressure p, the molar volume v and the temperature T. Theses kind of equations are generally referred as PVTEOS and have the advantage to provide both the liquid and vapour phases with a single equation (Frey et al., 2007).

With time, some improvements have been added to improve the quality of the approximation in both the general formula and in the way to compute the attraction parameter a and the repulsion parameter (or effective molecular volume) b.

The attractive parameter is often separated in a constant part a_c multiplied by a temperature dependant one $\alpha(T_R, \omega)$ such as $a = a_c \alpha(T_R, \omega)$.

The most common equations of state used in process simulation are mainly based on the Soave-Redlich-Kwong and Peng-Robinson EOS (Frey et al., 2007).

2.1.1. Soave-Redlich-Kwong

The Soave-Redlich-Kwong (SRK) is an improved Redlich-Kwong equation of state and has the original form (Soave, 1972):

$$p = \frac{RT}{v - b} - \frac{a_c \alpha(T_R, \omega)}{v(v + b)} \tag{2}$$

With the parameters:

$$a_c = 0.42747 \left(\frac{R^2 T_c^2}{Pc}\right)$$

$$b = 0.08664 \left(\frac{RT_c}{Pc}\right)$$

$$\alpha(T_R, \omega) = \left[1 + m(\omega)\left(1 - \sqrt{T_R}\right)\right]^2 \tag{3}$$

$$m(\omega) = 0.480 + 1.574\omega - 0.176\omega^2$$

2.1.2. Peng-Robinson

The Peng-Robinson (PR) equation is a modification of the SRK that allows better molar volume for liquids and better representation of liquid-vapour equilibrium for many mixtures (Valderrama, 2003). However, when considering the entire family of EOS derived from the SRK and PR, neither has a clear advantage in the accuracy of it's property predictions (Frey et al., 2007). It has the original form (Peng and Robinson, 1976):

$$p = \frac{RT}{v - b} - \frac{a_c \alpha(T_R, \omega)}{v(v + b) + b(v - b)} \tag{4}$$

With the parameters:

$$a_c = 0.45724\left(\frac{R^2 T_c^2}{Pc}\right)$$

$$b = 0.07780\left(\frac{RT_c}{Pc}\right)$$

$$\alpha(T_R, \omega) = \left[1 + m(\omega)\left(1 - \sqrt{T_R}\right)\right]^2 \tag{5}$$

$$m(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2$$
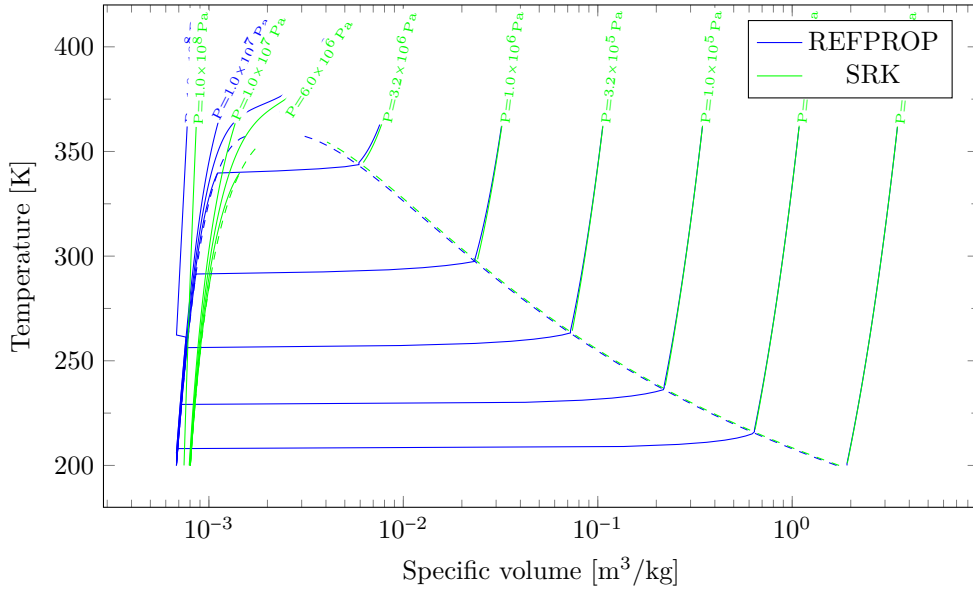
2.1.3. Volume translation

Figure 1: Isobar curves and saturation curve (dashed) on temperature/volume plot, comparison of SRK with REFPROP, fluid R407C

A correction to the molar volume of the form $v_c = v + c$ can be applied to the cubic equations of state. This correction is particularly interesting for mixtures as the molar volume of the pure fluid is different from the molar volume of the mixture.

The need for such correction can be seen in the FIGURE 1. A constant translation would correct most of the error on the liquid side, while having nearly no impact on the gaseous phase (the volume being order of magnitude higher).

Densities are usually known from experiments for the majority of pure fluids (an similarly for known mixtures) and tabulated in databases. Molar mass is constant for a given material and also generally known for pure fluids. So when molar volume is not directly known, density and molar mass are generally available to compute it.

It is common to use the molar volume at the reduce temperature $T_r = 0.7$ to compute the translation parameter (Schmid and Gmehling, 2012):

$$c = (v_{EOS} - v_{exp})\big|_{T_r = 0.7} \tag{6}$$

This constant volume translation can significantly improve the results for the saturated liquid densities in the low temperature range ($T_r < 0.8$), but fail near the critical temperature (Ahlers and Gmehling, 2001).

A solution to this can be to have a temperature dependant volume correction. Ji and Lempe (1997) suggest a dependency of the form:

$$c = \left.(v_{EOS} - v_{exp})\right|_{T=T_c} \frac{0.35}{0.35 + \eta \left|\alpha(T_R, \omega) - T_R\right|^{\gamma}} \tag{7}$$

Where $\alpha(T_R, \omega)$ is the same as in the one of the cubic equation of choice, and η and γ are obtained by matching experimental data. For SRK, Ji and Lempe (1997) propose the general formulation:

$$\eta = 23.010 e^{-38.267\left(\frac{1}{3} - z_c\right)} + 0.950$$
$$\gamma = 15.458 e^{-57.684\left(\frac{1}{3} - z_c\right)} + 0.635 \tag{8}$$

With z_c being the compressibility factor at the critical point.

A volume translated Peng-Robinson (VTPR) would be written (Schmid and Gmehling, 2012):

$$p = \frac{RT}{v + c - b} - \frac{a_c \alpha(T_R, \omega)}{(v + c)(v + c + b) + b(v + c - b)} \tag{9}$$

2.1.4. VTPR

Despite its name, the VTPR model is more than just a Volume Translated Peng-Robinson. It generally refers to a combination of the UNIFAQ group contribution mixture and a volume translation (Schmid and Gmehling, 2012; Schmid et al., 2014).

The equations of the model are developed in the Figure 2

Figure 2: Diagram of the VTPR equations. From source Schmid and Gmehling (2012)

The group contribution model discompose the different functional groups of the organic molecules and set interaction parameters between each of them. This gives a very interesting way to evaluate the interaction any mixture will have without the need to specifically test this mixture. This however has the cost to require to evaluate the interaction between all the functional groups and gives a slower model to solve.

This model is currently in development for CoolProp (VTPR).

Table 1: Mixing and combining rules in two-constant cubic EOS (Valderrama, 2003; Chen and Liu, 2007; Wong and Sandler, 1992)

Van der Waals	$a = \sum_i \sum_j x_i x_j a_{ij}; \quad a_{ij} = \sqrt{a_i a_j}$	$b = \sum_i \sum_j x_i x_j b_{ij}; \quad b_{ij} = \dfrac{b_i + b_j}{2}$
One parameter	$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij})$	$b_{ij} = \dfrac{b_i + b_j}{2}$
two parameters	$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij})$	$b_{ij} = \dfrac{b_i + b_j}{2}\,(1 - I_{ij})$
Panagiotopoulos-Reid (PR)		
two parameters	$a_{ij} = \sqrt{a_i a_j}\,[1 - k_{ij} + (k_{ij} - k_{ji} x_i)]$	$b_{ij} = \dfrac{b_i + b_j}{2}$
three parameters	$a_{ij} = \sqrt{a_i a_j}\,[1 - k_{ij} + (k_{ij} - k_{ji} x_i)]$	$b_{ij} = \dfrac{b_i + b_j}{2}\,(1 - I_{ij})$
General nonquadratic (GNQ)		
two parameters	$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij}); \quad k_{ij} = \delta_i x_i + \delta_j x_j$	$b_{ij} = \dfrac{b_i + b_j}{2}$
four parameters	$a_{ij} = \sqrt{a_i a_j}\,(1 - k_{ij}); \quad k_{ij} = \delta_i x_i + \delta_j x_j$	$b_{ij} = \dfrac{b_i(1 - \beta_i) + b_j(1 - \beta_j)}{2}$
Kurihara et al. (KTK) three parameters	$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} - \dfrac{(\tau - \phi)\,g^E_{RES}}{\ln\left(\frac{b-\phi}{b-\tau}\right)]}$ $g^E_{RES} = RT x_1 x_2 \left[\eta_1 + \eta_2(x_1 - x_2) + \eta_3(x_1 - x_2)^2\right]$	$b = \sum_i \sum_j x_i x_j b_{ij}; \quad b_{ij} = \dfrac{b_i + b_j}{2}$
Huron-Vidal	$a = b\left(\sum_i x_i \dfrac{a_i}{b_i} + \dfrac{g^E(x)}{C^*}\right)$	$b = \sum_i \sum_j x_i x_j b_{ij}; \quad b_{ij} = \dfrac{b_i + b_j}{2}$
Wong-Sandler	$a = b\left(\sum_i x_i \dfrac{a_i}{b_i} - A^E_\infty(x)\right)$	$b = \dfrac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \frac{\sum_i x_i \frac{a_i}{b_i} - A^E_\infty(x)}{RT}}$
one parameters V1		$\left(b - \dfrac{a}{RT}\right)_{ij} = \dfrac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}\,(1 - k_{ij})$
one parameters V2		$\left(b - \dfrac{a}{RT}\right)_{ij} = \dfrac{b_i + b_j}{2} - \dfrac{\sqrt{a_i a_j}\,(1 - k_{ij})}{RT}$
three parameters		$\left(b - \dfrac{a}{RT}\right)_{ij} = \dfrac{b_i(1 - l_i) + b_j}{2} - \dfrac{\sqrt{a_i a_j}\,(1 - k_{ij})}{RT}$

2.2. Mixing rules

A summary of the most common mixing rules for two constants EOS can be found in the TABLE 1.

It worth noting that it is possible to simplify the b constant in the basic Van der Waals mixing rule:

$$
\begin{aligned}
b &= \sum_i \sum_j x_i x_j b_{ij} \\
&= \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} \\
&= \sum_i \sum_j x_i x_j \frac{b_i}{2} + \sum_i \sum_j x_i x_j \frac{b_j}{2} \\
&= 2 \left(\sum_i \sum_j x_i x_j \frac{b_i}{2} \right) \\
&= \sum_i \sum_j x_i x_j b_i \\
&= \sum_i (\sum_j x_j) x_i b_i \\
&= \sum_i x_i b_i
\end{aligned}
\tag{10}
$$

2.3. Software

2.3.1. RefProp

RefProp is a commercial software developed by NIST (Lemmon et al., 2013).

It has different models such as Helmholtz equations of state and translated Peng-Robinson equation (PRT).

This software is used as a reference value to compare the accuracy of the different models.

2.3.2. CoolProp

CoolProp is an open-source software CoolProp (2016).

It has different models such as the Helmholtz equations of state, IF97, Incompressible models, and different cubic equations of states.

The Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) models are used with the general form:

$$
p = \frac{RT}{v - b} + \frac{a(T)}{(v + \Delta_1 b)(v + \Delta_2 b)}
\tag{11}
$$

For SRK, $\Delta_1 = 0$; $\Delta_2 = 1$.
For PR, $\Delta = 1 \pm \sqrt{2}$.

This allows to have a single implementation to cover both cases.

This equation is used to define the residual non-dimensional Helmholtz energy and its derivatives as explained in (**?**).

The residual non-dimensional Helmholtz energy and its derivatives are afterwards used to compute the other thermodynamic properties.

3. Volume translation implementation

In this work, the volume translation is considered as a constant value c.

The cubic equations of states for Soave-Redlich-Kwong and Peng-Robinson are implemented in COOL-PROP in the general form seen in equation 11.

The volume translation can be added in this general form as:

$$p = \frac{RT}{v + c - b} + \frac{a(T)}{(v + c + \Delta_1 b)(v + c + \Delta_2 b)} \tag{12}$$

3.1. Solving the cubic equation

The cubic equation is solved in the function rho_Tp_cubic who uses the temperature and pressure to solves the cubic and give back the density solution(s).

The equation 12 is thus rewritten in term of density:

$$p = \frac{RT}{\frac{1}{\rho} + c - b} + \frac{a(T)}{\left(\frac{1}{\rho} + c + \Delta_1 b\right)\left(\frac{1}{\rho} + c + \Delta_2 b\right)} \tag{13}$$

This equation can be simplified by introducing:

$$d_1 = c - b \tag{14}$$
$$d_2 = c + \Delta_1 b \tag{15}$$
$$d_3 = c + \Delta_2 b \tag{16}$$

$$p = \frac{RT\rho}{1 + d_1 \rho} + \frac{a(T)\rho^2}{(1 + d_2 \rho)(1 + d_3 \rho)} \tag{17}$$

Then expresses as a polynomial of the density ρ:

$$0 = -p \tag{18}$$
$$+ \rho \left(RT - p(d_1 + d_2 + d_3)\right) \tag{19}$$
$$+ \rho^2 \left(RT(d_2 + d_3) - p(d_1 d_2 + d_1 d_3 + d_2 d_3) - a(T)\right) \tag{20}$$
$$+ \rho^3 (RT d_2 d_3 - p d_1 d_2 d_3 - d_1 a(T)) \tag{21}$$

The coefficients of this 3rd order polynomial are then sent to an analytic cubic equation solver to give the one to 3 solutions for density.

3.2. Preparing for the other thermodynamic properties

To compute the other values, CoolProp uses the residual non-dimensional Helmholtz energy and it's derivatives. First the equation 13 is reformulated as a function of the non dimensional density $\delta = \frac{\rho}{\rho_r}$ and reciprocal reduced temperature $\tau = \frac{T_r}{T}$. Further explanation on the choice of the reducing parameters ρ_r and T_r are available in (**?**).

This leads to:

$$p = \frac{T_r}{\tau} \frac{R}{\frac{1}{\delta \rho_r} + c - b} + \frac{a(\tau)}{\left(\frac{1}{\delta \rho_r} + c + \Delta_1 b\right)\left(\frac{1}{\delta \rho_r} + c + \Delta_2 b\right)} \tag{22}$$

or

$$p = \frac{T_r}{\tau} \frac{\delta \rho_r r}{1 + (c - b)\delta \rho_r} + \frac{\delta^2 \rho_r^2 a(\tau)}{(1 + (c + \Delta_1 b)\delta \rho_r)(1 + (c + \Delta_2 b)\delta \rho_r)} \tag{23}$$

The derivative with respect to δ of the residual non-dimensional Helmholtz energy is given by (**?**):

$$\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau = \frac{p\tau}{\delta^2 \rho_r R T_r} - \frac{1}{\delta} \tag{24}$$

Inserting equation 23 into equation 24 leads to:

$$\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau = \frac{(b-c)\rho_r}{1-(b-c)\delta\rho_r} - \frac{\tau a(\tau)}{RT_r} \frac{\rho_r}{(1+(b\Delta_1+c)\delta\rho_r)(1+(b\Delta_2+c)\delta\rho_r)} \tag{25}$$

The value of the residual non-dimensional Helmholtz energy can be obtained by integrating this equation 25. The result can be decomposed to the form:

$$\alpha^r = \psi^{(-)} - \frac{\tau a(\tau)}{RT_r}\psi^{(+)} \tag{26}$$

With the two integrals:

$$\psi^{(-)} = \int_0^\delta \frac{(b-c)\rho_r}{1-(b-c)\delta\rho_r}\mathrm{d}\delta \tag{27}$$

$$= -\ln\left(1-(b-c)\delta\rho_r\right) \tag{28}$$

$$\psi^{(+)} = \int_0^\delta \frac{\rho_r}{(1+(b\Delta_1+c)\delta\rho_r)(1+(b\Delta_2+c)\delta\rho_r)}\mathrm{d}\delta \tag{29}$$

$$= \frac{\ln\left(\dfrac{1+(b\Delta_1+c)\delta\rho_r}{1+(b\Delta_2+c)\delta\rho_r}\right)}{b(\Delta_1-\Delta_2)} \tag{30}$$

$\Delta_1 - \Delta_2 \neq 0$ is required but satisfied for PR and SRK.

