Technische Universität Braunschweig

Molecular simulation studies on the thermophysical properties of fluoropropene refrigerants and their mixtures

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Thermophysical Properties for Technical Thermodynamics, Rostock, 2013

Motivation

- Different fluoropropenes are currently considered as refrigerants, either as pure compounds or as components in low GWP refrigerant mixtures
- The lack of experimental data for the pure compounds and their mixtures hampers studies on their performance in technical applications

$\Rightarrow$ Development of a force field model for reliable predictions of their thermophysical properties by molecular simulation studies to complement experimental data.

Force Field Development

- fully flexible all-atoms ‘class 1’ force field

$$U_{conf} = \sum_{i=1}^{N-1} \sum_{j>i}^{N} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

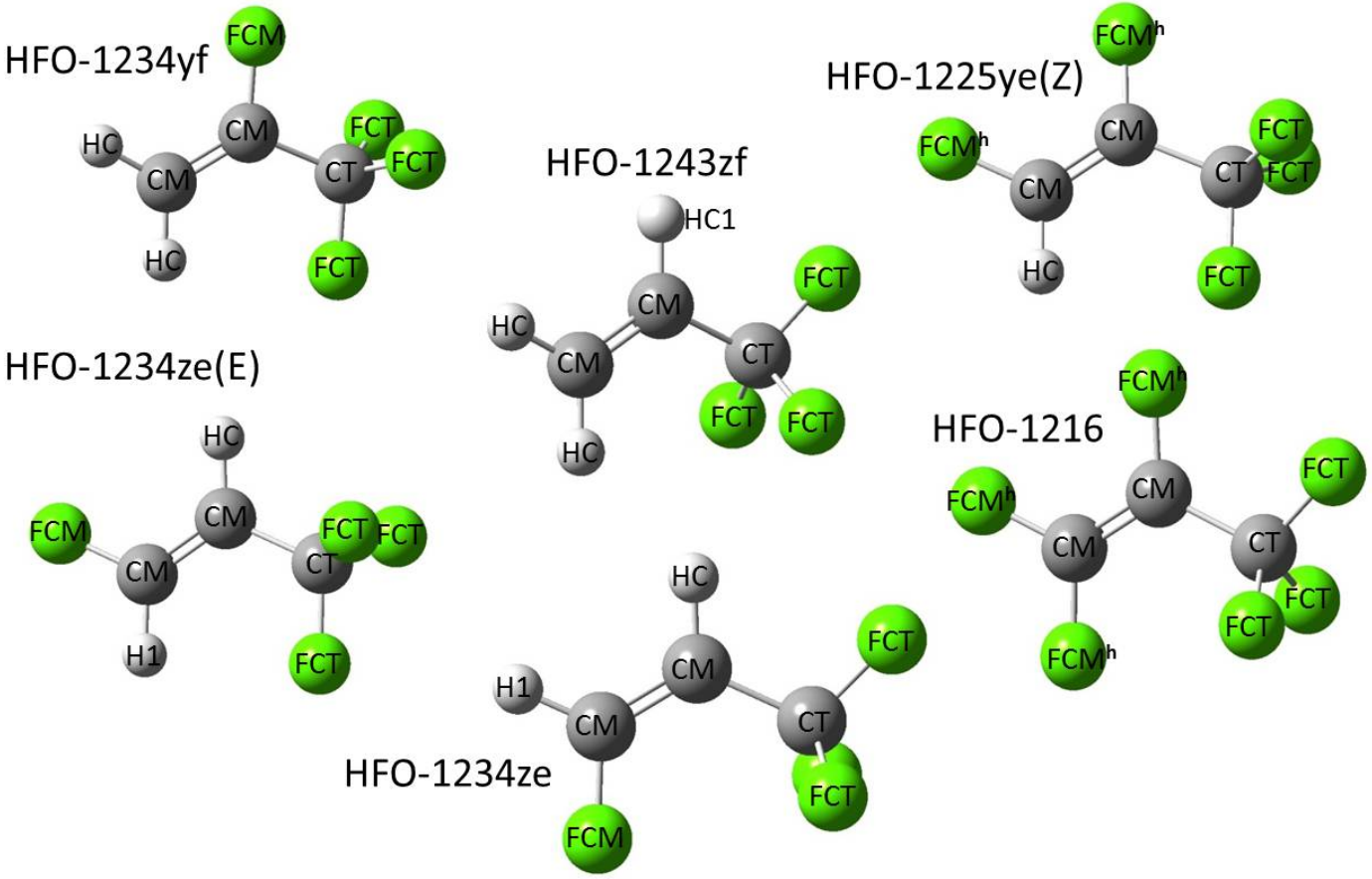
$$+ \sum_{bonds} k_r \left(r - r_0 \right)^2 + \sum_{angles} k_\theta \left(\theta - \theta_0 \right)^2$$

$$+ \sum_{dihedral} k_\chi \left[1 + cos \left(n\chi - \delta \right) \right]$$

- transferable parameters (Lennard-Jones (LJ), intramolecular terms)

Force Field Development

Compounds directly considered at the moment:

