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

Force Field Development

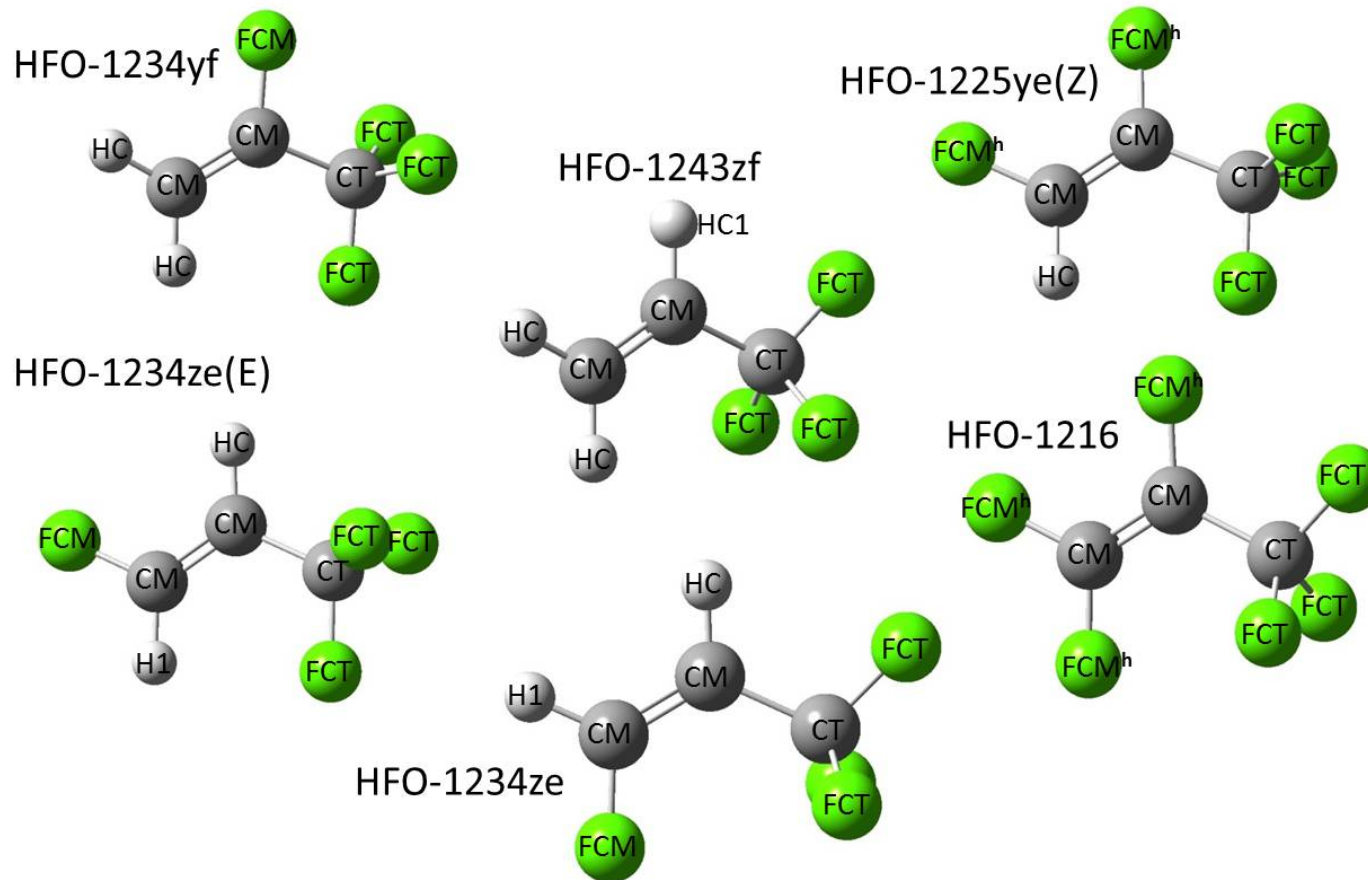
- fully flexible all-atoms 'class 1' force field

$$U_{conf} = \sum_{i=1}^{N-1} \sum_{j>i}^N \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$
$$+ \sum_{bonds} k_r (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2$$
$$+ \sum_{dihedral} k_\chi [1 + \cos(n\chi - \delta)]$$

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

Force Field Development

Compounds directly considered at the moment:

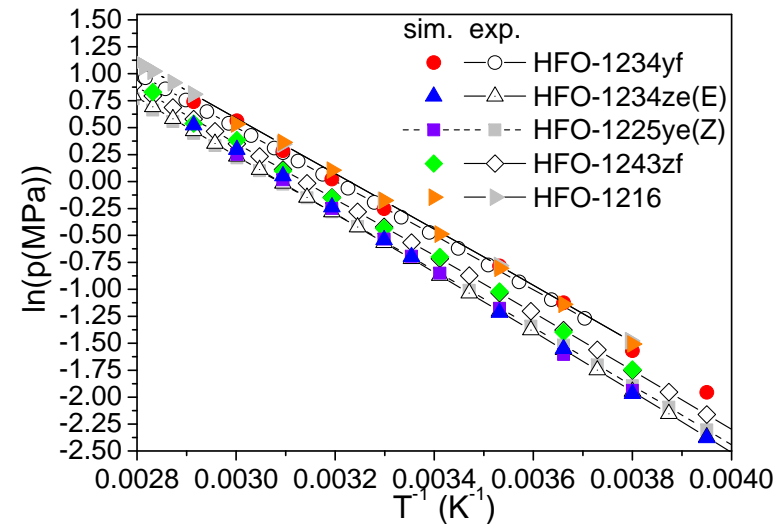
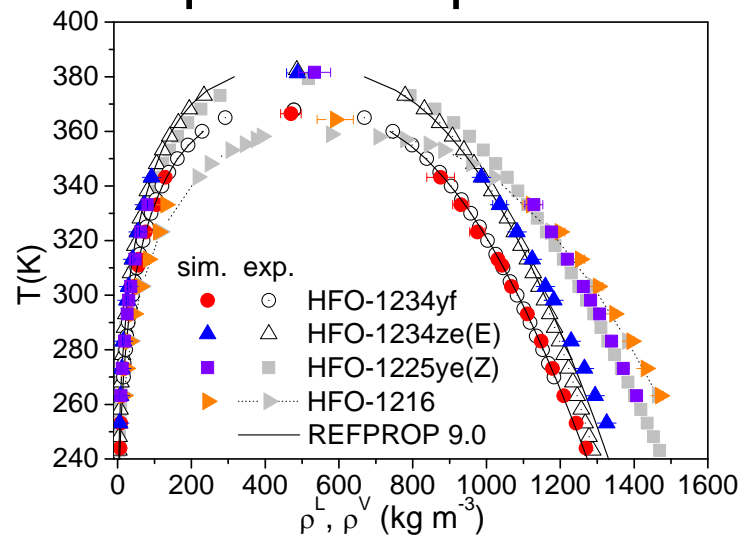


Force Field Development

- 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 perturbed 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

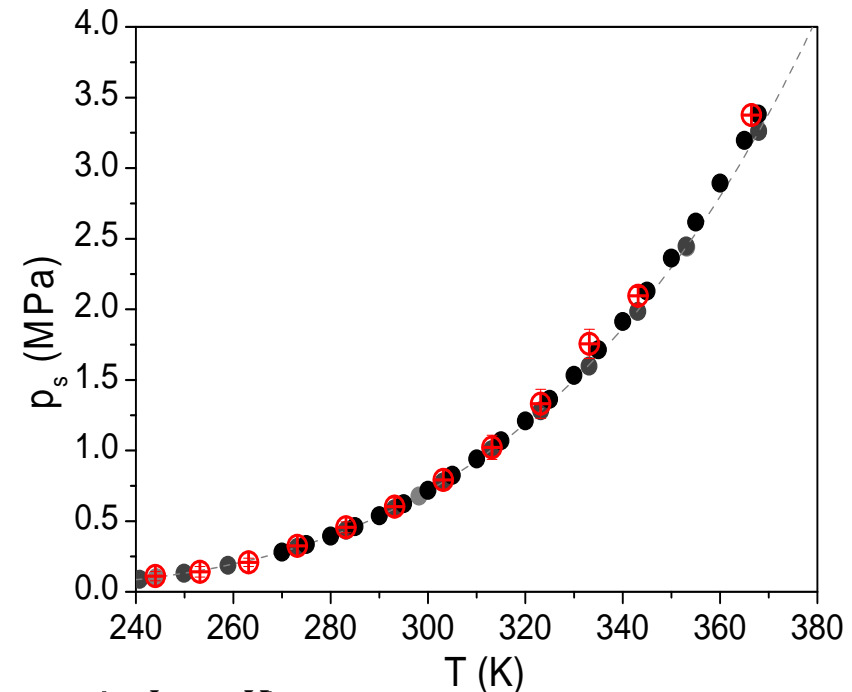
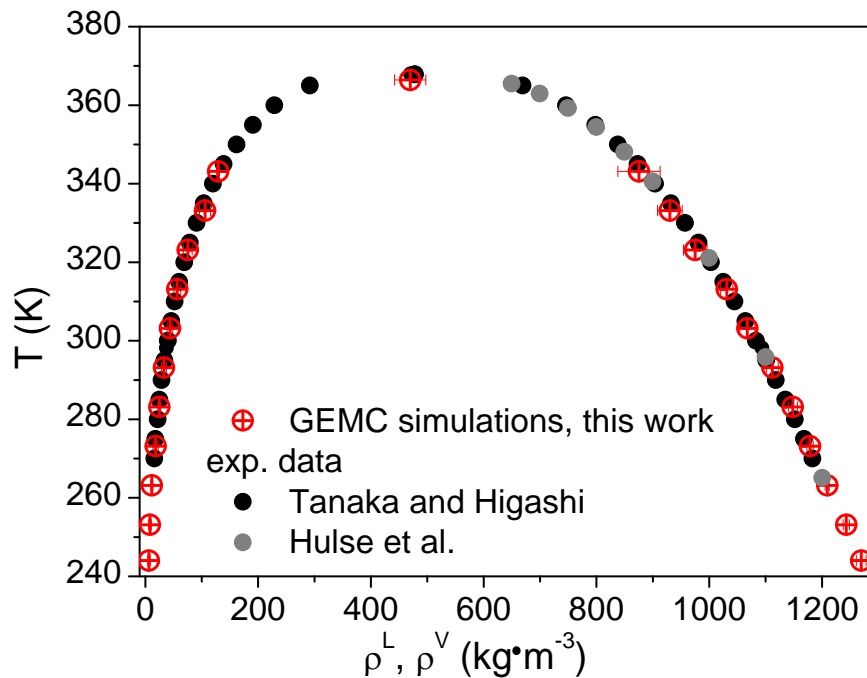
by Gibbs ensemble (GEMC) simulations on the VLE of the different pure compounds