Several derivatives with respect to τ and δ at constant composition are required in CoolProp. Some of them are not impacted by the volume translation and can be found in (**?**) and the one affected are developed in the supplementary material.

4. Comparison

To evaluate the accuracy of the cubic equation of state models is done by comparing with recognised thermodynamic software and experimental data. All the fluids studies here are already quite well studied fluids, this will allows to compare the models with a known reference. This gives an overview of what can be expected for fluids that have not been yet studied enough to have an accurate state model.

Only a small portion of the studied fluids are displayed here. You will find many other graphics in the supplementary material.

4.1. Pure fluid

A large data set of experimental data has been collected by NIST for pure fluid who gracefully allowed its use for this work.

The part in use here are temperature-pressure-density data and temperature-quality-density data. The experimental density is compared to the one computed from the different equations of state by the pressure and temperature input or temperature-quality input. The density deviation is defined by:

$$E_\rho = \frac{\|\rho_{data} - \rho_{calc}\|}{\rho_{data}} \tag{31}$$

In order to enhance data displaying, any deviation bigger than 100% has been caped to 100%. This approximation was considered reasonable as a magnitude of 100% deviation is already not acceptable.

The box plot (as in Figure 3) indicate the repartition of the deviation values. The lower bar represent the minimal deviation value, the first bar of the rectangle represent the first quartile, the middle bar the median, the upper bar of the rectangle the third quartile and the upper bar the maximal value.

This allows to know that, for instance in Figure 3, for fluid R134A, 75% of the data for RefProp and HEOS are under 0.2% of deviation to the experimental data and half of the data under 0.04% of deviation.

In order to have a general overview of where the differences occurs, isobars in temperature volume plot have also been done. These plots however do not include the experimental data.
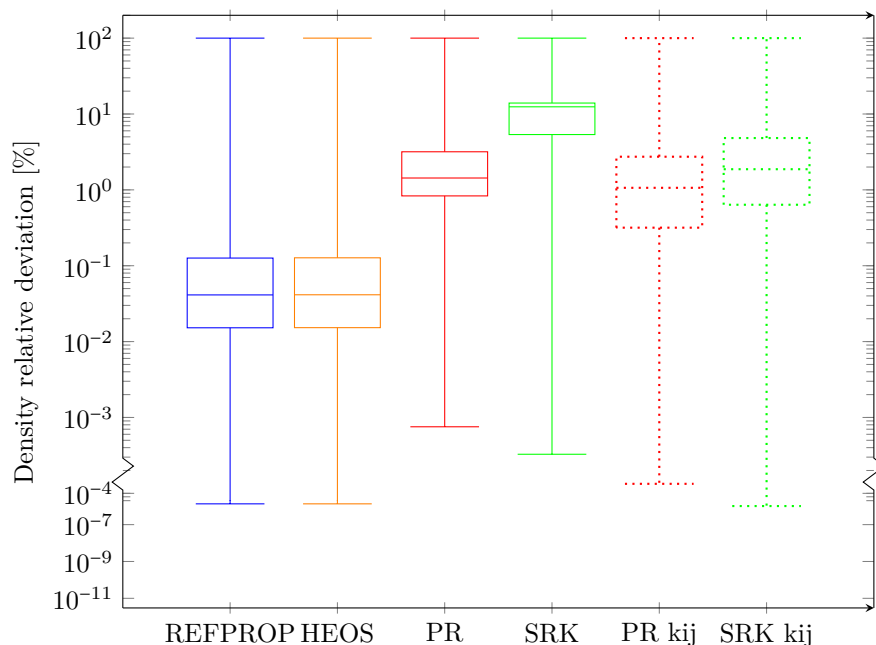

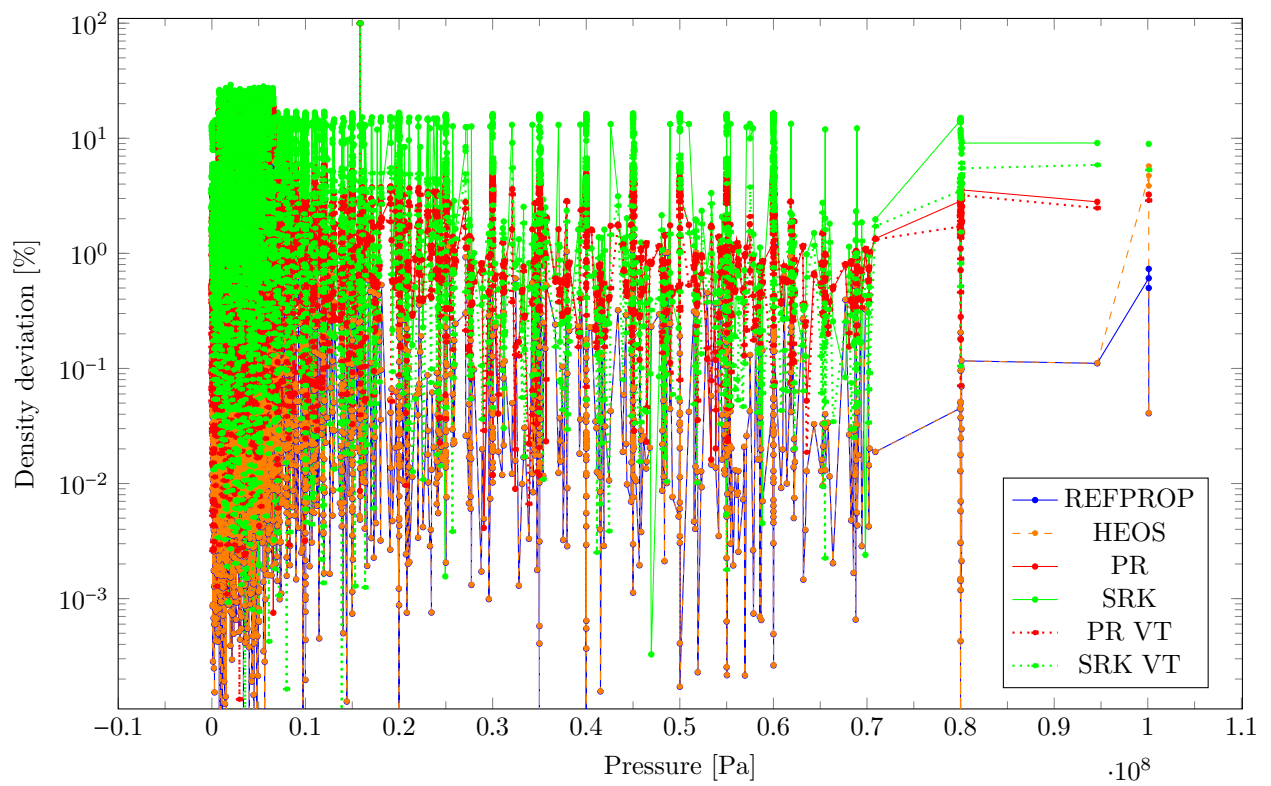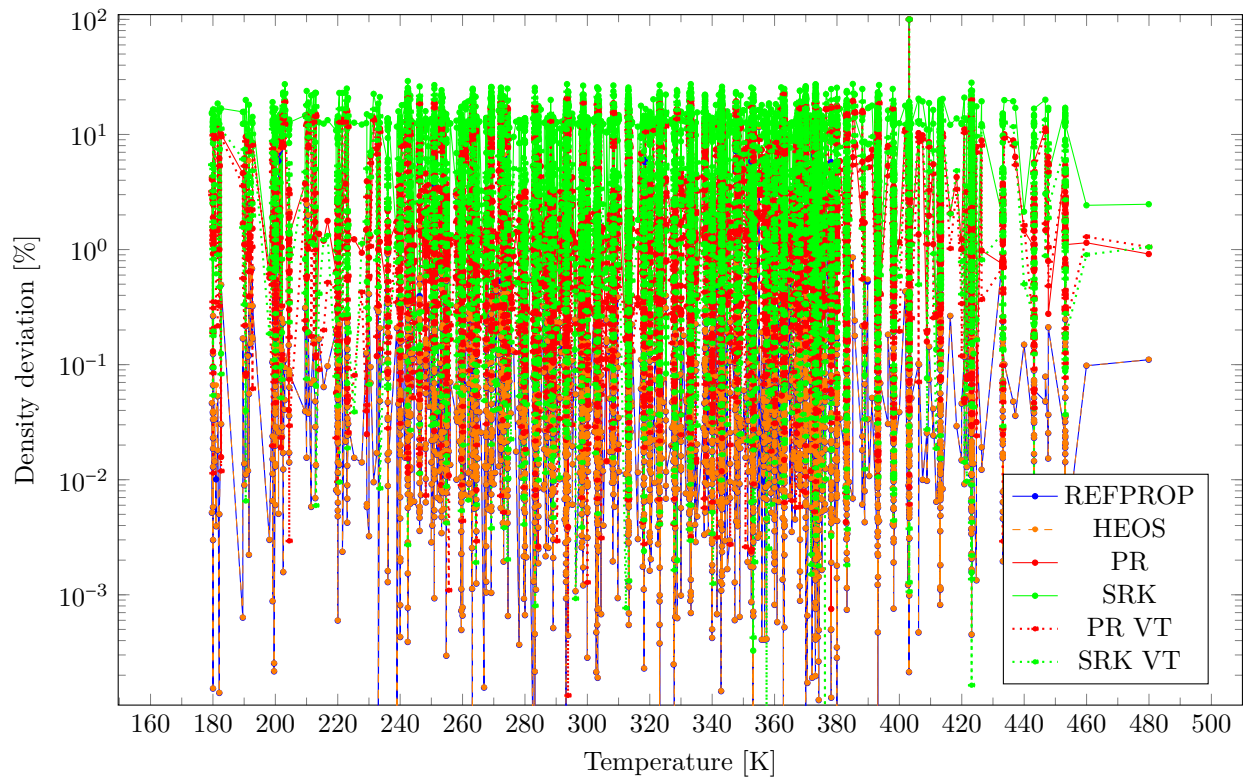Figure 3: Relative density deviation to experimental data for fluid R134A

Figure 4: Density dependence on the temperature and pressure for fluid R134A

For a lot of pure fluids, it can be observed as in Figures 3 and 4 that RefProp and the HEOS model of CoolProp gives very similar results. It however happens that the model differs slightly as can be observed in the Figure 5 and 6.

The maximal deviation with fluid R134A tops at least 100% (Figures 3) for all EOS, but it can be observed in Figure 4 that this is the case for only one point at a bit more than 400 K and 15 MPa. This is probably an invalid data point. If we exclude this outlier, the deviations for fluid R134A are under 3% for all HEOS.
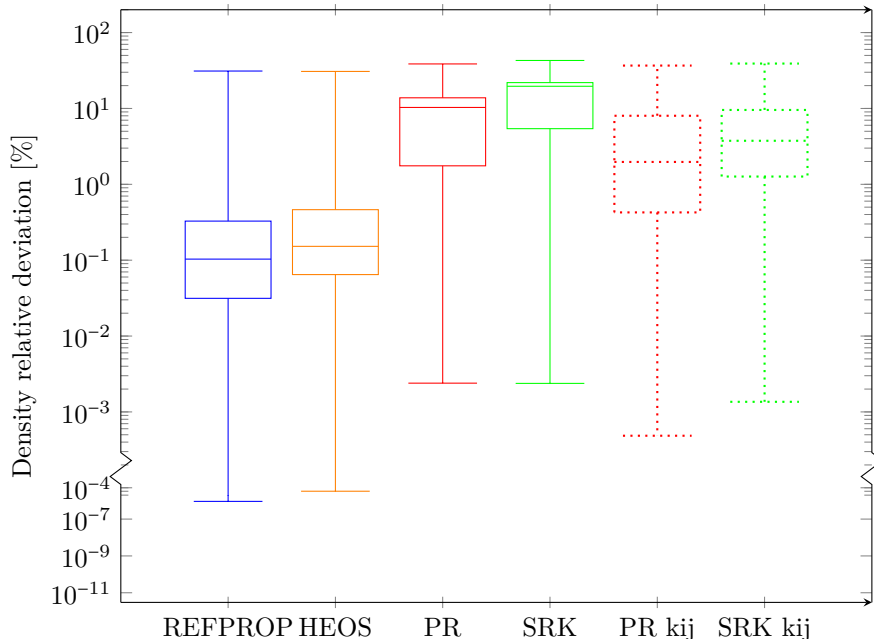
Figure 5: Relative density deviation to experimental data for fluid R41

For these pure fluid density comparison, the Cubic models give significantly worst deviations compared to the Helmholtz equations of state.

When looking at the isobars (Figure 7), it can be seen that a big part of the difference between the HEOS and the cubics looks like a translation in volume in the liquid phase.

A volume translation parameter has been computed by making the difference between the volume of the respective cubic and RefProp at a reduced temperature of $0.7T_{\text{crit}}$. This introduce RefProp's own error, but correct most of the translation error.

We can see in the Figures 3, 4, 5 and 6 that the effect is generally positive, reducing significantly the deviation. This effect depends of course on the actual translation which is not the same for al fluid and also depend on the cubic equation in use (PR or SRK).

The specific effect of this translation can be seen on the Figures 8 and 9.

The constant translation parameter correct a big part of the volume translation issue, but do not correct it entirely. Near critical values still have a significant deviation (see Figures 8 and 9). A more complex temperature dependant parameter could potentially improve the behaviour in that area.