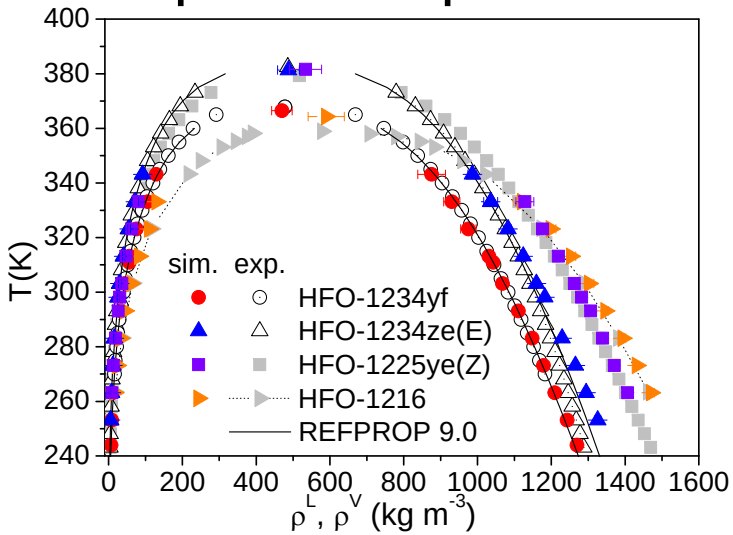


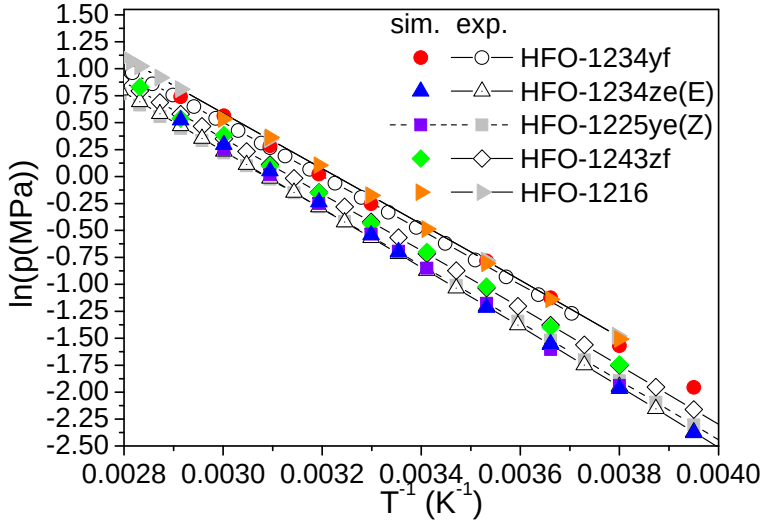
Force Field Development

- nominal bond lengths r_0 and bond angles θ_0 from ab initio optimizations (DFT: B3LYP/DGDZVP)
- force constants k_r, k_Θ and k_χ from ab initio optimizations for perturbated geometries
- ab initio CHELPG charges q_i (HF/6-31G*)
- LJ parameters ε_{ii}, σ_{ii} adjusted to fine-tune agreement with experimental data:
  - CM, FCM: ΔH_{vap}, p_s of C_2F_4
  - HC, H1: AMBER parameter
  - CT, FCT: ρ^L, p_s of HFO-1234yf, HFO-1243zf
  - FCM^h: ρ^L, p_s of HFO-1225ye(Z)