	$T_{c, \text{sim}}$ (K)	$T_{c, \text{exp}}$ (K)	$\rho_{c, \text{sim}}$ (kg m^{-3})	$\rho_{c, \text{exp}}$ (kg m^{-3})	$p_{c, \text{sim}}$ (MPa)	$p_{c, \text{exp}}$ (MPa)	$T_{b, \text{sim}}$ (K)	$T_{b, \text{exp}}$ (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

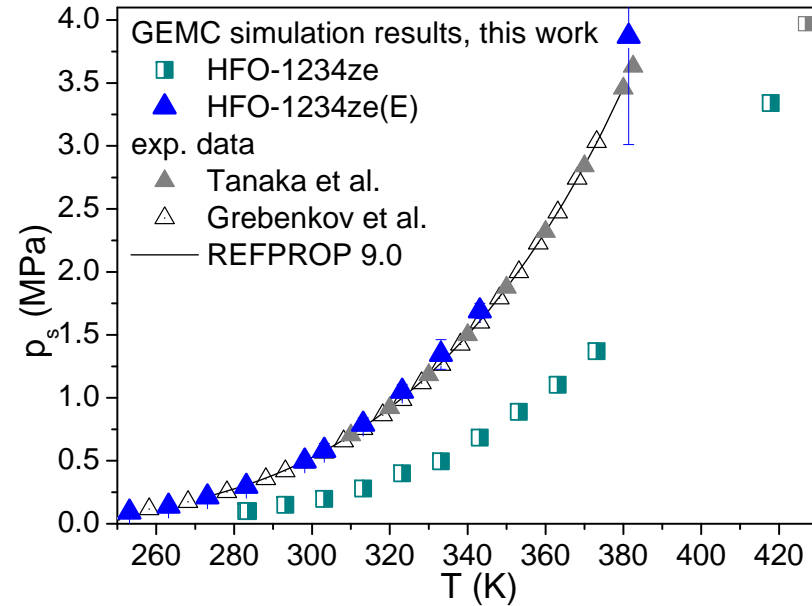
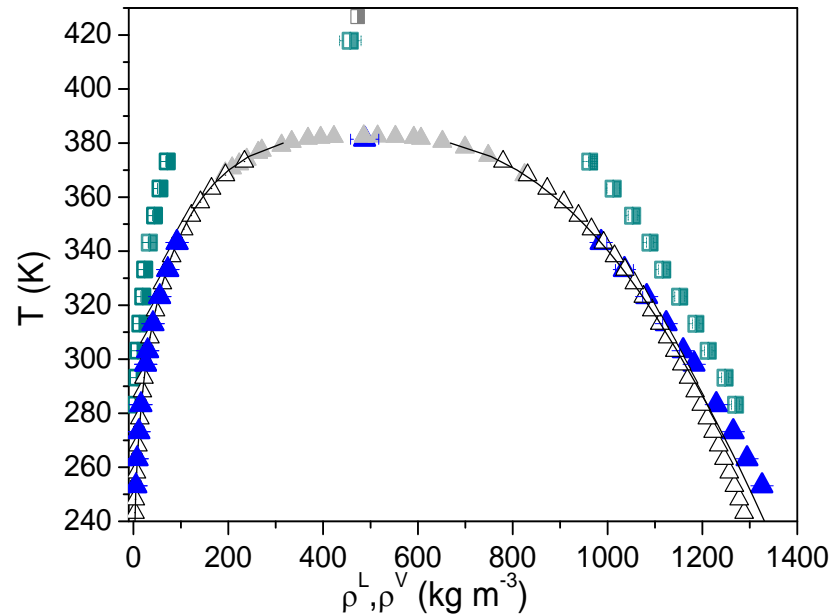


The simulated saturated densities (ρ^L, ρ^V) and vapor pressures (p_s) agree with the experimental data within their error bars

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

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

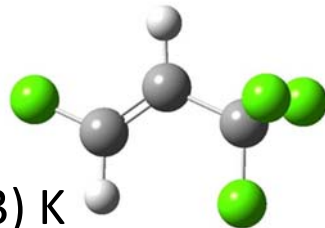
Only with individual q_{ij} but no adjusted LJ parameters



HFO-1234ze(E)

$$T_b^{exp} = 254.15 \text{ K}$$

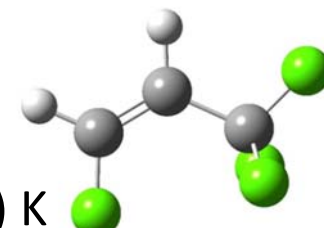
$$T_b^{sim} = (254.9 \pm 2.3) \text{ K}$$