For some fluids, the Peng-Robinson model gives better results than the Soave-Redlich-Kwong (as can be seen for R134A 3 and R41 5), but this is not always the case. Carbon monoxide for instance is better represented by the SRK model than PR as can be seen in Figure 10 and 11, but the PR becomes more accurate with volume translation. Some others, like the MethylPalmitate have quite good volume translated SRK (12 and 11).
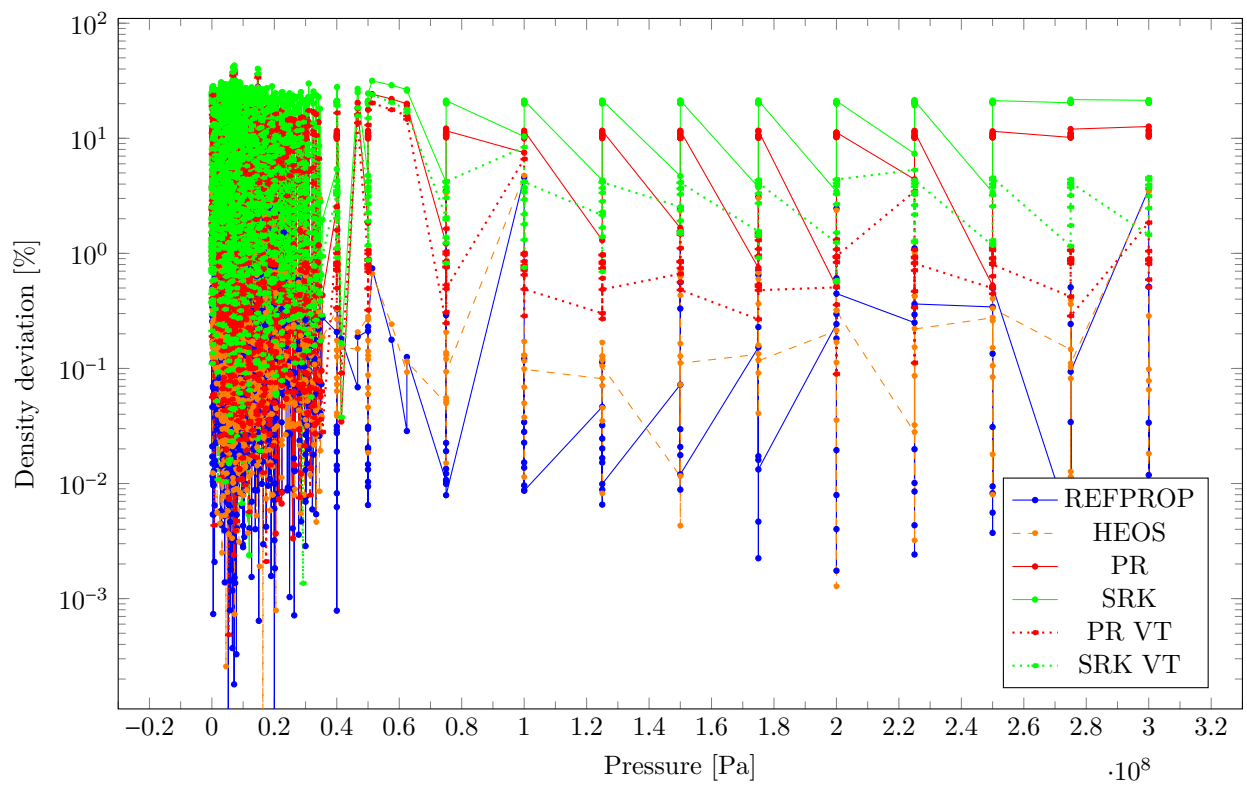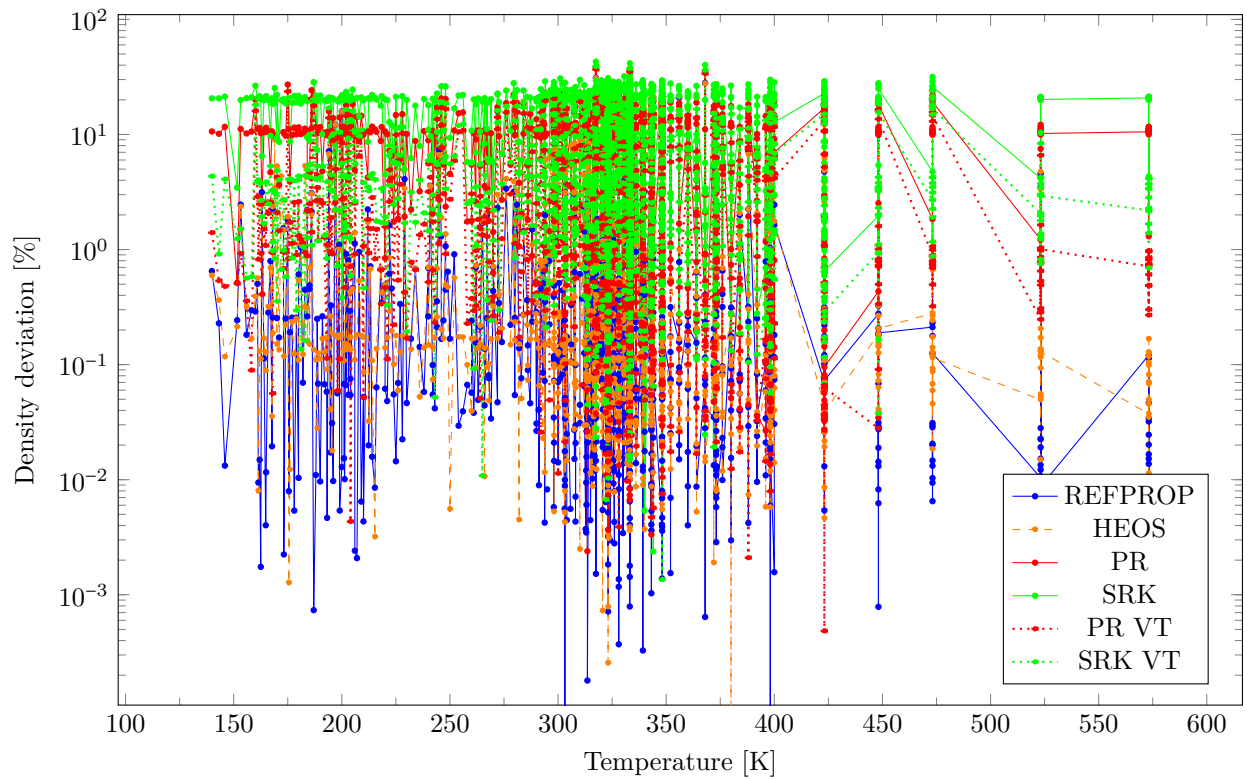
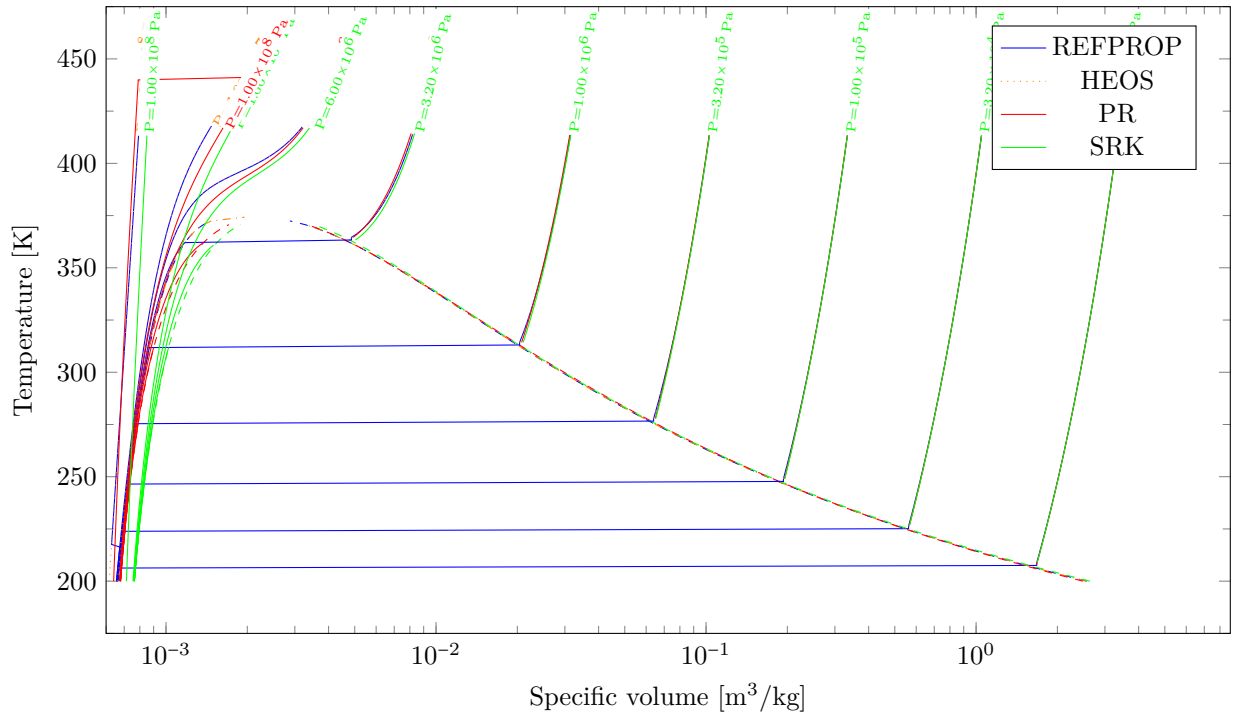Figure 6: Density dependence on the temperature and pressure for fluid R41

Figure 7: Isobar curves and saturation curve (dashed) on temperature/volume plot, fluid R134A
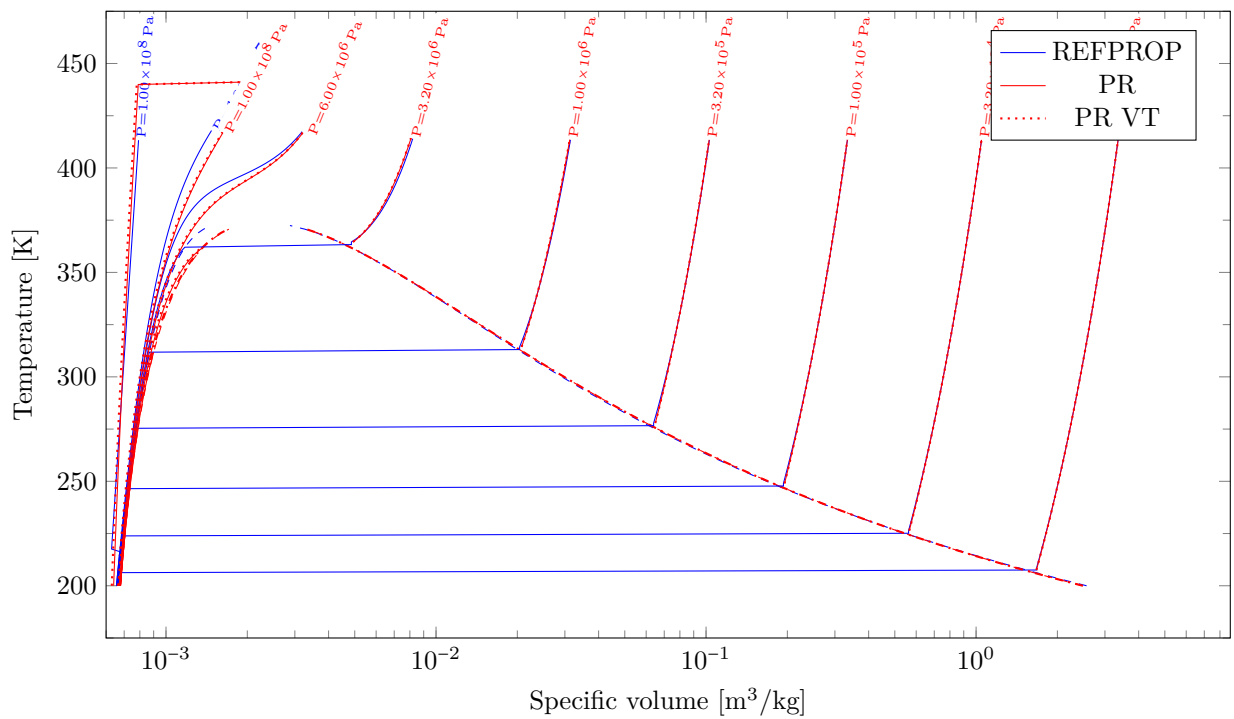

Figure 8: Isobar curves and saturation curve (dashed) on temperature/volume plot, comparison of PR with REFPROP, fluid R134A
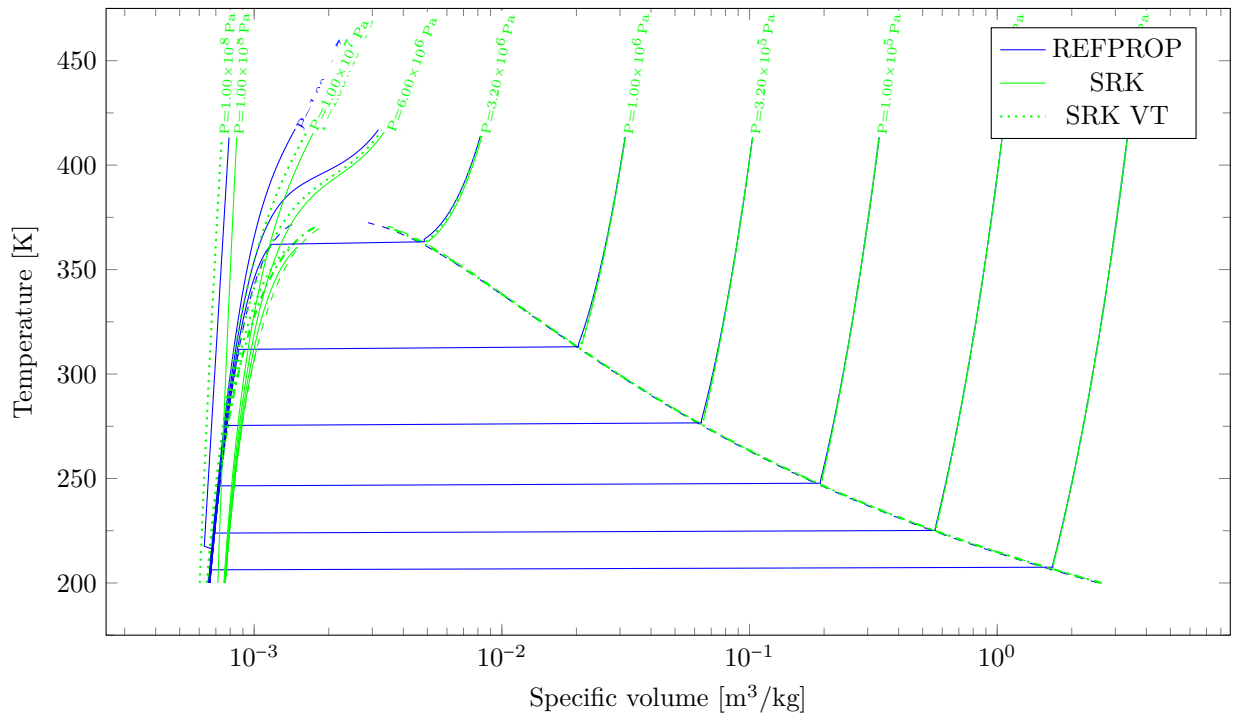
Figure 9: Isobar curves and saturation curve (dashed) on temperature/volume plot, comparison of SRK with REFPROP, fluid R134A
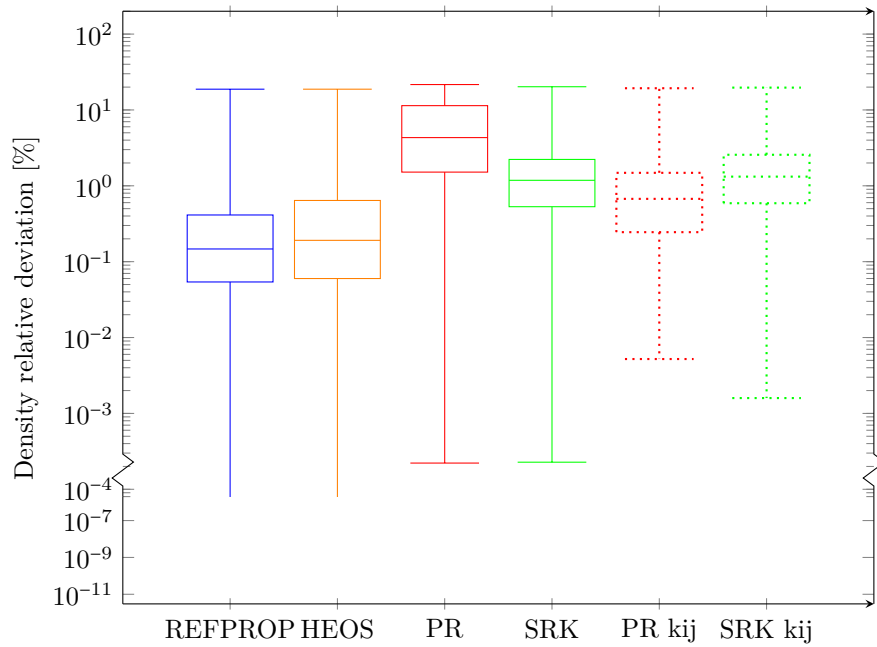