Validation of the Force Field

by Gibbs ensemble (GEMC) simulations on the VLE of the different pure compounds

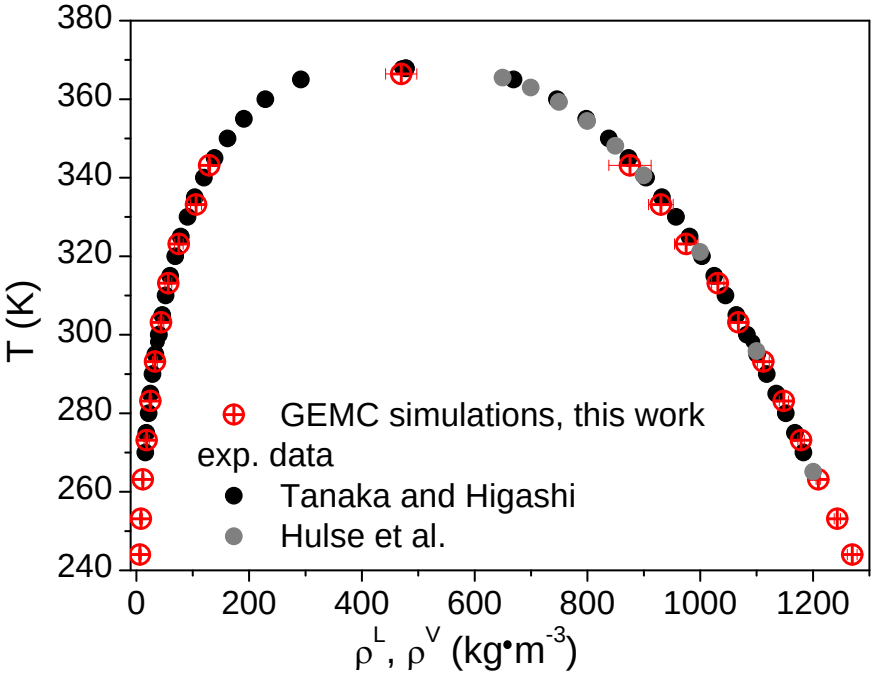


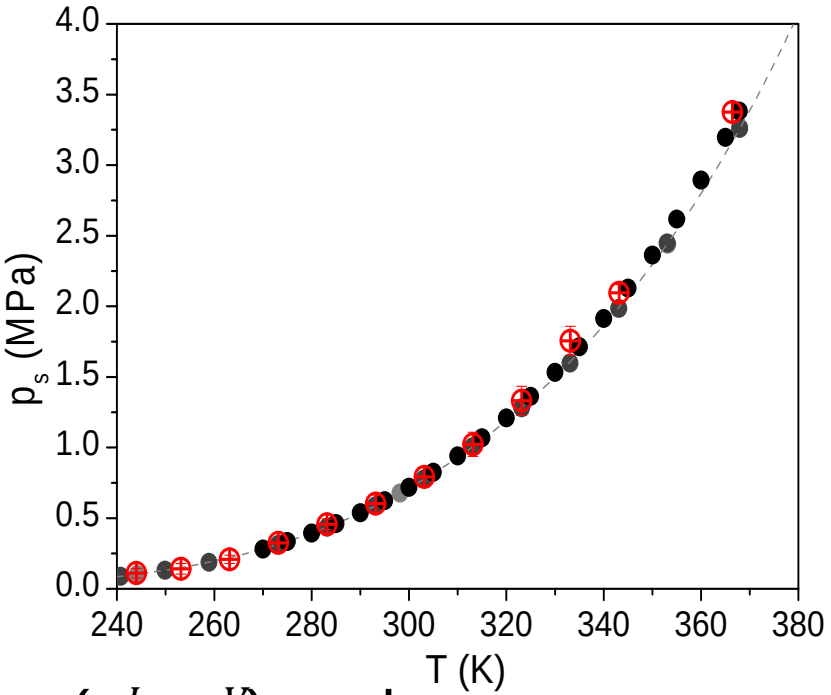


	$T_{c,sim}$ (K)	$T_{c,exp}$ (K)	$\rho_{c.sim}$ (kg m^{-3})	$\rho_{c.exp}$ (kg m^{-3})	$p_{c,sim}$ (MPa)	$p_{c,exp}$ (MPa)	$T_{b,sim}$ (K)	$T_{b,exp}$ (K)
HFO-1234yf	366.6 ± 9.5	367.9	470 ± 26	478	3.38 ± 0.73	3.26-3.38	243.3 ± 3.5	243.8
HFO-1243zf	375.5 ± 14.5	376.2-380.8	422± 40	455.22-462.2	3.56 ± 1.1	3.61-3.79	250.1 ± 4.3	249.3
HFO-1216	364.3 ± 13.2	358.93	590 ± 49	579.03	3.34 ±1.13	3.136	242.4 ± 6.6	243.6
HFO-1234ze(E)	381.4 ± 10.7	382.51	487 ± 29	486	3.87 ± 0.86	3.632	254.9 ± 2.3	254.15
HFO-1225ye(Z)	381.6 ± 15.7	378.2	534 ± 43	527	3.67 ± 1.15	3.183	254.2 ± 3.1	253.5

Validation of the Force Field

GEMC simulation results for the VLE of HFO-1234yf



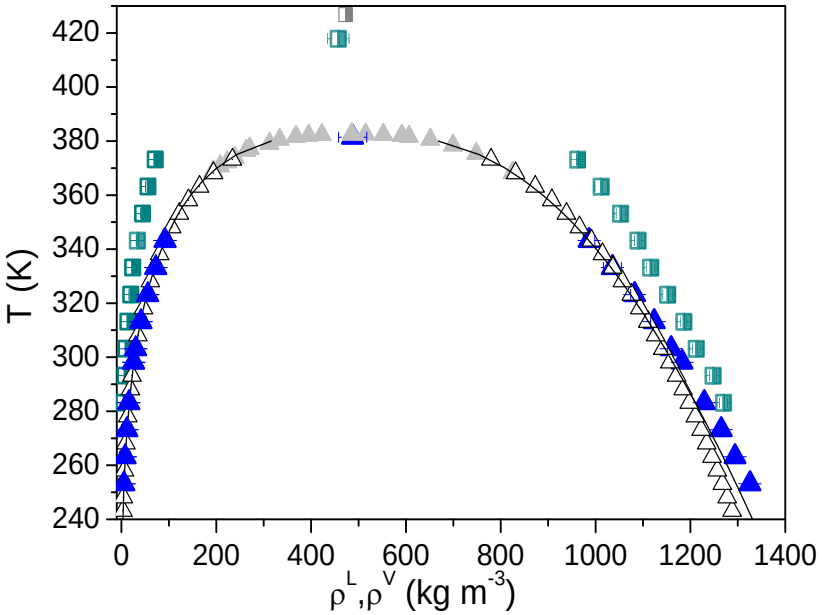


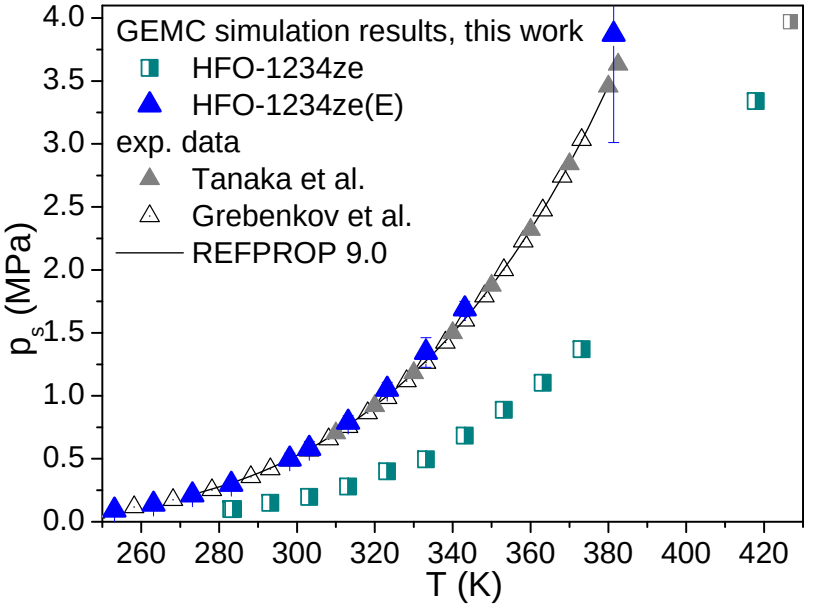
The simulated saturated densities (ρ^L, ρ^V) and vapor pressures (p_s) agree with the experimental data within their error bars

GR, E. J. Maginn, J. Phys. Chem. Letters 1 (2010) 93-96.