HFO-1234ze

$$T_b^{exp} = 282.15 \text{ K}$$

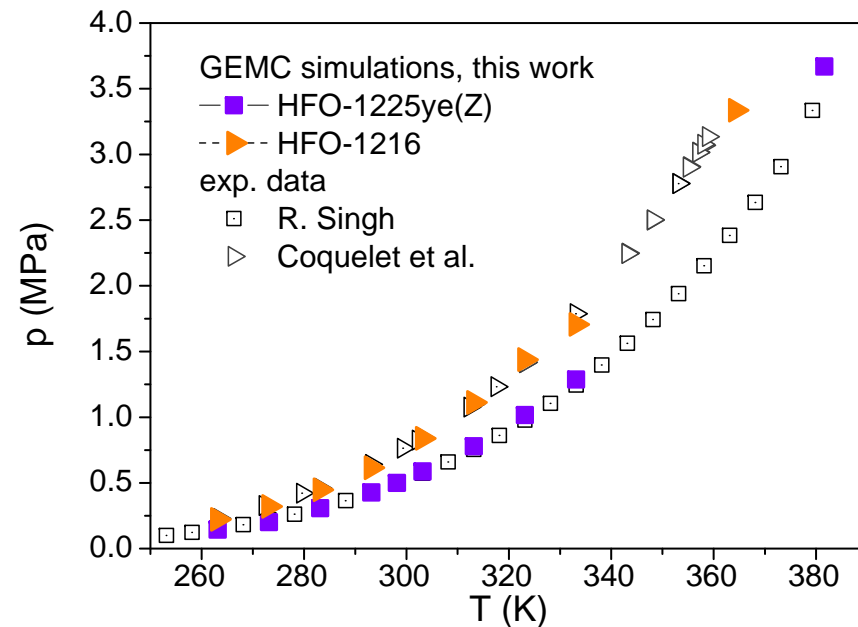
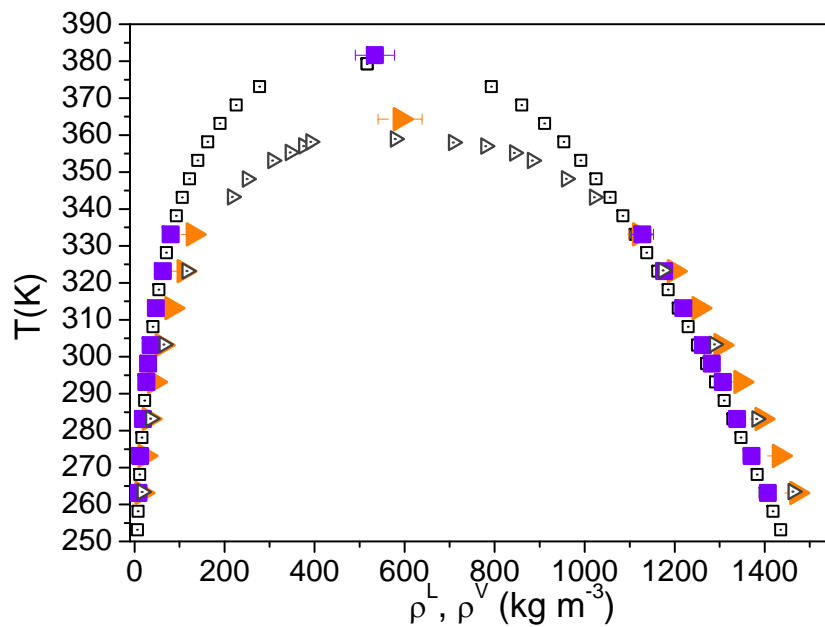
$$T_b^{sim} = (283.6 \pm 3.5) \text{ K}$$



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)