Figure 10: Relative density deviation to experimental data for fluid CARBON MONOXIDE
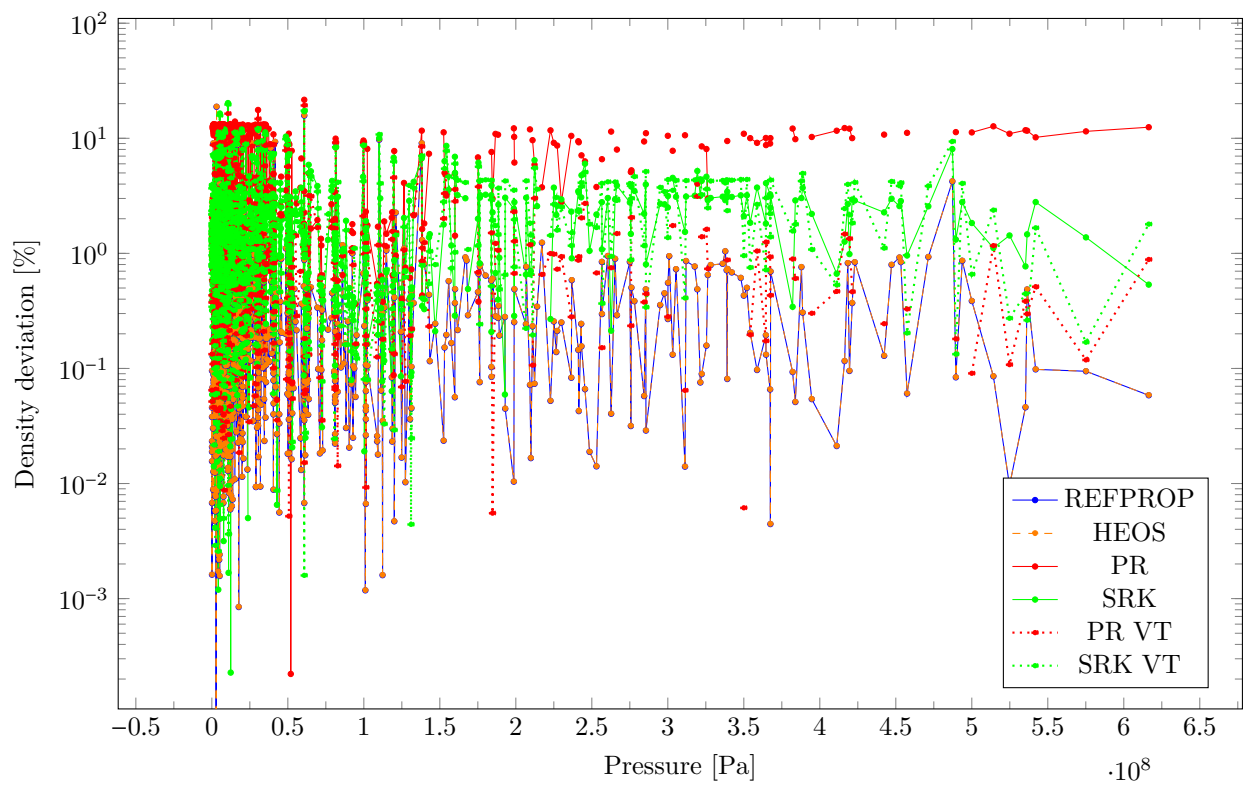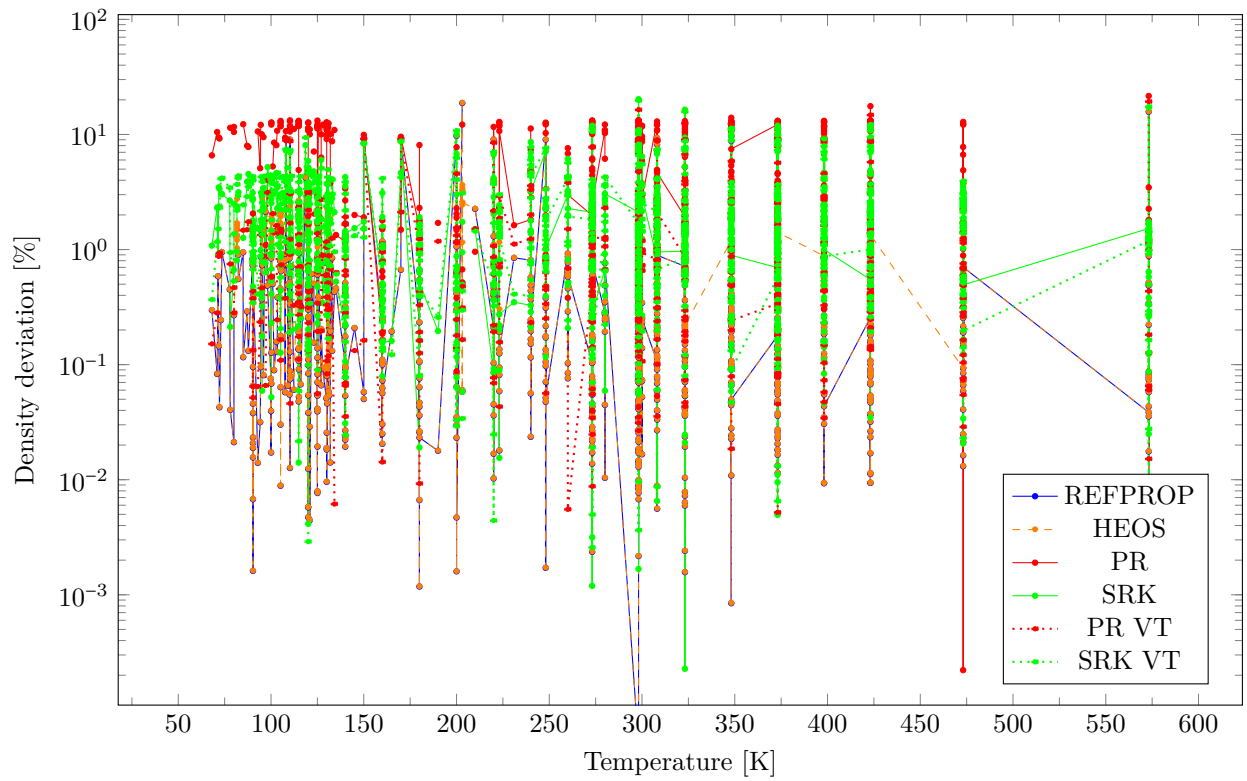
Figure 11: Density dependence on the temperature and pressure for fluid Carbon Monoxide
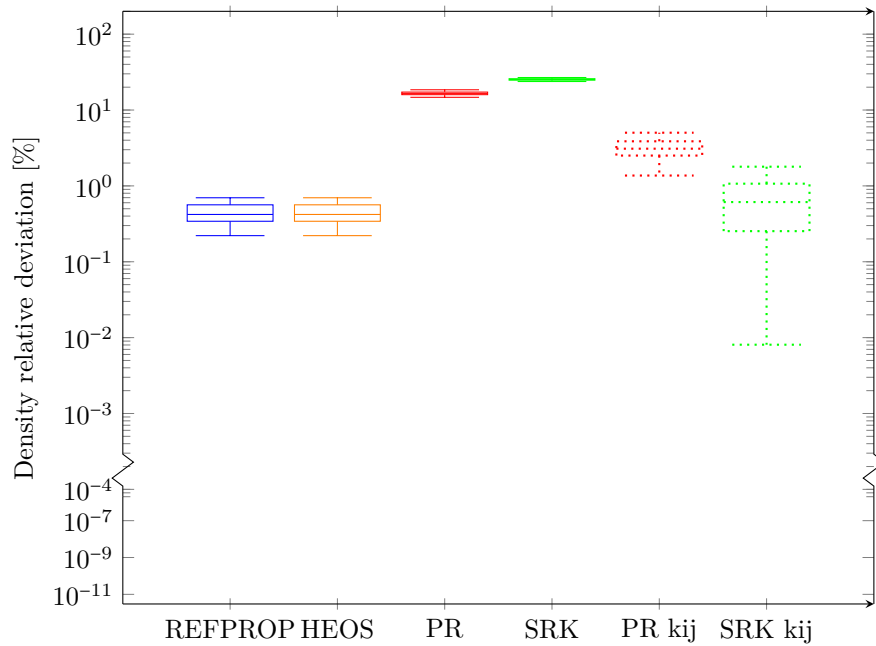
Figure 12: Relative density deviation to experimental data for fluid METHYLPALMITATE

It can also be noted that sometimes some EOS do not gives results when other ones gives, or gives unacceptable deviations ($\geq 100\%$) where others gives more reasonable results as for the fluid n-Dodecane (14 and 15).

In a general manner, the relative deviations do not seem to be much affected by the temperature nor the pressure value 4, 6, 11, 13 and 15. This means that the absolute deviation (the deviation in Pa or K) will increase proportionally with the pressure and the temperature.
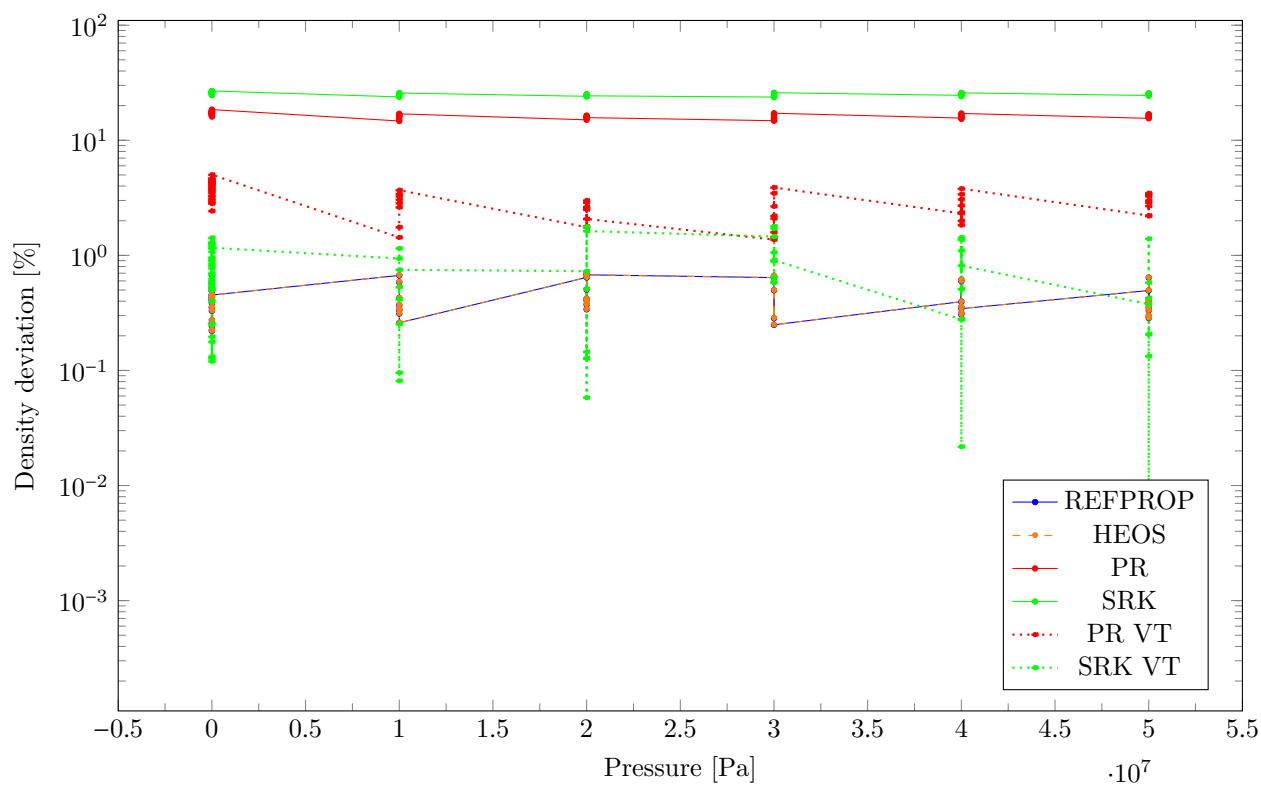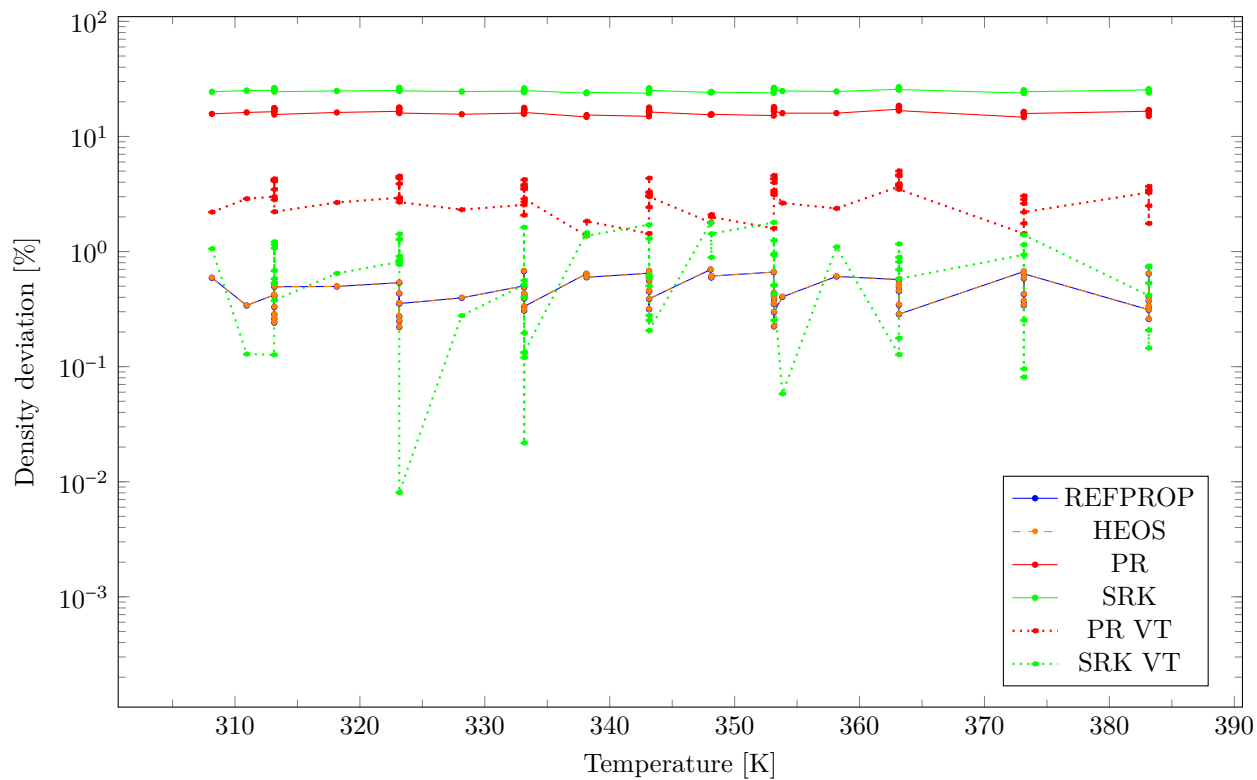
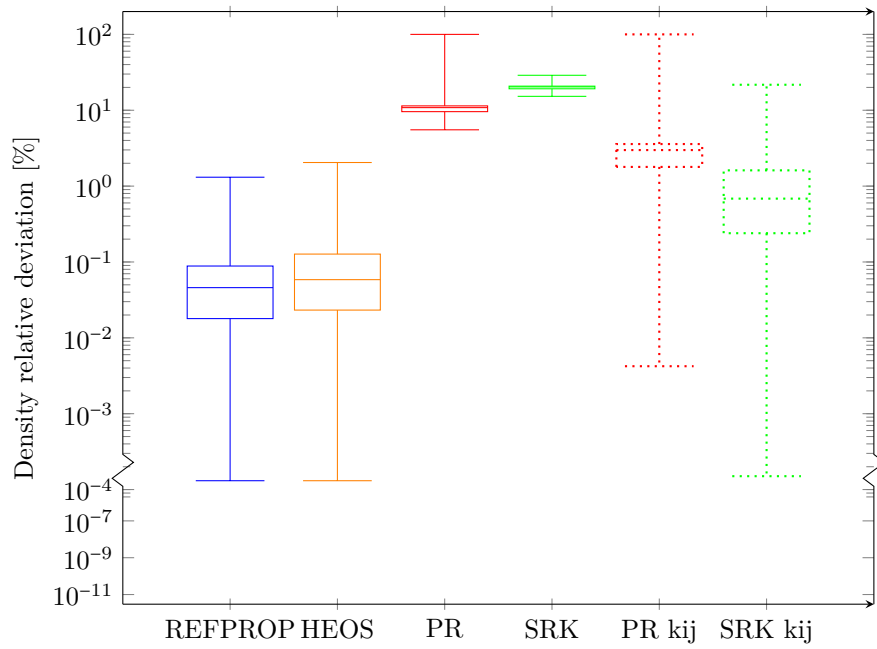Figure 13: Density dependence on the temperature and pressure for fluid METHYLPALMITATE