Application to HFO-1234ze(E) and HFO-1234ze

Only with individual q_i, but no adjusted LJ parameters

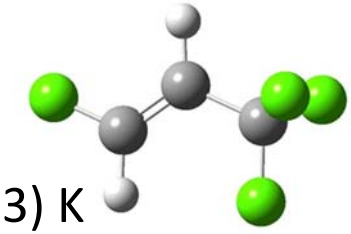




HFO-1234ze(E)

T_b^{exp} = 254.15 K

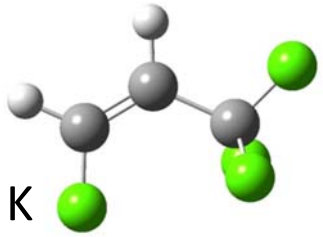
T_b^{sim} = (254.9 ± 2.3) K



HFO-1234ze

T_b^{exp} = 282.15 K

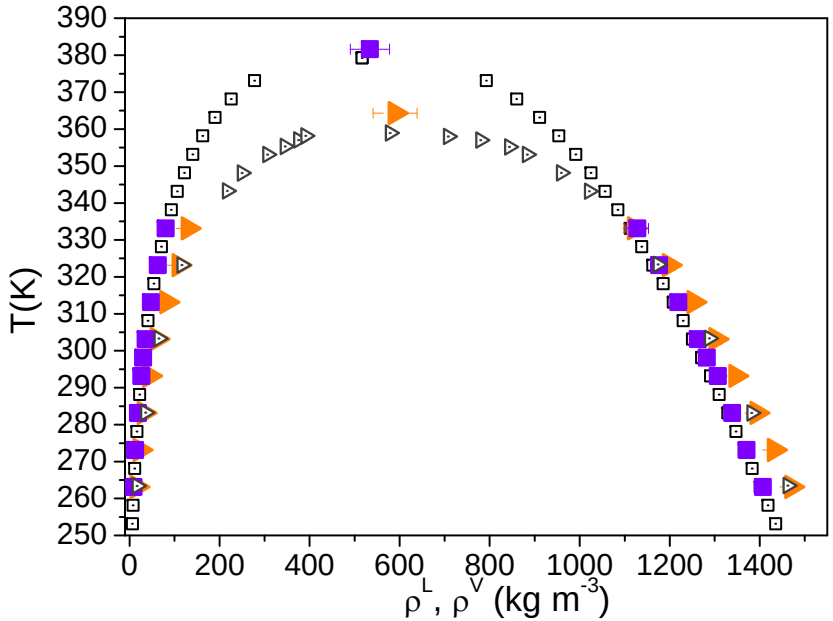
T_b^{sim} = (283.6 ± 3.5) K

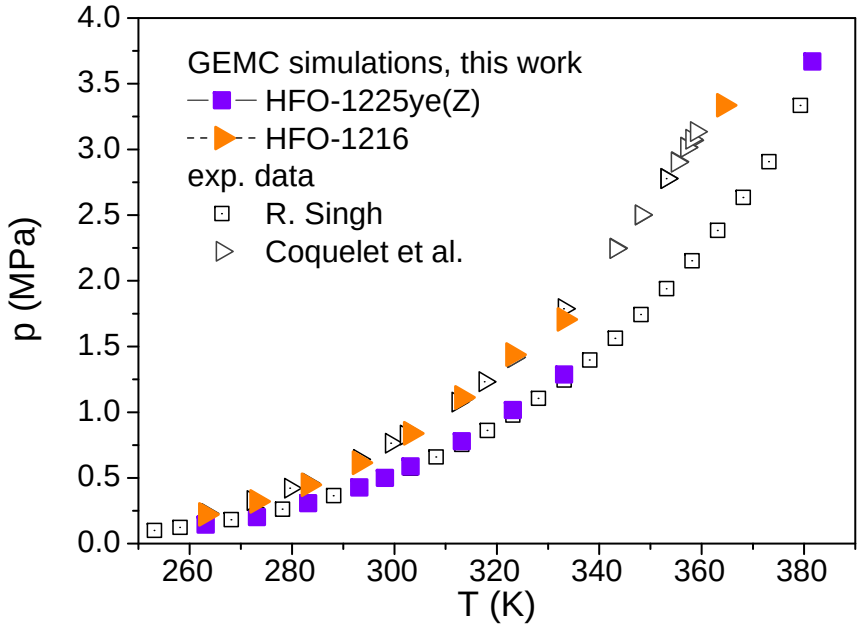


GR, J. Phys. Chem. B 116 (2012) 5744-5751

GEMC results for HFO-1225ye(Z) and HFO-1216

Modified FCM^{h} parameter required for fluoropropenes with > 4 fluorine atoms, adjusted to exp. data for HFO-1225ye(Z)



