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

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Molecular simulation studies on fluoropropene refrigerants

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.
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**Force Field Development**

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

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

- transferable parameters (Lennard-Jones (LJ), intramolecular terms)
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**Force Field Development**

Compounds directly considered at the moment:

- HFO-1234yf
- HFO-1234ze(E)
- HFO-1234ze
- HFO-1243zf
- HFO-1216
- HFO-1225ye(Z)
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**Force Field Development**

- nominal bond lengths $r_0$ and bond angles $\theta_0$ from ab initio optimizations (DFT: B3LYP/DGDZVP)
- force constants $k_r$, $k_{\theta}$ and $k_{\chi}$ from ab initio optimizations for perturbated geometries
- ab initio CHELPG charges $q_i$ (HF/6-31G*)
- LJ parameters $\varepsilon_{ii}$, $\sigma_{ii}$ adjusted to fine-tune agreement with experimental data:
  - CM, FCM: $\Delta H_{vap}$, $p_s$ of $\text{C}_2\text{F}_4$
  - HC, H1: AMBER parameter
  - CT, FCT: $\rho_l$, $p_s$ of HFO-1234yf, HFO-1243zf
  - FCM$^h$: $\rho_l$, $p_s$ of HFO-1225ye(Z)
Validation of the Force Field
by Gibbs ensemble (GEMC) simulations on the VLE of the different pure compounds

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

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Validation of the Force Field

GEMC simulation results for the VLE of HFO-1234yf

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

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

Only with individual $q_i$, but no adjusted LJ parameters

HFO-1234ze(E)

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

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

HFO-1234ze

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

$T_b^{\text{sim}} = (283.6 \pm 3.5)$ K
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GEMC results for HFO-1225ye(Z) and HFO-1216
Modified FCM\textsuperscript{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

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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
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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
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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
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**MD simulations on CO$_2$ + R-1234yf / R-1234ze(E) mixtures**

Prediction of thermophysical properties in the liquid phase, e.g. densities $\rho(T, x_{CO_2})$ and viscosities $\eta(T, x_{CO_2})$ 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 $\varepsilon_{ij}$ or $\sigma_{ij}$

$\Rightarrow$ tested for CO$_2$ + R-134a
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Simulation studies on the MAC refrigerant AC-6 (R-445A)

Liquid phase properties

\[ T = 315 \text{ K}, \ p = 1.6 \text{ MPa} : \]
\[ \rho = (1099.6 \pm 16.7) \frac{kg}{m^3} \]
\[ \eta = (0.147 \pm 0.012) \text{ mPas} \]

\[ T = 300 \text{ K}, \ p = 1.6 \text{ MPa} : \]
\[ \rho = (1158.6 \pm 13.4) \frac{kg}{m^3} \]
\[ \eta = (0.181 \pm 0.013) \text{ mPas} \]

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)
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Thank You!