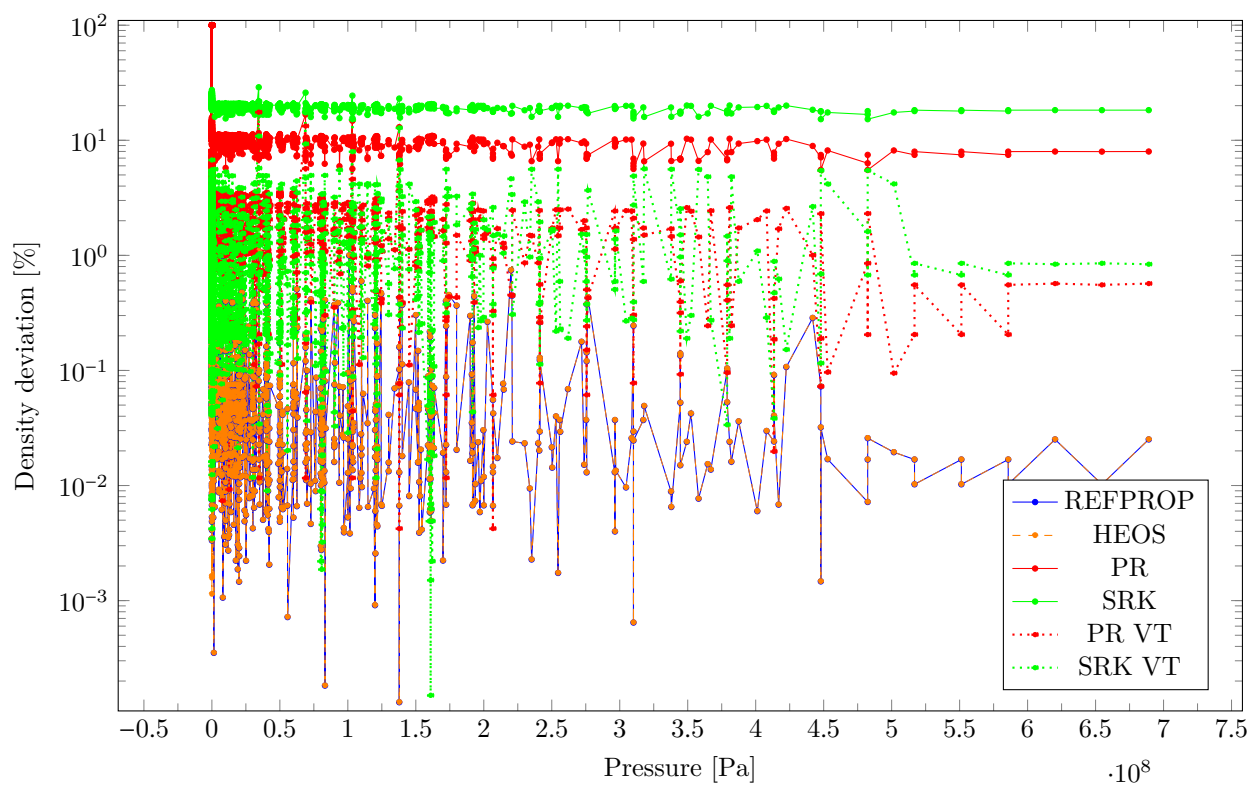Figure 14: Relative density deviation to experimental data for fluid n-Dodecane
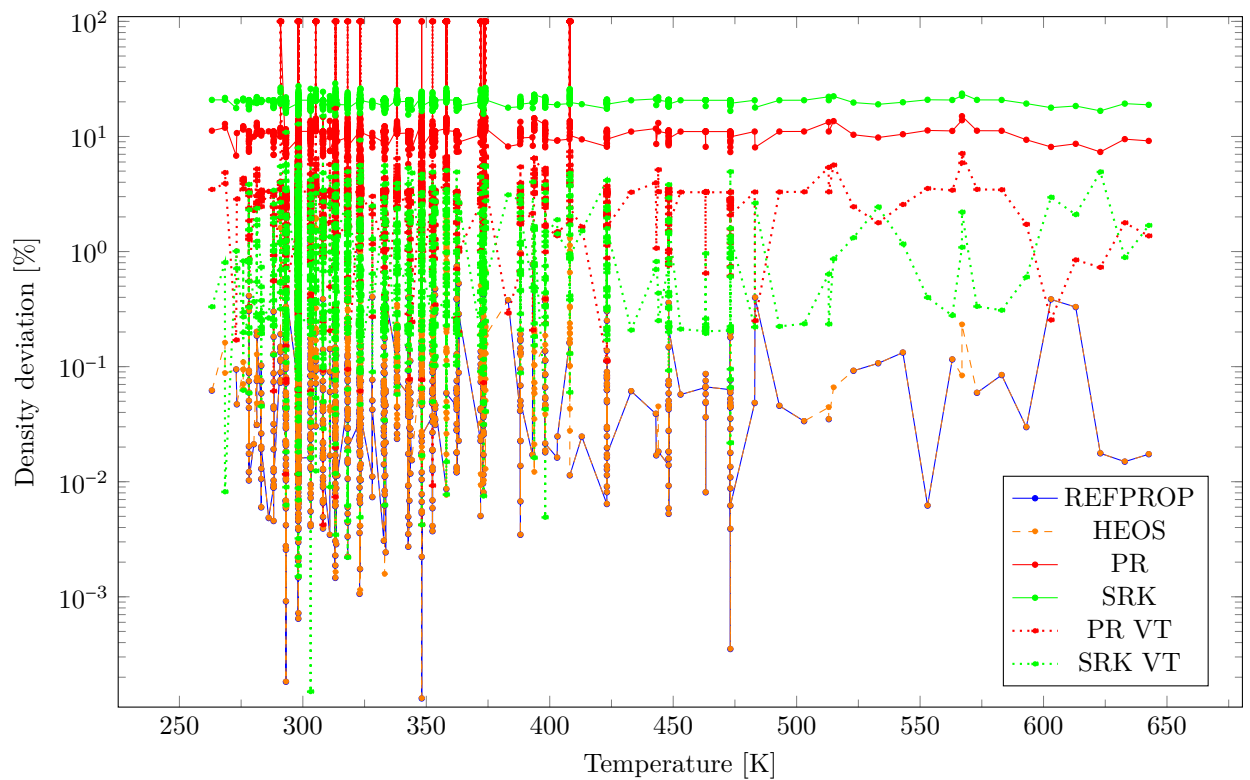
Figure 15: Density dependence on the temperature and pressure for fluid N-DODECANE

4.2. Binary mixtures

An other data set of experimental data has been collected by NIST for mixtures, but only containing vapour-liquid equilibrium (VLE) data.

These data consist of the molar fraction of each component and the temperature and pressure. The molar fraction at a given temperature and pressure are specified to be either liquid or gaseous, which allows to define the quality (0 or 1).

Two values where computed thanks to the state models: the temperature from the pressure and the quality, and the pressure from the temperature and quality. The deviation between the computed values and the experimental data where then computed as following:

$$E_T = \frac{\|T_{data} - T_{calc}\|}{T_{data}} \tag{32}$$

$$E_p = \frac{\|p_{data} - p_{calc}\|}{p_{data}} \tag{33}$$

The effect of the volume translation has not been evaluated here, as no density/volume data where provided.

As these are mixtures, there is the possibility to use an interaction parameter. The one currently implemented in CoolProp is the Van der Waals mixing rules with one parameter k_{ij}. For this work, the interaction parameter was fitted to minimize the deviation to experimental data with Brent's method. The error to minimise was expressed as follow:

$$\bar{E} = \sum \left| E_T + 0.1 E_p \right| \tag{34}$$

were E_T and E_p are from equations 32 and 33.

The difference of results between pure temperature or pure pressure errors where not significant. The pressure term has been weighted by 0.1 as it's magnitude was around 10 times bigger than the deviation in term of temperature.

With the mixture, the differences between RefProp and CoolProp's HEOS are a bit more marked as can be seen in Figure 16. Depending on the fluid, RefProp can be better than CoolProp's HEOS, especially when it comes to near critical data where the later tend to gives very wrong values (see Figure 18), but the Figure 19 is a good example where CoolProp's HEOS is far better.

On the cubic's side, the results for the liquid-vapour equilibrium seems extremely good and comparable with RefProp and CoolProp's HEOS. It is interesting to notice that the volume translation problem occurring with density and volume value do not seem to be a weight for these VLE data.

A very important thing to notice with the mixture R1234YF-R134A is the influence of the molar fraction on the deviation (Figure 20). RefProp and the two cubics (without the binary interaction parameter k_{ij}) have a deviation that considerable increases (around 10 times bigger) when mixing the two fluid compared to the pure fluids, with a maximum around equimolar composition. This is the kind of behaviour that is expected when using two sufficiently different fluids, the way they interact together is different to the way they interact with themselves.

This effect is reduced with the interaction model, and it appears that CoolProp's HEOS have a good interaction model for this mixture. This is also corrected for the cubic by the k_{ij} interaction parameter. This explains the better behaviour of CoolProp's HEOS and the cubics with interaction parameter for this particular mixture.

Other mixtures like R134A-R32 are more similar and don't benefit that much from a better mixing rule (Figure 17). This lead to more homogeneous deviations between the EOS.

Again, the variation of temperature and pressure on the relative deviation seems minimal except when approaching to the critical point.

The temperature deviations are significantly smaller than the pressure deviations for all EOS.
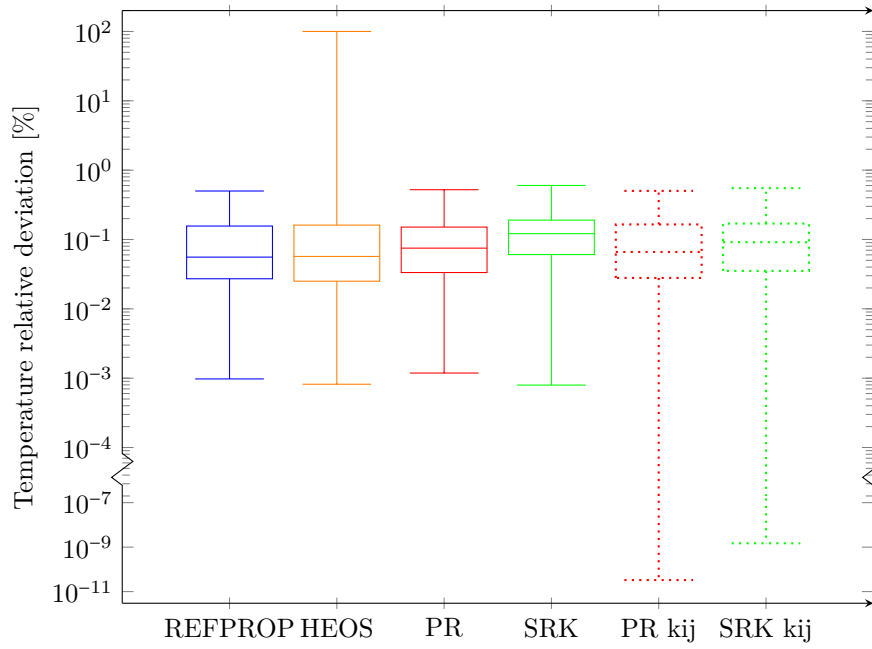
(a) Temperature deviation
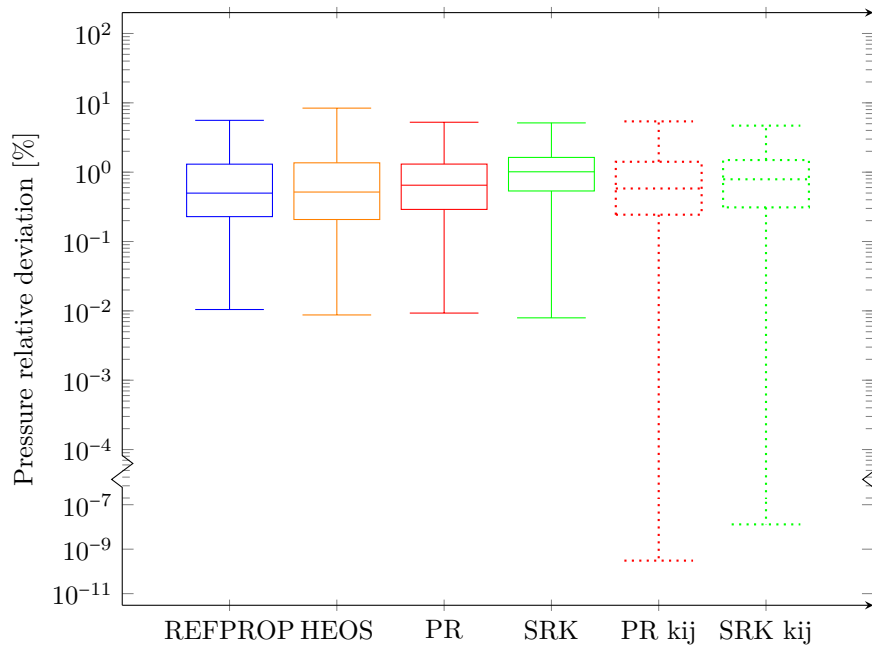
(b) Pressure deviation