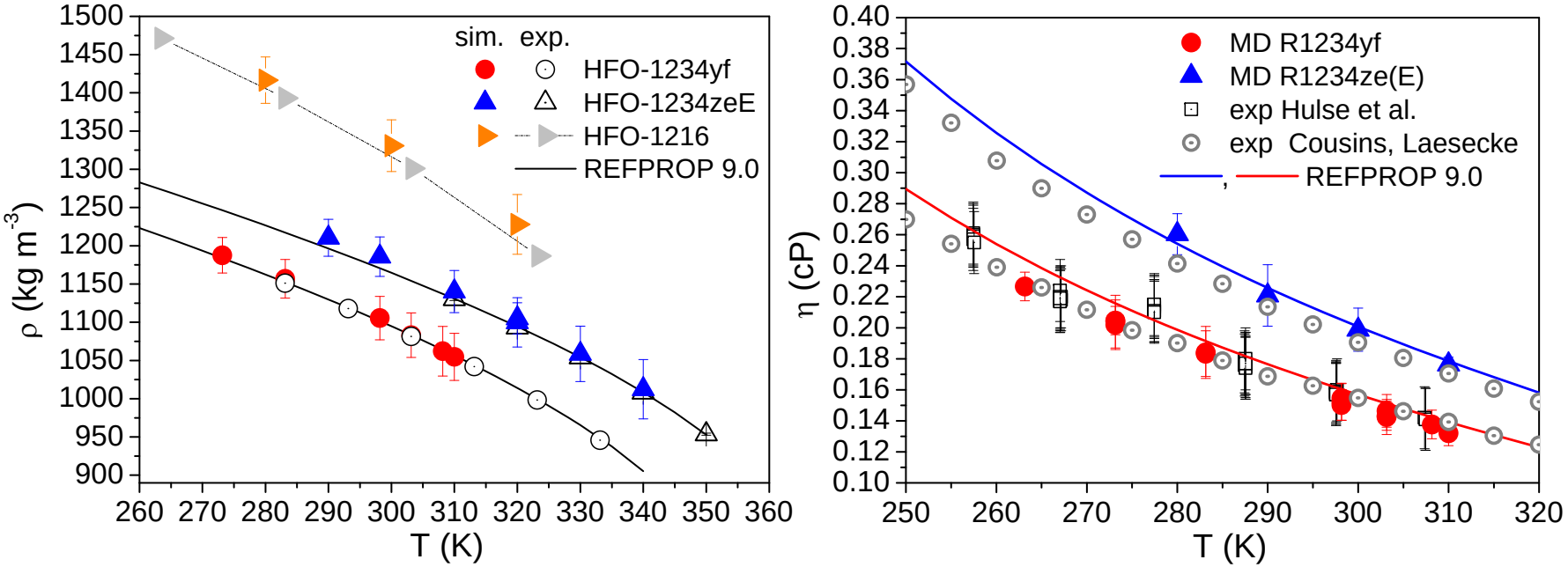


Good reproduction of the VLE of HFO-1216 using the same LJ parameters attests the good transferability of the force field

GR, J. Phys. Chem. B 116 (2012) 5744-5751

Prediction of other thermophysical properties

e.g. liquid densities $\rho(T)$ and viscosities $\eta(T)$ at $p = 2\ MPa$

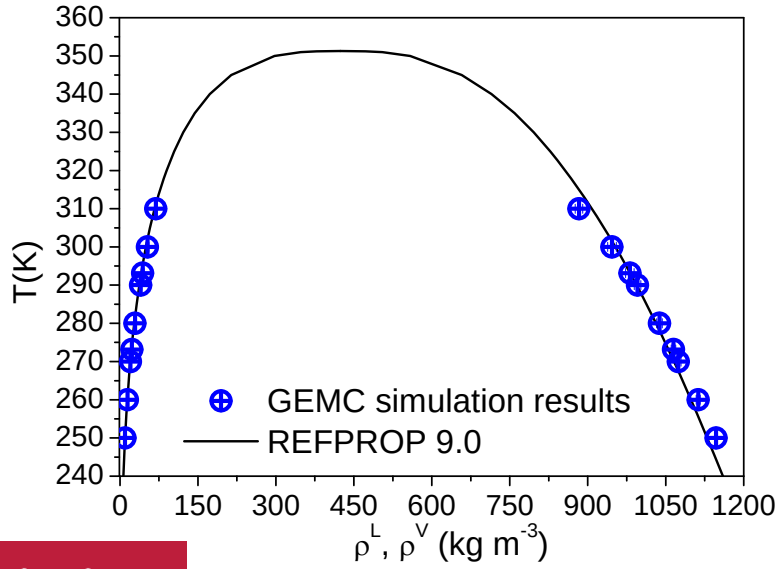


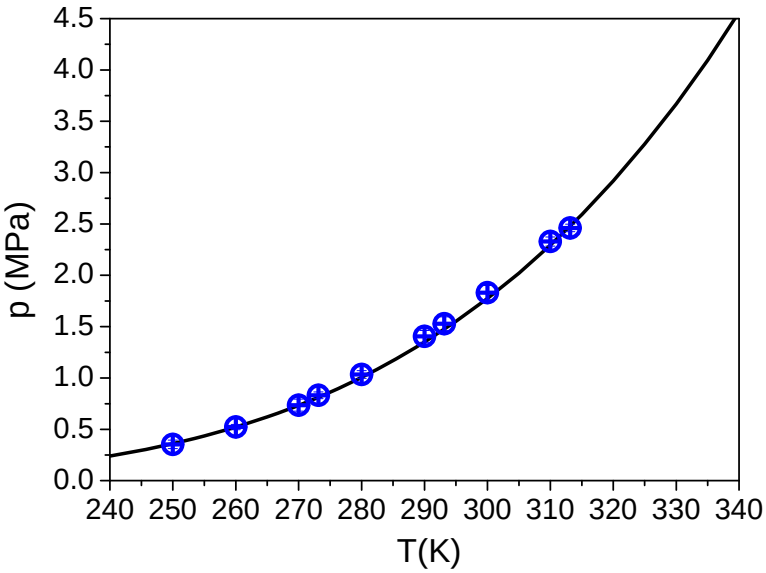
Force field also enables reliable predictions for properties not included in its parameterization.

Predictions for the VLE of refrigerant blends with R-32

Binary mixtures R-32 + R-1234yf and R-32 + R-1234ze(E) as candidates to replace R-410A in domestic heat pump and air conditioning systems