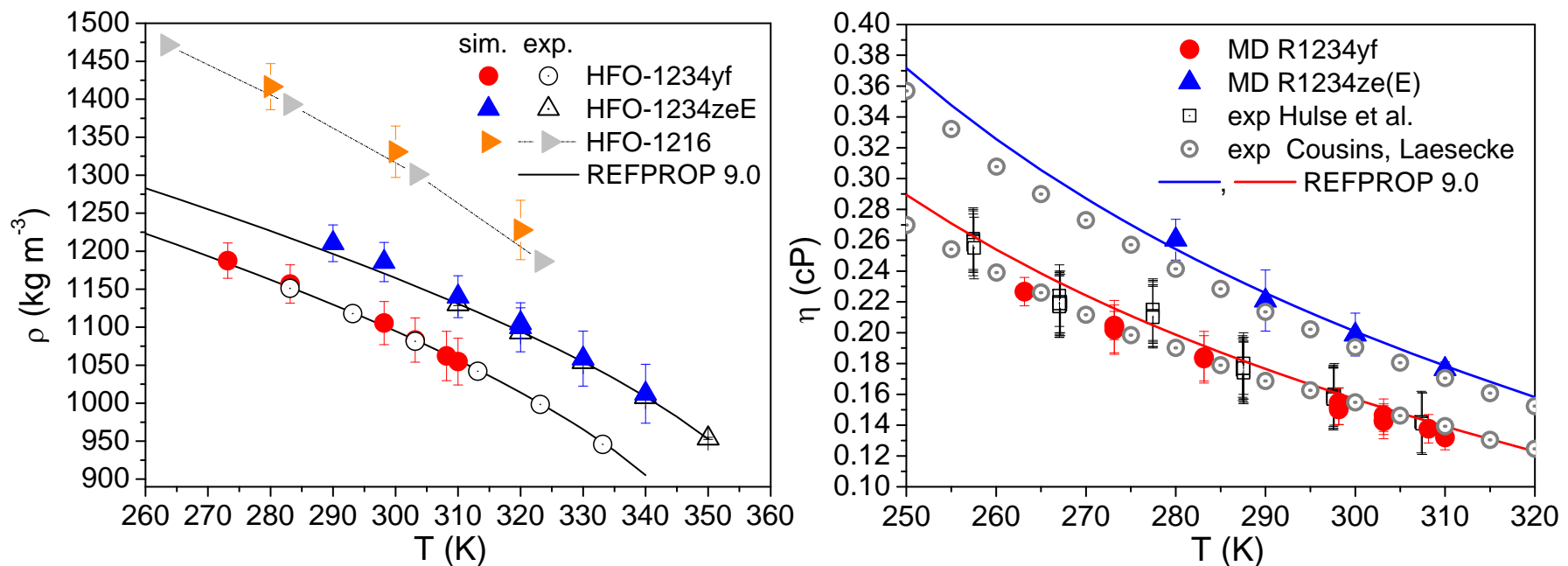


Good reproduction of the VLE of HFO-1216 using the same LJ parameters attests the good transferability of the force field

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 $p = 2 \text{ MPa}$

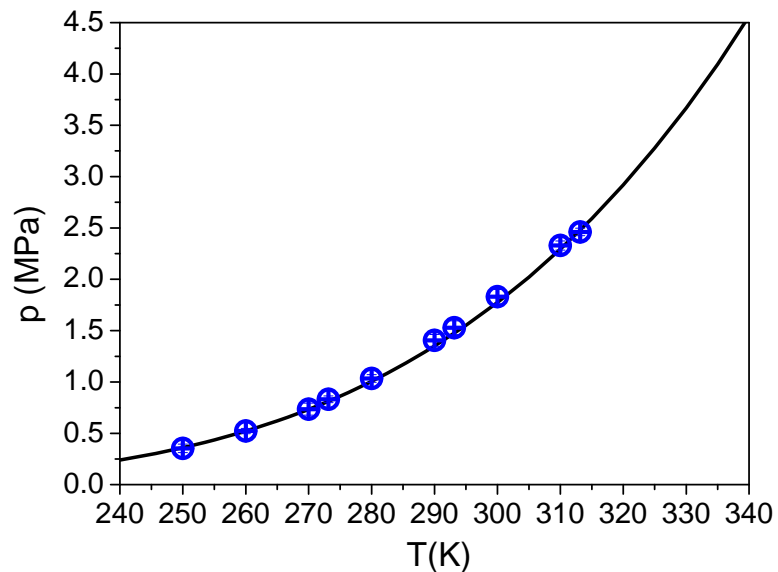
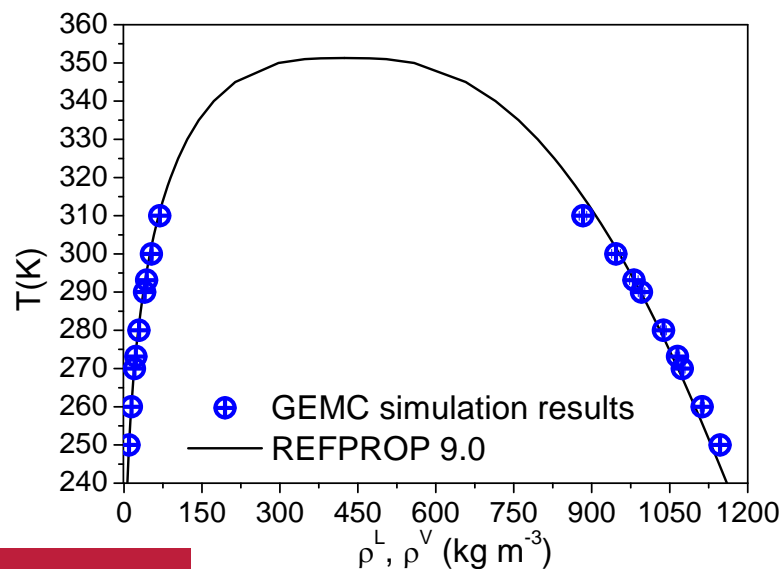


Force field also enables reliable predictions for properties not included in its parameterization.