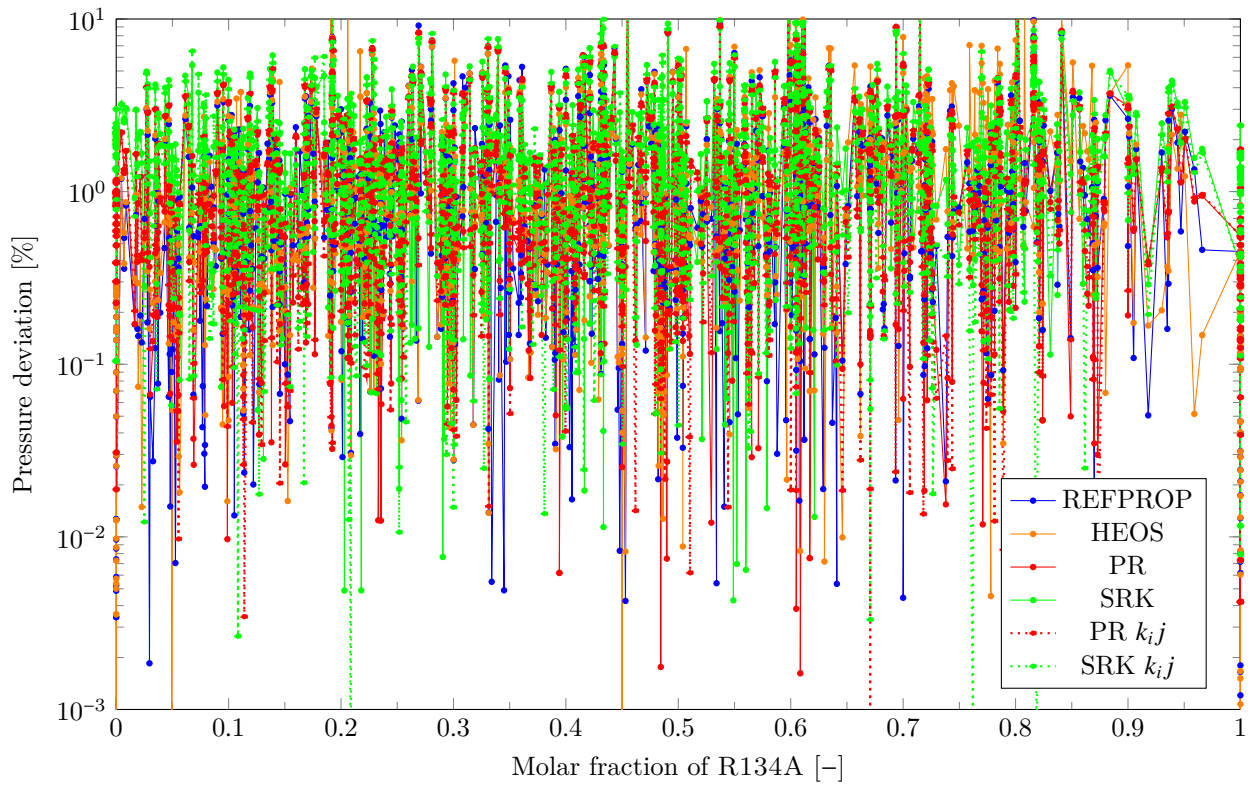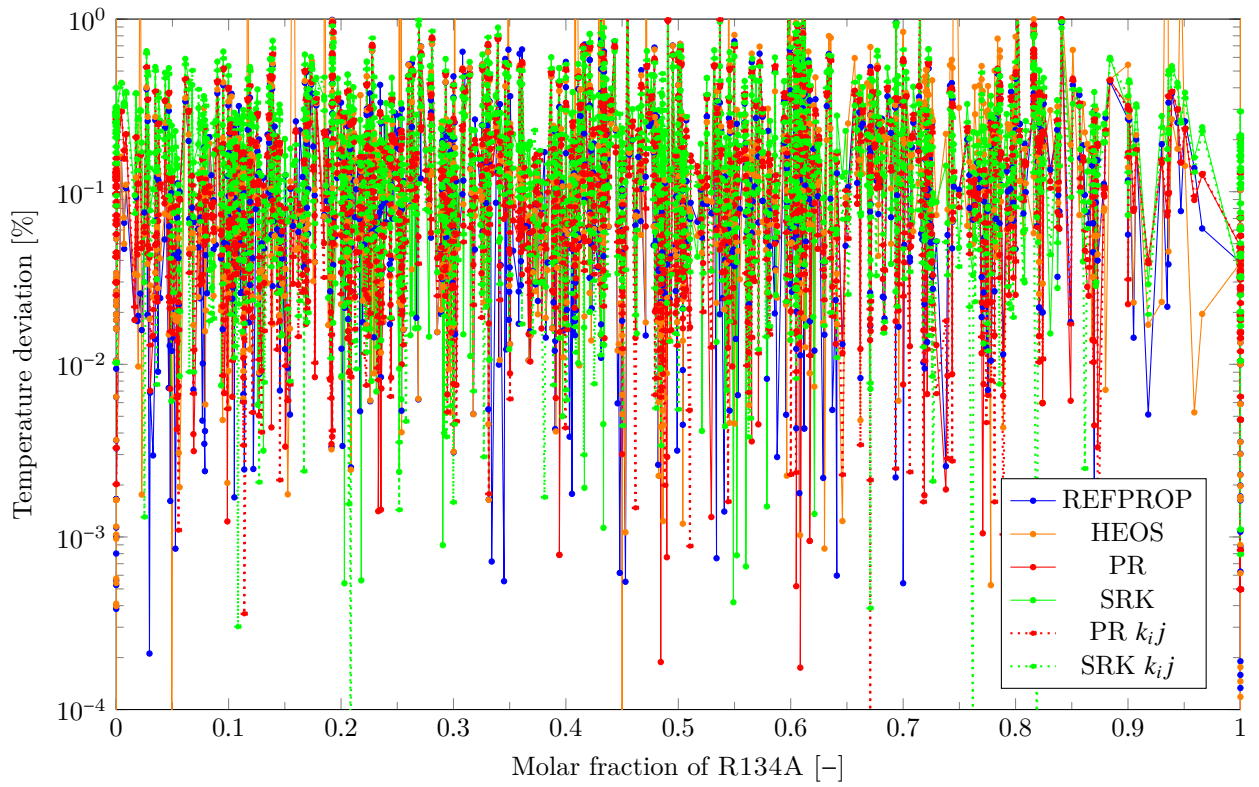Figure 16: Relative deviation to experimental saturation data for mixtures based on R125 and R134A

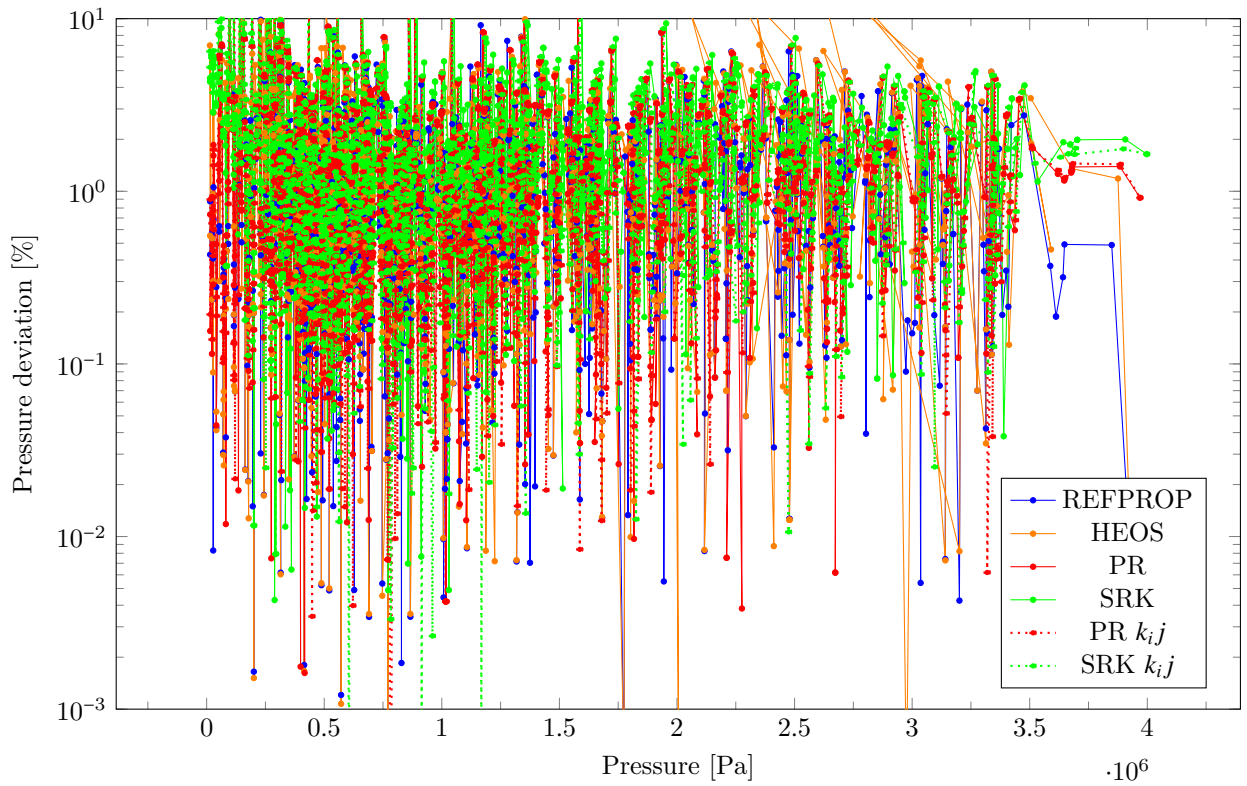Figure 17: Dependence on the molar fraction for the binary mixture R134A-R32
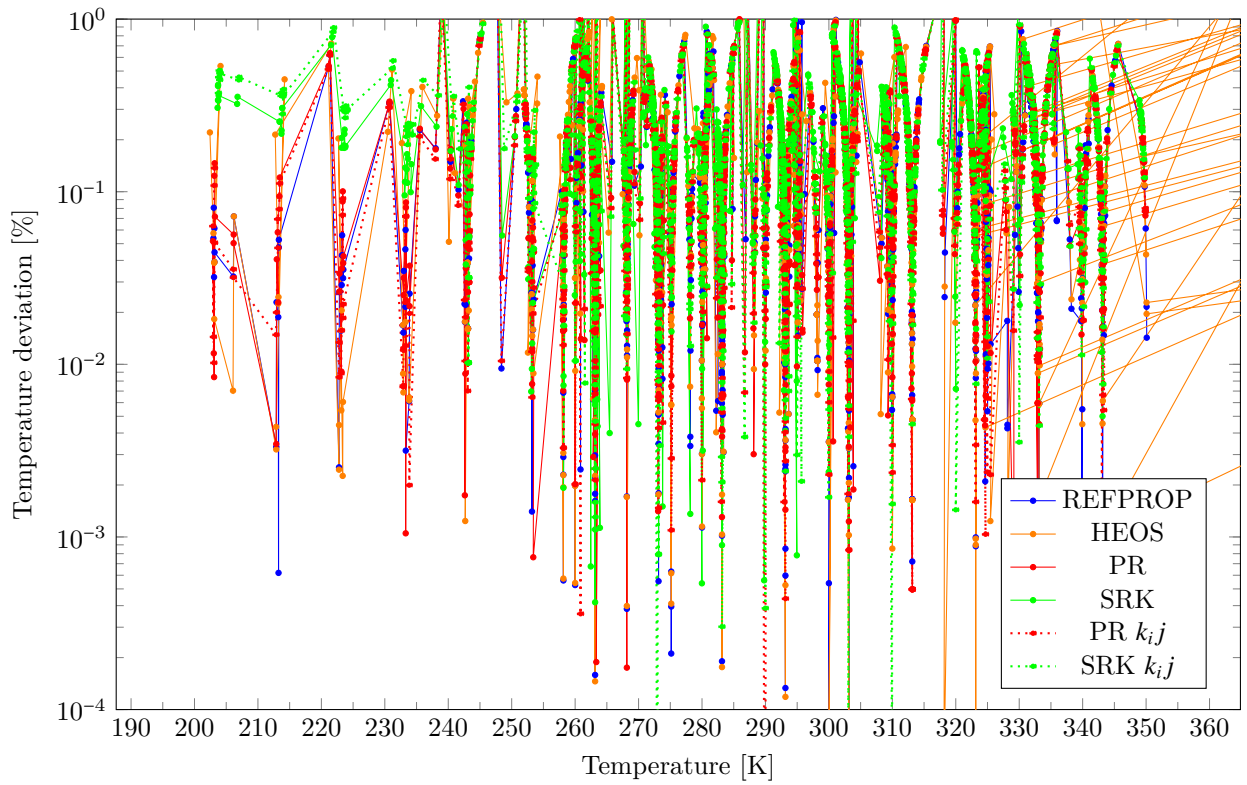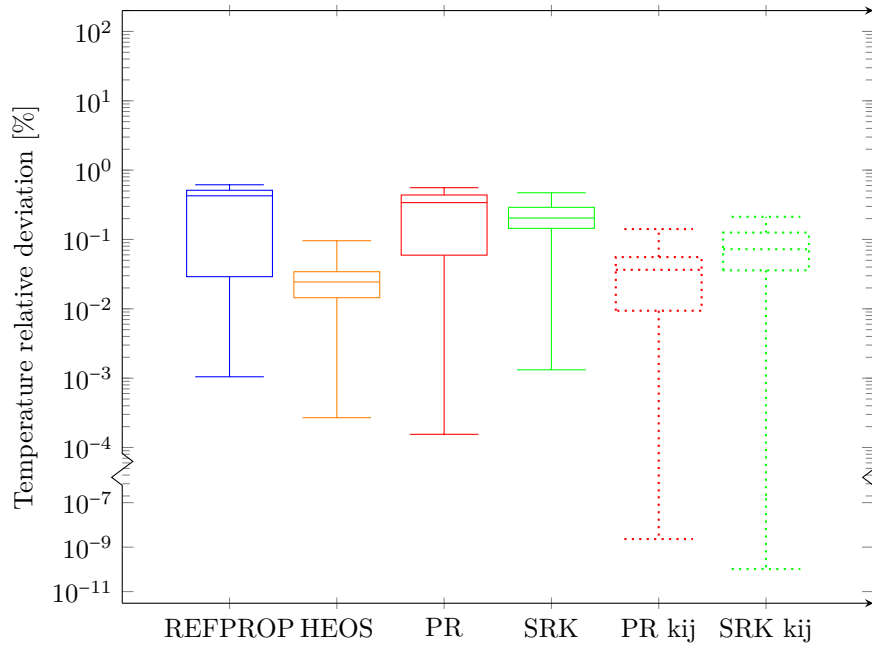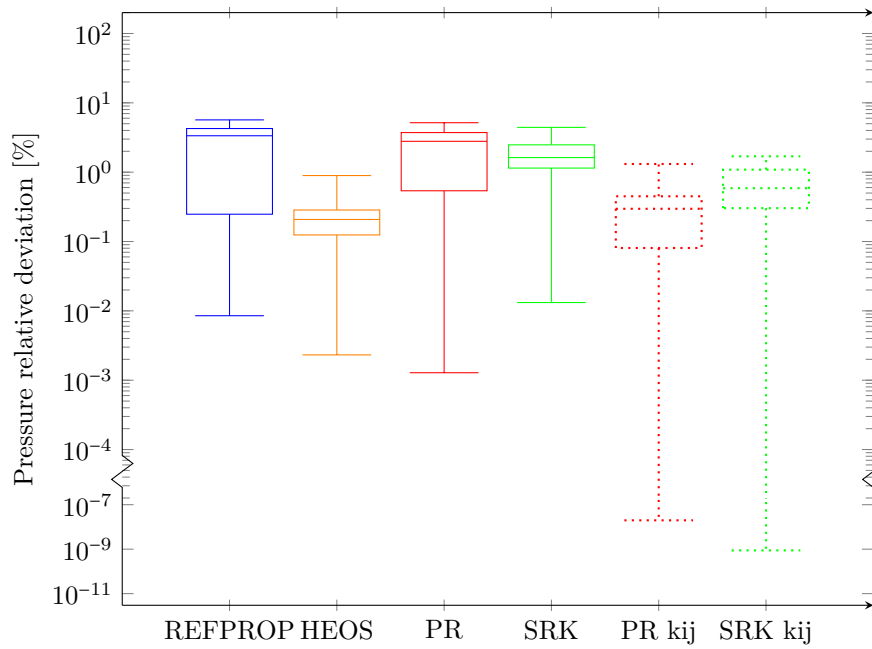
Figure 18: Dependence on the temperature and pressure for the binary mixture R134A-R32