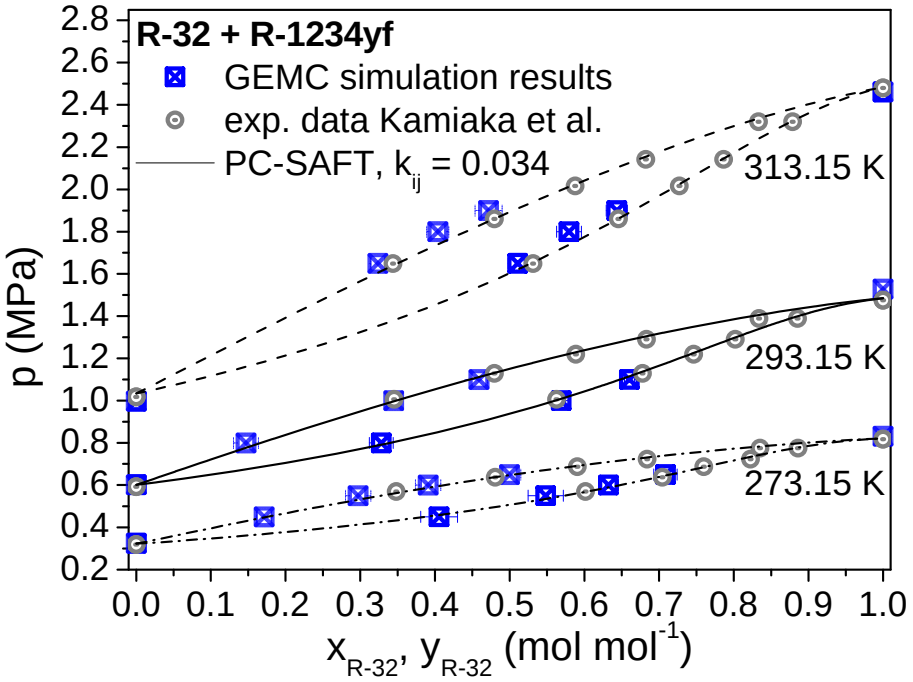
⇒ New flexible all atoms model for R-32, compatible with fluoropropene force field

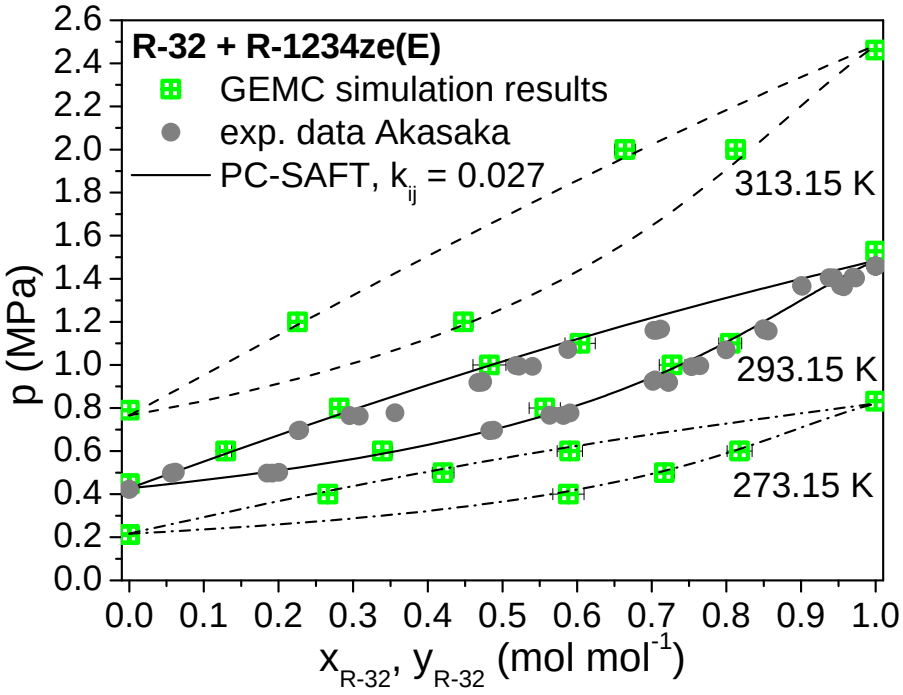




Predictions for the VLE of refrigerant blends with R-32

- GEMC simulations for R-32 + R-1234yf / R-1234ze(E) with new R-32 model and Lorentz-Berthelot combining rule
- no adjusted interaction parameters in GEMC simulations