Predictions for the VLE of refrigerant blends with R-32

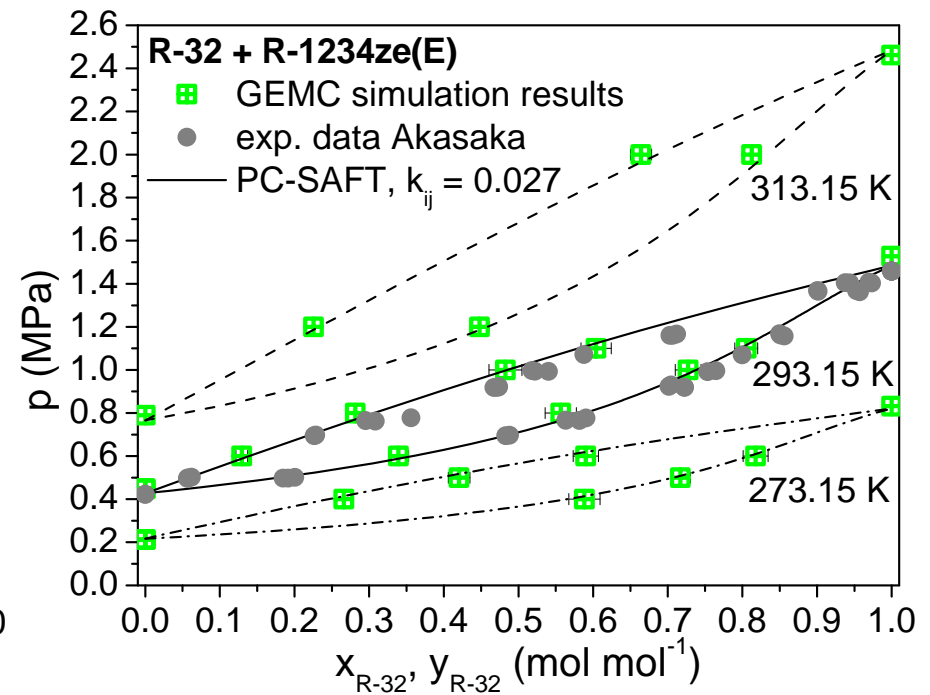
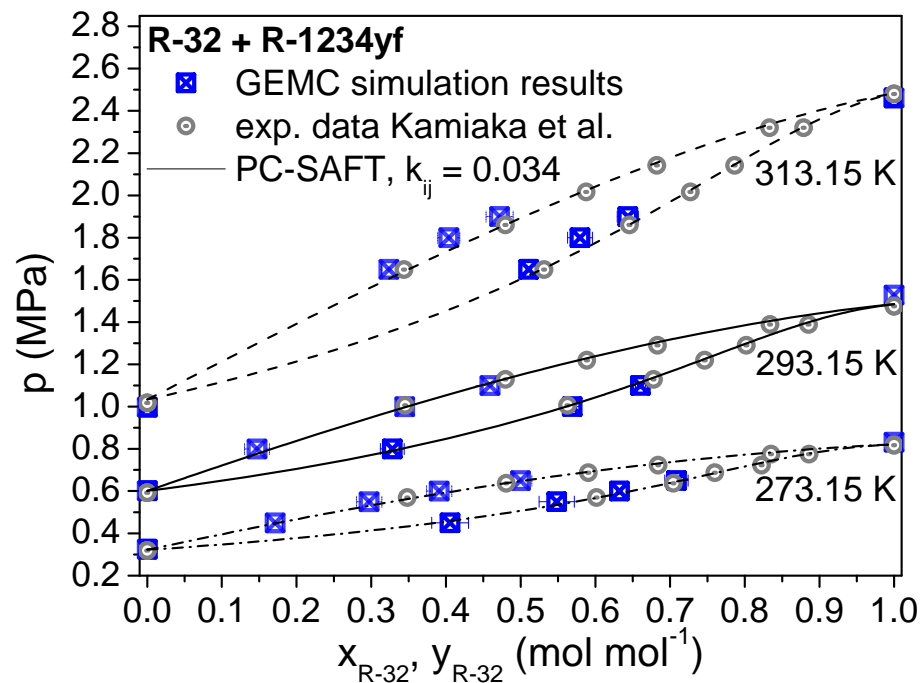
Binary mixtures R-32 + R-1234yf and R-32 + R-1234ze(E) as candidates to replace R-410A in domestic heat pump and air conditioning systems

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



Predictions for the VLE of refrigerant blends with R-32

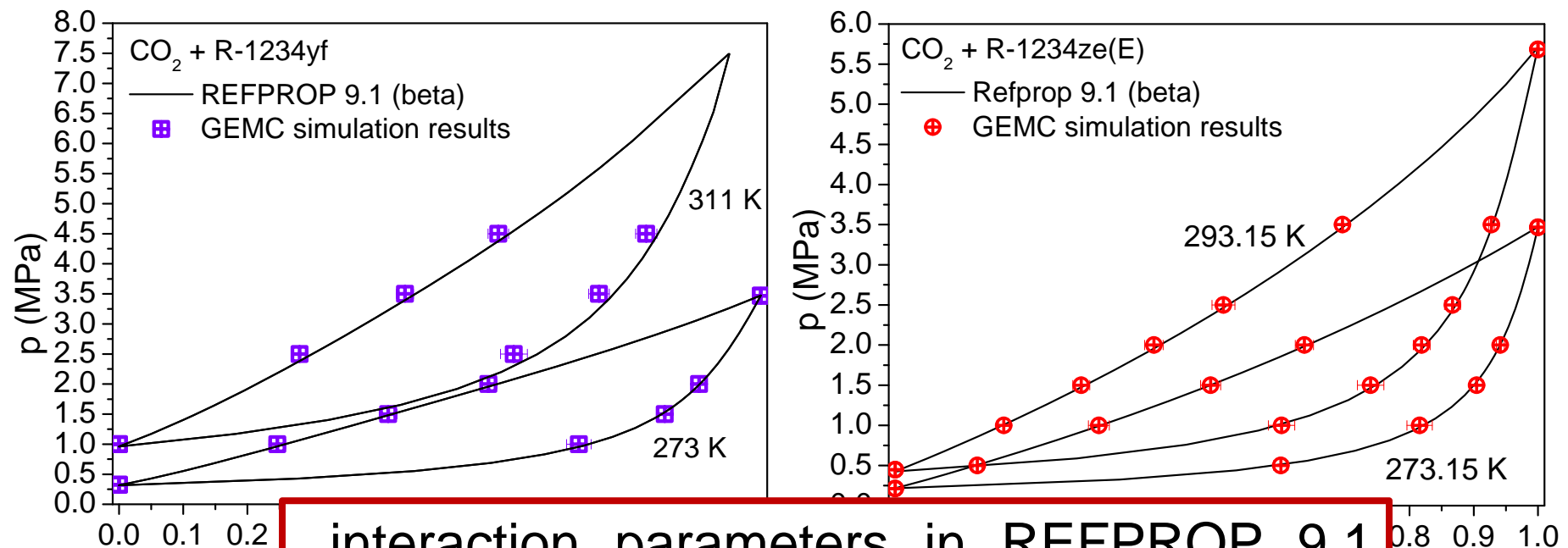
- GEMC simulations for R-32 + R-1234yf / R-1234ze(E) with new R-32 model and Lorentz-Berthelot combining rule
- no adjusted interaction parameters in GEMC simulations