(a) Temperature deviation

(b) Pressure deviation

Figure 19: Relative deviation to experimental saturation data for mixtures based on R1234YF and R134A
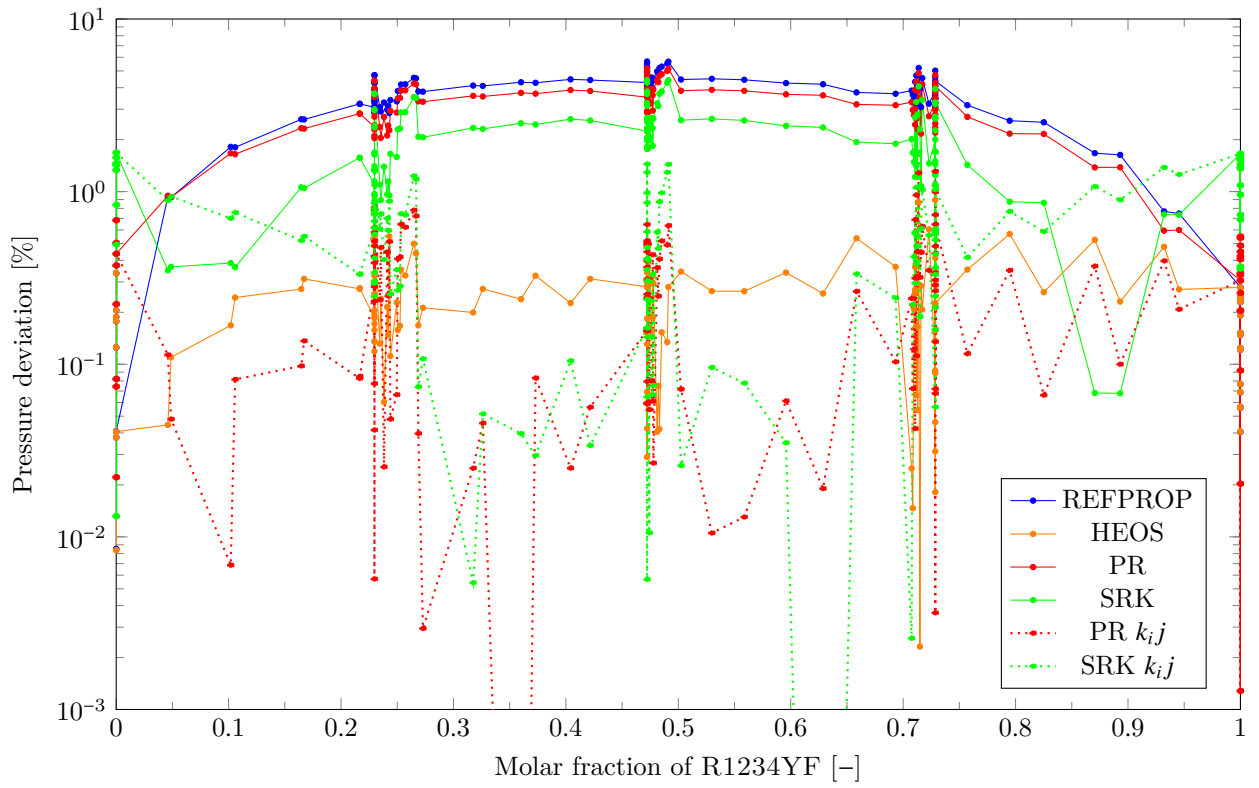
Figure 20: Dependence on the molar fraction for the binary mixture R1234YF-R134A
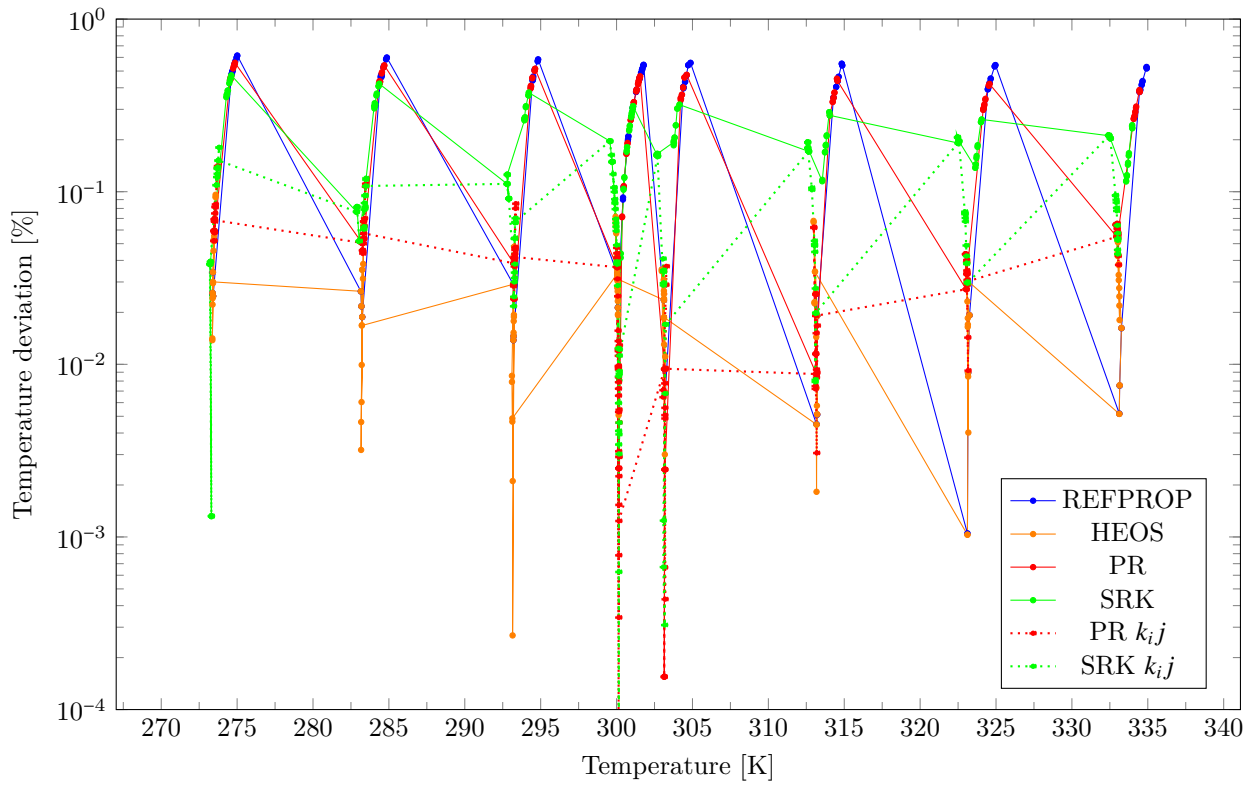
Figure 21: Dependence on the temperature and pressure for the binary mixture R1234YF-R134A

4.3. Ternary mixtures

The ternary mixtures are from the same data set as the binaries. The binary interaction parameters k_{ij} where fitted with the binary mixture and reused here.

The results for the ternary mixtures are similar to the ones from the binaries.
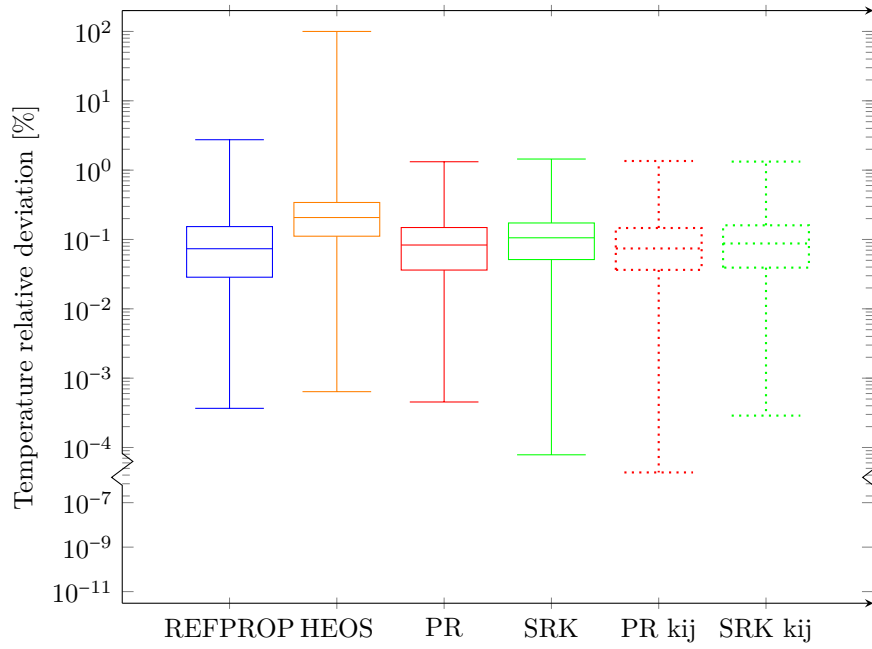
(a) Temperature deviation
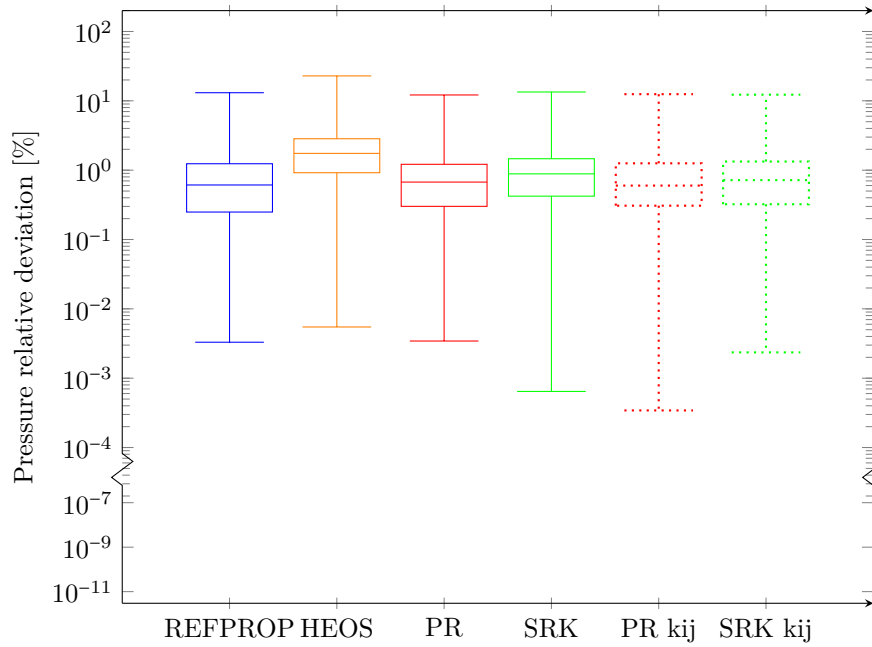
(b) Pressure deviation