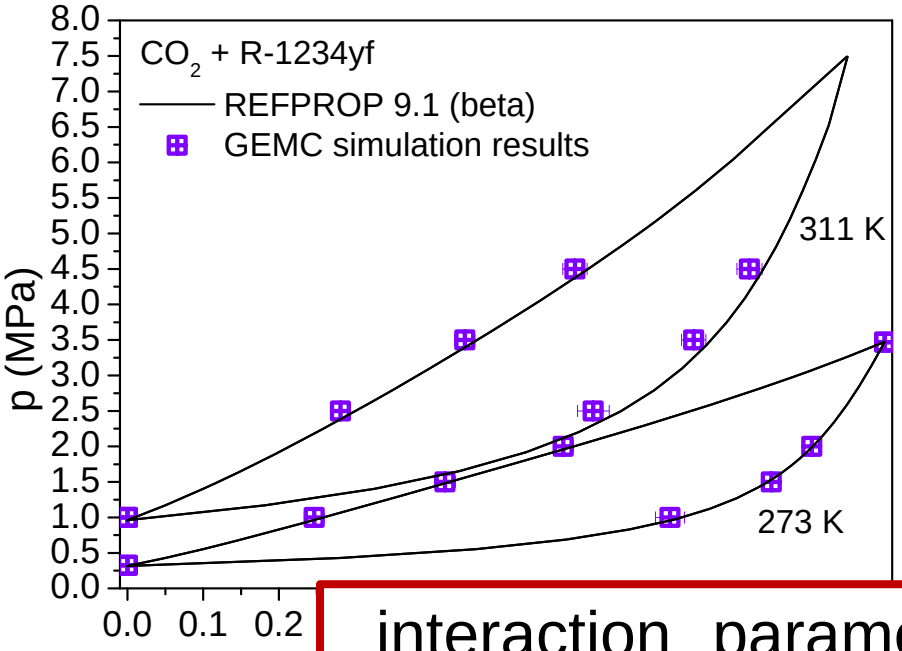


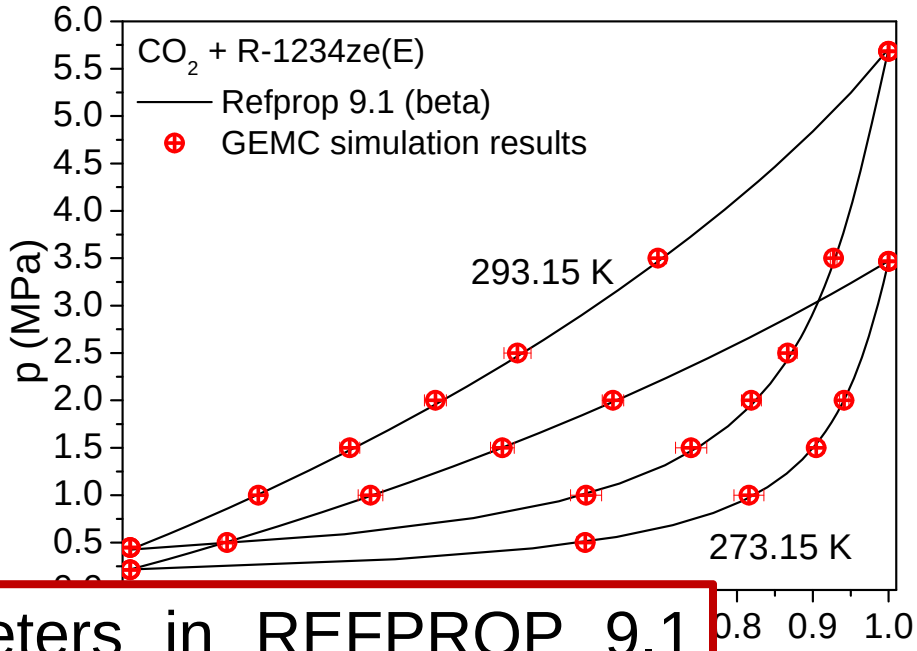


Predictions for the VLE of binary mixture with CO_2

GEMC simulations for CO_2 + R-1234yf / R-1234ze(E)

- TraPPE CO_2 model and Lorentz-Berthelot combing rule
- no adjusted interaction parameters in GEMC simulations

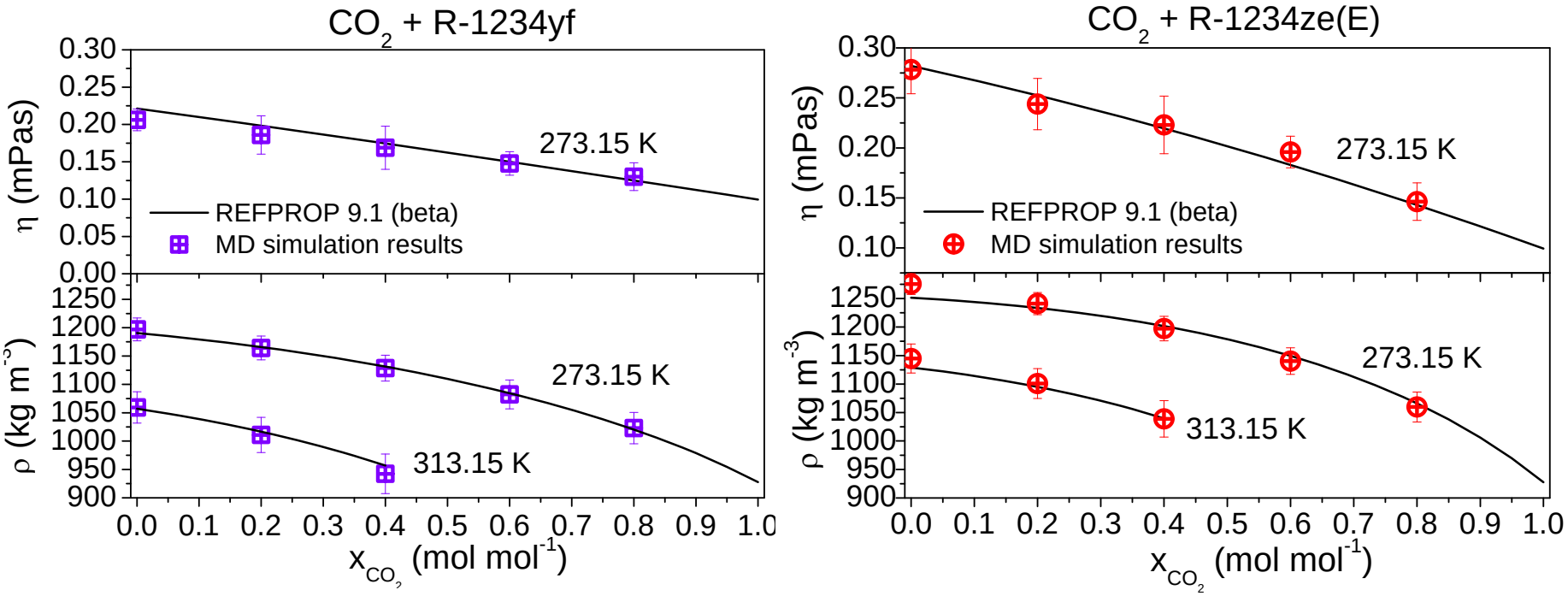




interaction parameters in REFPROP 9.1 fitted to GEMC simulation results for VLE

MD simulations on CO_2 + R-1234yf / R-1234ze(E) mixtures

Prediction of thermophysical properties in the liquid phase, e.g. densities $\rho(T, x_{CO2})$ and viscosities $\eta(T, x_{CO2})$ at $p = 3.5\ MPa$