Predictions for the VLE of binary mixture with CO₂

GEMC simulations for CO₂ + R-1234yf / R-1234ze(E)

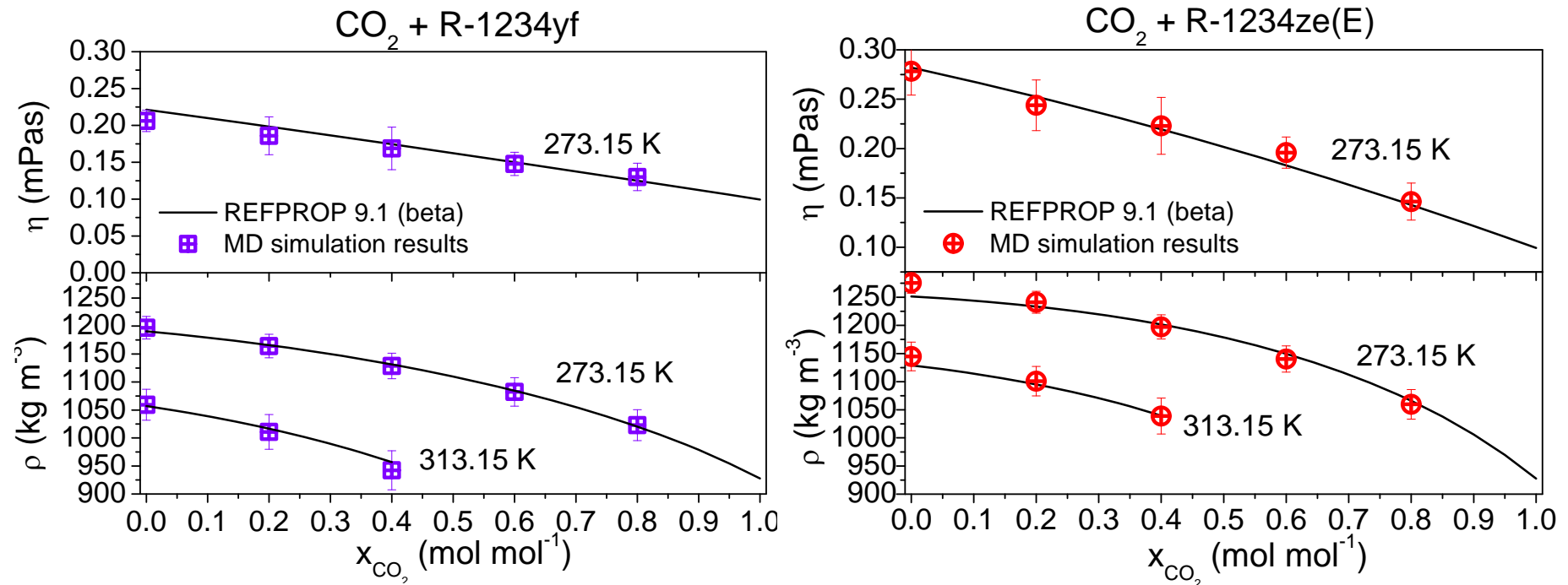
- TraPPE CO₂ model and Lorentz-Berthelot combining rule
- no adjusted interaction parameters in GEMC simulations



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

MD simulations on CO₂ + R-1234yf / R-1234ze(E) mixtures

Prediction of thermophysical properties in the liquid phase, e.g. densities $\rho(T, x_{CO_2})$ and viscosities $\eta(T, x_{CO_2})$ at $p = 3.5 \text{ MPa}$