Figure 22: Relative deviation to experimental saturation data for mixtures based on R125, R32 and R134A
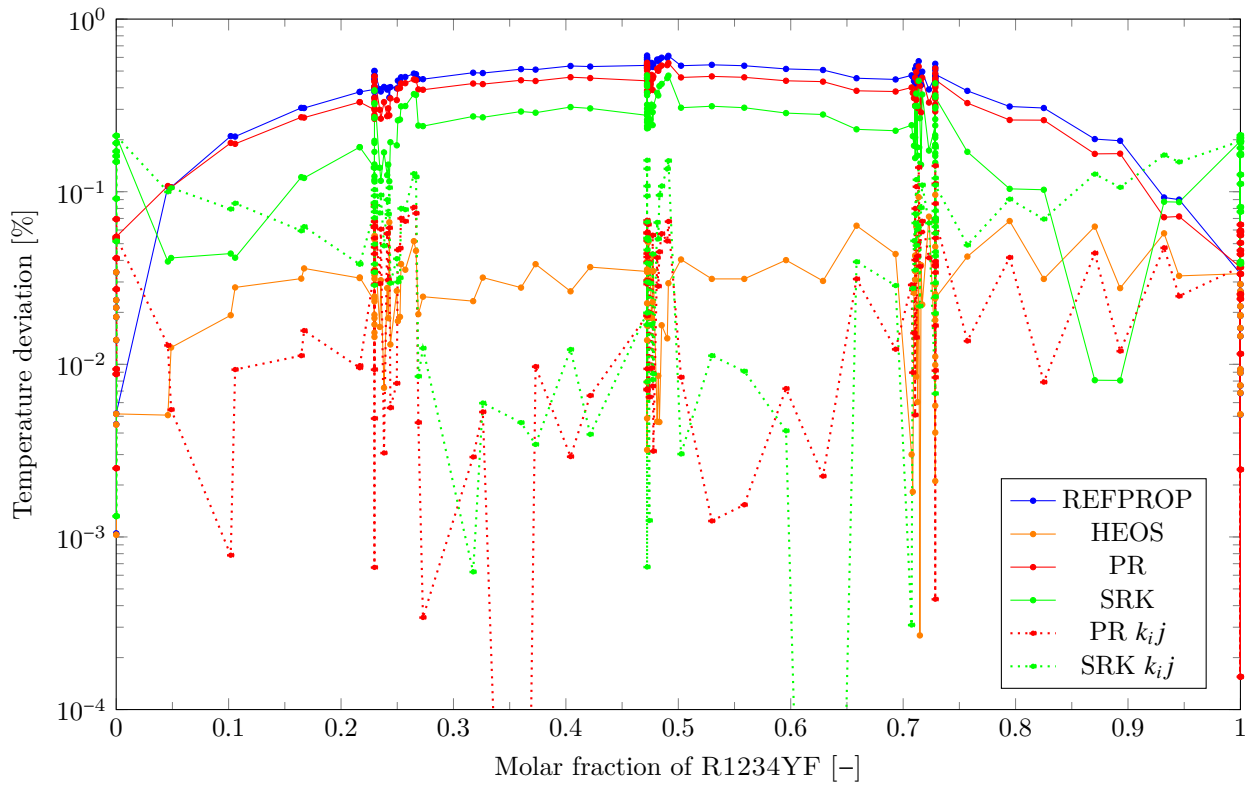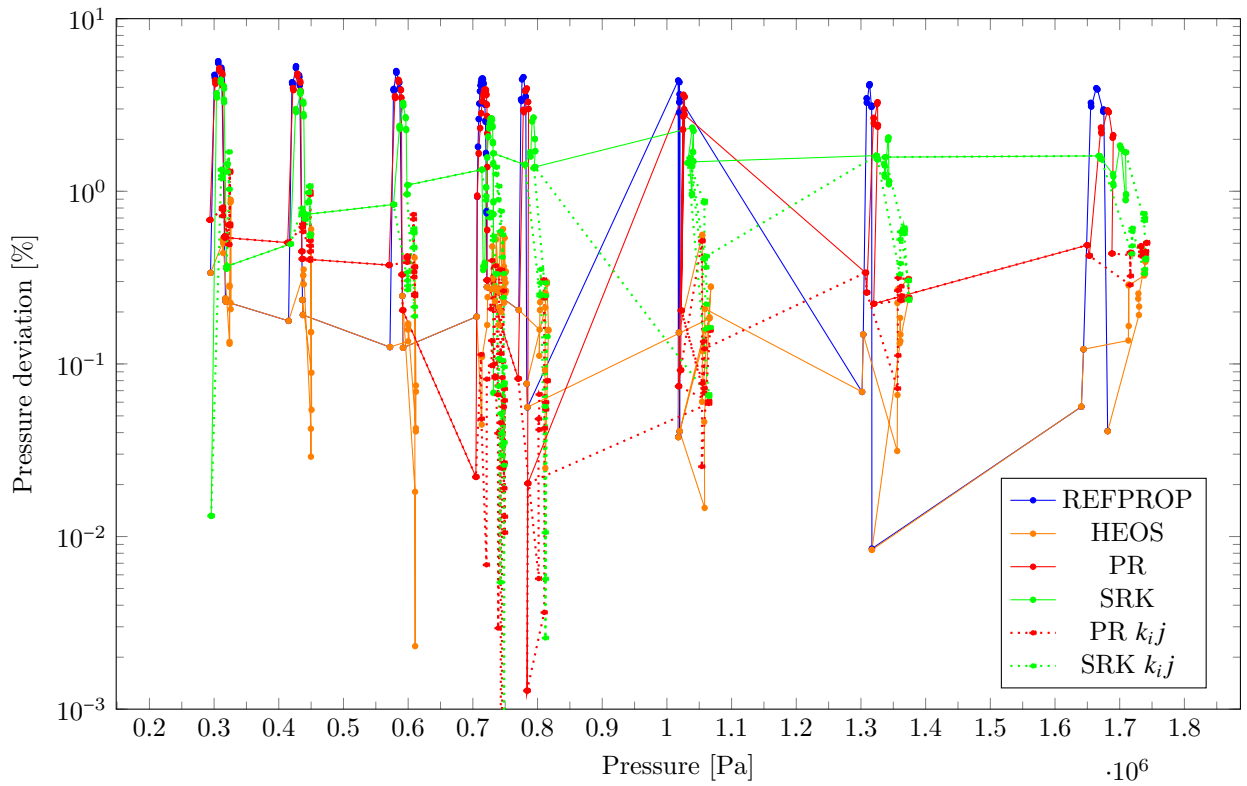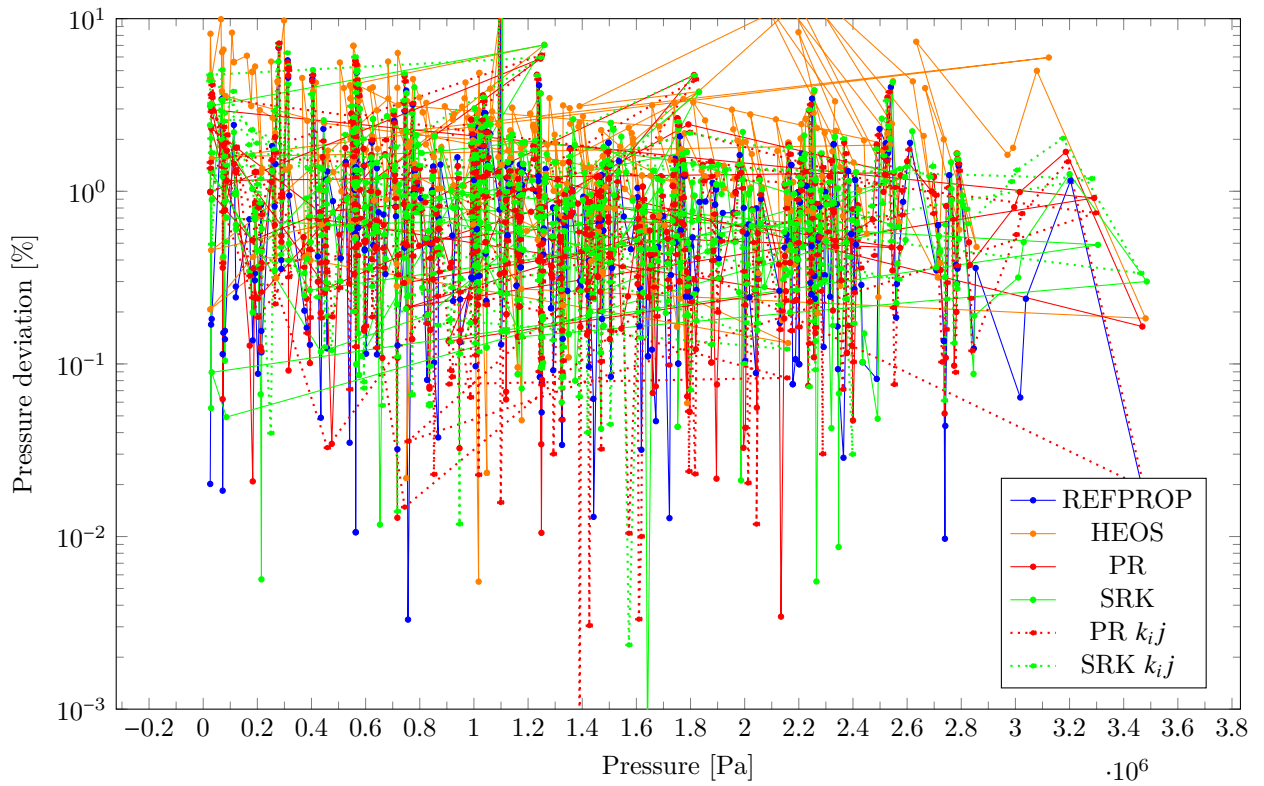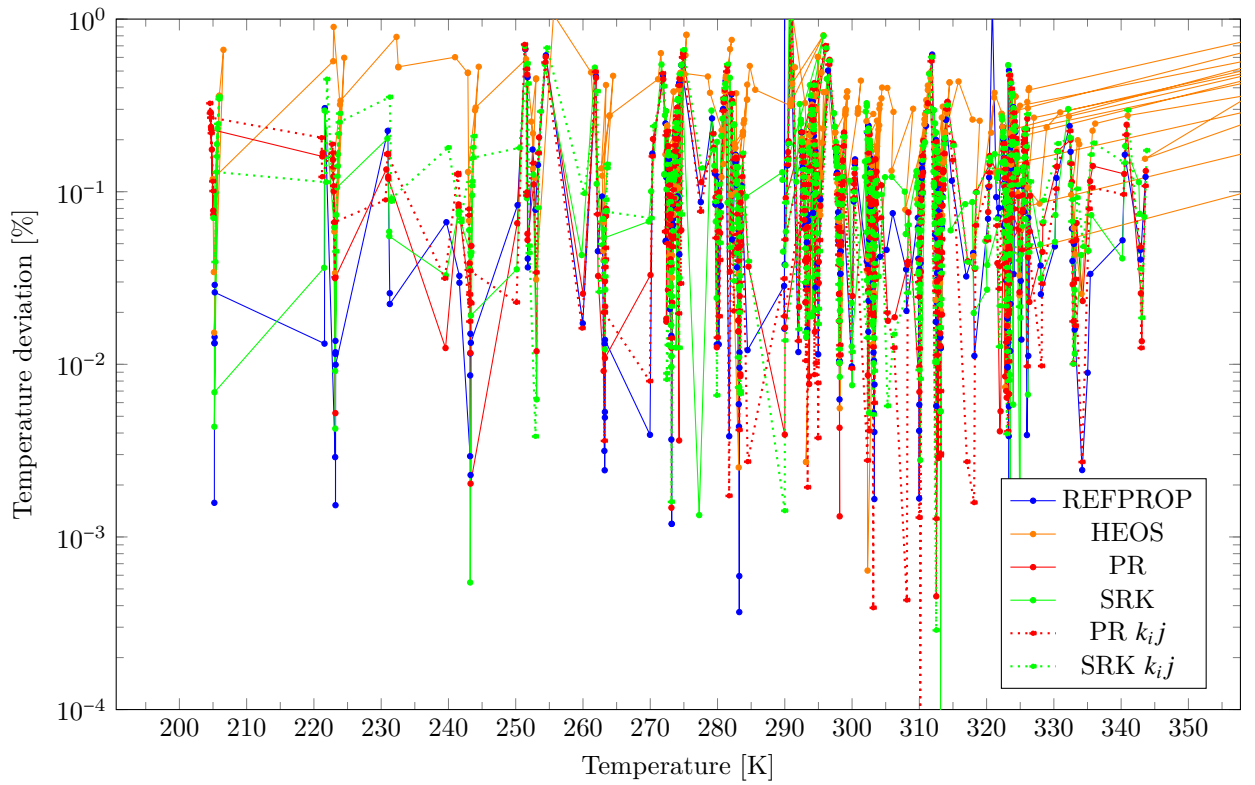
Figure 23: Dependence on the temperature and pressure for the ternary mixture R125-R32-R134A

5. Acknowledgements

I would like to thank the professor Sylvain Quoilin for having given to me the opportunity to make this master thesis abroad. This was a very interesting experience which allowed me to practice English and meet an other culture.

I have a big thank to give to the DTU team who took care of me in Denmark: the professor Fredrik Haglind, and the two post doctorates Maria E. Mondejar Montagud and Jorrit Wronski. It was a real pleasure to work with them.

I also thanks Ian Bell, our contact at NIST who manage to provide us with the database and without who CoolProp would not exist.

6. Conclusions

The simple cubic equations of state do not always gives satisfying results to compute density. This can however be mostly corrected with a simple translation coefficient requiring a single measurement of saturated liquid, and more complex translation models could potentially give more accurate results.

The cubic equations of states are very effective at modelling the liquid vapour equilibrium, competing with well recognise software.

Depending on the interaction between the fluid constituting the mixtures, all models benefit from binary interaction knowledge. This is sometimes integrated in the software, but would generally be an issue with not yet well studied mixtures. A simple coefficient (to be determined experimentally or approximated) can be used to improve greatly the results of cubic equations when the interaction between the fluids is significant. An alternative would be to approximate the interaction with the UNIFAQ model as it is done with the VTPR. Determination of models to approximate the binary interaction parameters depending on the type of fluid used would be an interesting subject for complementary study.

More complex models can be used for the attractive parameter like the Mathias-Copeman and the TWU equations. They both require 3 supplementary parameters and are already implemented in CoolProp. Their impact could be interesting for a further study.

The speed of the models are not compared in this work. The comparison would be interesting, but it is useful to notice CoolProp also provide a tabular interface which allows for extremely fast properties computation when the tables have been generated (with a small loss of accuracy).

The cubic equations of states gives a wide range of possibilities from the simplest and fast model but slightly lacking accuracy to more complex and accurate models. They provide a great tool for evaluation of fluids when few data are available.

Ahlers, J., Gmehling, J., 2001. Development of an universal group contribution equation of state. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state. Fluid Phase Equilibria 191 (1-2), 177–188.
URL http://www.sciencedirect.com/science/article/pii/S0378381201006264/pdfft?md5=86daea9e53bace87587e62b056b3007e&pid=1-s2.0-S0378381201006264-main.pdf

Bell, I., Jäger, A., 2016a. Helmholtz energy transformation of common cubic equations of state for use with pure fluids and mixtures. Journal of Research of the National Institute of Standards and Technology 121 (July), 238–263.
URL https://www.researchgate.net/publication/304186500_Helmholtz_Energy_Transformations_of_Common_Cubic_Equations_of_State_for_Use_with_Pure_Fluids_and_Mixtures

Bell, I. H., Jäger, A., 2016b. Intermediate Terms, 1–14.

Bell, I. H., Jäger, A., 2016c. Supplementary Information to accompany Helmholtz energy transformations of common cubic equations of state for use with pure fluids and mixtures. No. 5.

Chen, W.-Y., Liu, J., 2007. Mathcad Modules for Supercritical Fluid Extraction based on Mixing Rules. Appendix A - Mixing Rules (662), 1–10.
URL http://home.olemiss.edu/{~}cmchengs/Extraction/AppendixA_MixingRules.doc

CoolProp, 2016. Cubic Equations of State.
URL http://www.coolprop.org/coolprop/Cubics.html

Faúndez, C. a., Valderrama, J. O., 2009. Low pressure vapor–liquid equilibrium in ethanol+congener mixtures using the Wong–Sandler mixing rule. Thermochimica Acta 490 (1-2), 37–42.
URL http://www.sciencedirect.com/science/article/pii/S0040603109000999/pdfft?md5=65533f85d53569eeebae29e565402cc4&pid=1-s2.0-S0040603109000999-main.pdf

Frey, K., Augustine, C., Ciccolini, R. P., Paap, S., Modell, M., Tester, J., 2007. Volume translation in equations of state as a means of accurate property estimation. Fluid Phase Equilibria 260 (2), 316–325.
URL http://www.sciencedirect.com/science/article/pii/S0378381207004591/pdfft?md5=c750d4ea93f662a13b87183c76a8654e&pid=1-s2.0-S0378381207004591-main.pdf

Ji, W.-R., Lempe, D., 1997. Density improvement of the SRK equation of state. Fluid Phase Equilibria 130 (1-2), 49–63.
URL http://www.sciencedirect.com/science/article/pii/S0378381296031901

Lemmon, E. W., Huber, M. L., McLinden, M. O., 2013. Reference Fluid Thermodynamic and Transport Properties-REFPROP, version 9.1.
URL http://www.nist.gov/srd/upload/REFPROP9.PDF

López, J. A., Cardona, C. A., 2006. Phase equilibrium calculations for carbon dioxide+n-alkanes binary mixtures with the Wong–Sandler mixing rules. Fluid Phase Equilibria 239 (2), 206–212.
URL http://www.sciencedirect.com/science/article/pii/S0378381205004565

Martin, J. J., 1967. Equations of State—Applied Thermodynamics Symposium. Industrial & Engineering Chemistry 59 (12), 34–52.
URL http://dx.doi.org/10.1021/ie50696a008$\delimiter"026E30F$nhttp://pubs.acs.org/doi/pdf/10.1021/ie50696a008

Martin, J. J., 1979. Cubic Equations of State-Which? Industrial & Engineering Chemistry Fundamentals 18 (2), 81–97.
URL http://dx.doi.org/10.1021/i160070a001

Meng, L., Duan, Y. Y., Wang, X. D., 2007. Binary interaction parameter kij for calculating the second cross-virial coefficients of mixtures. Fluid Phase Equilibria 260 (2), 354–358.
URL http://www.sciencedirect.com/science/article/pii/S0378381207004323/pdfft?md5=e3b19d08e08099003d28392a4450f768&pid=1-s2.0-S0378381207004323-main.pdf

Peng, D.-Y., Robinson, D. B., 1976. A New Two-Constant Equation of State. Industrial & Engineering Chemistry Fundamentals 15 (1), 59–64.
URL http://pubs.acs.org/doi/abs/10.1021/i160057a011

Schmid, B., Gmehling, J., 2012. Revised parameters and typical results of the VTPR group contribution equation of state. Fluid Phase Equilibria 317, 110–126.
URL http://dx.doi.org/10.1016/j.fluid.2012.01.006

Schmid, B., Schedemann, A., Gmehling, J., 2014. Extension of the VTPR group contribution equation of state: Group interaction parameters for additional 192 group combinations and typical results. Industrial and Engineering Chemistry Research 53 (8), 3393–3405.

Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. Chemical Engineering Science 27 (6), 1197–1203.
URL http://ac.els-cdn.com/0009250972800964/1-s2.0-0009250972800964-main.pdf?_tid=cd3fc6c8-1dbd-11e6-a8de-00000aacb35d&acdnat=1463661351_8f1dbe034b52854e2d97cd6d80b7b56b

Valderrama, J. O., 2003. The State of the Cubic Equations of State. Industrial & Engineering Chemistry Research 42 (8), 1603–1618.
URL http://pubs.acs.org/doi/abs/10.1021/ie020447b

Valderrama, J. O., Marambio, L. E., Silva, A. a., 2002. Mixing rules in cubic equations of state applied to refrigerant mixtures. Journal of Phase Equilibria 23 (6), 495–501.
URL http://download.springer.com/static/pdf/558/art{%}3A10.1361{%}2F105497102770331181.pdf?originUrl=http://link.springer.com/article/10.1361/105497102770331181{&}token2=exp=1463652668{~}acl=/static/pdf/558/art{%}253A10.1361{%}252F105497102770

Wong, D. S. H., Sandler, S. I., 1992. A Theoretically Correct Mixing Rule for Cubic Equations of State 38 (5).
URL http://onlinelibrary.wiley.com/doi/10.1002/aic.690380505/epdf