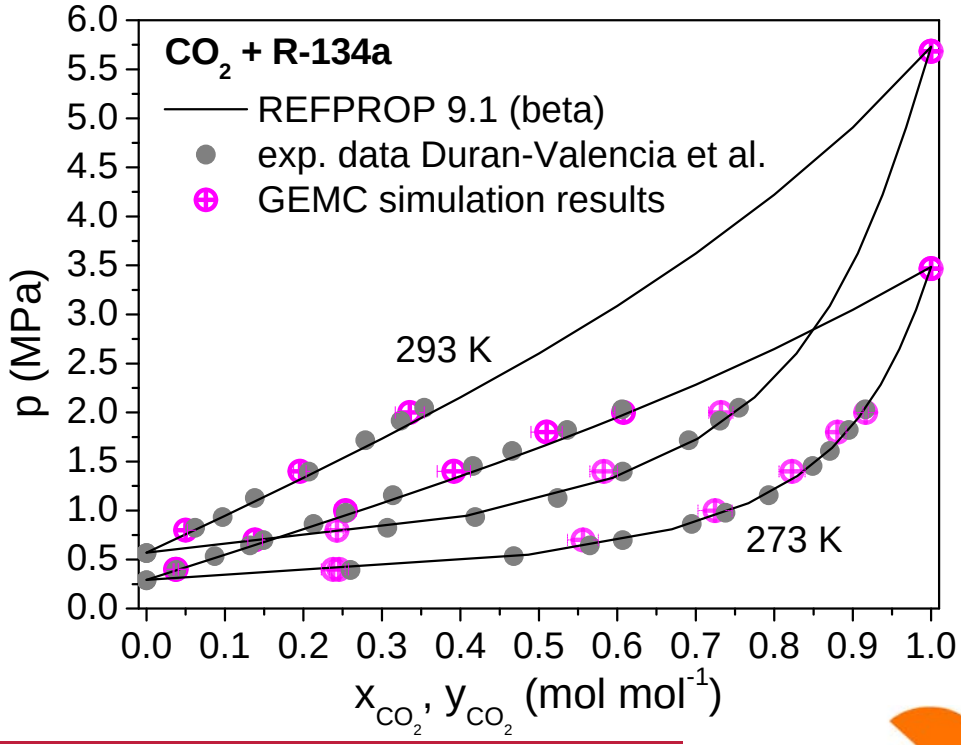


Simulation studies on the new MAC refrigerant AC-6

AC-6 : 6 % CO_2 + 9 % R-134a + 85 % R-1234ze(E) (by mass)

- R-1234ze(E) this work + TraPPE CO_2 model, as before
- R-134a model by Peguin et al.
- no adjusted ε_{ij} or σ_{ij}

$\Rightarrow$ tested for CO_2 + R-134a



Simulation studies on the MAC refrigerant AC-6 (R-445A)

Liquid phase properties

$T = 315\,K,\ p = 1.6\,MPa:$

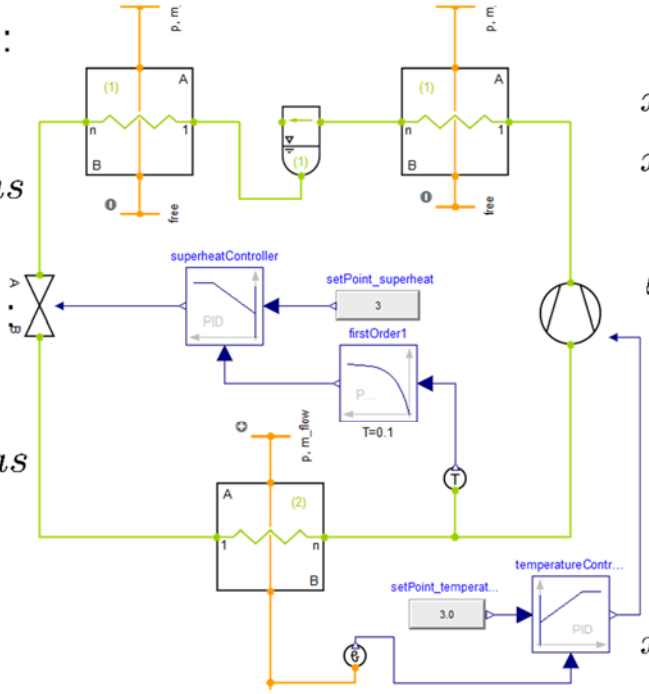
$\varrho = (1099.6 \pm 16.7)\,\frac{kg}{m^3}$

$\eta = (0.147 \pm 0.012)\,mPas$

$T = 300\,K,\ p = 1.6\,MPa:$

$\varrho = (1158.6 \pm 13.4)\,\frac{kg}{m^3}$

$\eta = (0.181 \pm 0.013)\,mPas$



VLE properties

$T = 320\,K,\ p = 1.68\,MPa:$

$x_1' = 0.119,\ x_2' = 0.092\ (\pm 0.006)$

$x_1'' = 0.383,\ x_2'' = 0.082\ (\pm 0.004)$

$\varrho' = (1076.0 \pm 7.0)\,kg\,m^{-3}$

$\varrho'' = (67.3 \pm 2.0)\,kg\,m^{-3}$

$T = 278\,K,\ p = 0.35\,MPa:$

$x_1' = 0.028,\ x_2' = 0.081\ (\pm 0.004)$

$x_1'' = 0.215,\ x_2'' = 0.096\ (\pm 0.007)$

$\varrho' = (1246.0 \pm 8.1)\,kg\,m^{-3}$

$\varrho'' = (15.9 \pm 0.1)\,kg\,m^{-3}$

Conclusion

- transferable force field for the fluoropropenes HFO-1234yf, -1234ze(E), -1234ze, -1243zf, -1225ye(Z), -1216
- validation of the force field by GEMC simulations on the VLE properties of the different pure compounds
- also yields reliable predictions for thermophysical properties not used in parameterization
- enables studies on mixtures without adjusted interaction parameters
- application for simulation studies on refrigerant blends of R-1234yf and R-1234ze(E) with R-32 and CO_2, and on AC-6 (CO_2 + R-134a + R-1234ze(E) = R-445A)

Acknowledgement

- DFG for the Research Fellowship (RA 946/2-1)
- Prof. Edward Maginn and his group @ ND
- Dr. Eric Lemmon @ NIST, Boulder for fitting binary interaction parameters for REFPROP 9.1 to GEMC simulation results for CO_2 + R-1234yf and CO_2 + R-1234ze(E)

Thank You!