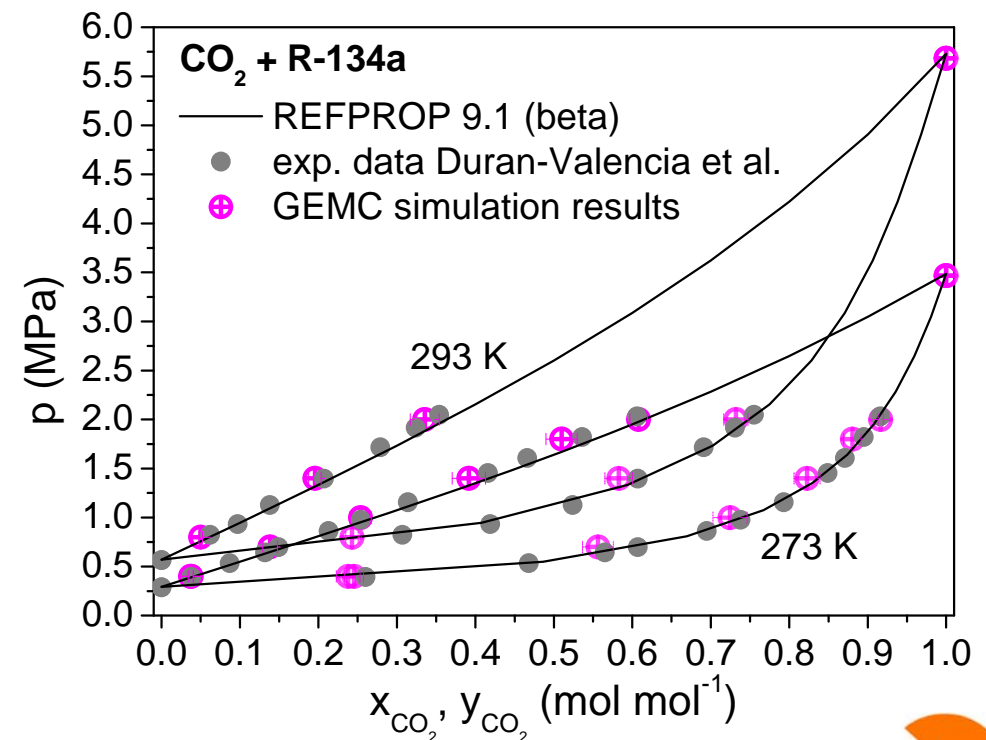


Simulation studies on the new MAC refrigerant AC-6

AC-6 : 6 % CO₂ + 9 % R-134a + 85 % R-1234ze(E) (by mass)

- R-1234ze(E) this work + TraPPE CO₂ model, as before
- R-134a model by Peguin et al.
- no adjusted ϵ_{ij} or σ_{ij}

⇒ tested for CO₂ + R-134a



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

Liquid phase properties

$$T = 315 \text{ K}, p = 1.6 \text{ MPa} :$$

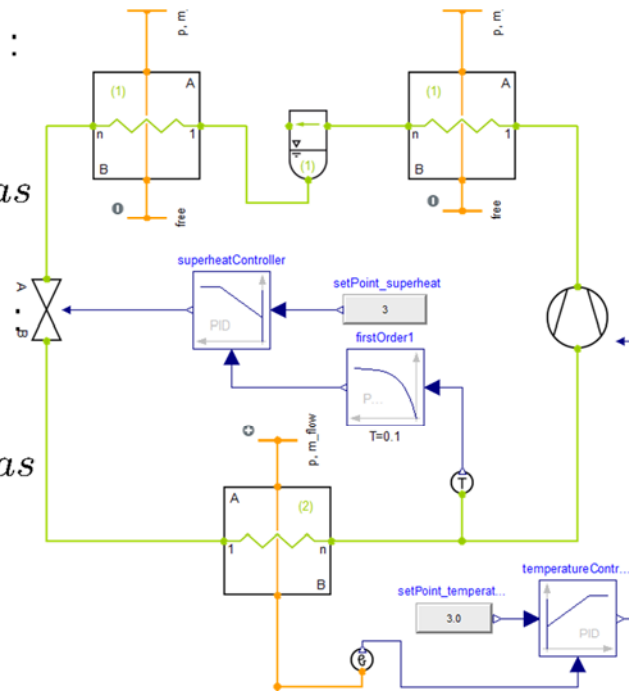
$$\rho = (1099.6 \pm 16.7) \frac{\text{kg}}{\text{m}^3}$$

$$\eta = (0.147 \pm 0.012) \text{ mPas}$$

$$T = 300 \text{ K}, p = 1.6 \text{ MPa}$$

$$\rho = (1158.6 \pm 13.4) \frac{\text{kg}}{\text{m}^3}$$

$$\eta = (0.181 \pm 0.013) \text{ mPas}$$



VLE properties

$$T = 320 \text{ K}, p = 1.68 \text{ MPa} :$$

$$x'_1 = 0.119, x'_2 = 0.092 (\pm 0.006)$$

$$x''_1 = 0.383, x''_2 = 0.082 (\pm 0.004)$$

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

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

$$T = 278 \text{ K}, p = 0.35 \text{ MPa} :$$

$$x'_1 = 0.028, x'_2 = 0.081 (\pm 0.004)$$

$$x''_1 = 0.215, x''_2 = 0.096 (\pm 0.007)$$

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

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

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 CO₂, and on AC-6 (CO₂ + 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 CO₂ + R-1234yf and CO₂ + R-1234ze(E)

Thank You!