Int J Thermophys (2010) 31:462–474
DOI 10.1007/s10765-010-0764-2

Monte Carlo Simulation of Vapor–Liquid Equilibria for Perfluoropropane (R-218) and 2,3,3,3-Tetrafluoropropene (R-1234yf)

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Received: 22 December 2009 / Accepted: 18 May 2010 / Published online: 9 June 2010

Abstract Thermophysical properties of two refrigerants (perfluoropropane and 2,3,3,3-tetrafluoropropene) were computed using Monte Carlo methods with the OPLS-AA (Optimized Potentials for Liquid Simulations-All Atoms) forcefield. Original OPLS-AA parameters were extended to include an F atom attached to a double bond in 2,3,3,3-tetrafluoropropene and modified to produce the correct stationary geometry for this compound. The results of the simulations for critical parameters, saturated densities, saturated pressures, liquid densities, and vaporization enthalpies are in good agreement with available experimental data and equation of state models. Systematic deviations between the experimental data and the predicted values were observed for liquid densities and saturated pressures, suggesting that further refinement of forcefield parameters that can lead to better accuracy may be possible.

Keywords Perfluoropropane · R-218 · 2,3,3,3-Tetrafluoropropene · R-1234yf · Monte Carlo · VLE

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1 Introduction

Thermophysical properties of refrigerants are of key importance in terms of determining their usability. As the demand for new refrigerants with low environmental impact grows [1,2], so does the need for efficient means of assessing their thermophysical properties. While accurate experimental measurements are preferable, they are usually very time- and labor-intensive. Therefore, various estimation methods are widely used, especially during initial exploratory stages when evaluation of candidates with respect to their usability as industrial refrigerants is performed. The estimation of thermophysical properties is traditionally performed with a range of empirical methods [3]. However, recent advances in methods based on molecular simulations (e.g., Monte Carlo or molecular dynamics) [4,5] open new possibilities for estimation of thermophysical properties by more theoretically sound means. Unlike empirical approaches that use different estimation methods for each individual property, potentially leading to inconsistencies among them, molecular simulation methods produce property values that are consistent with each other. Molecular modeling is also capable of generating all the information necessary to produce equation of state models. On the other hand, the accuracy of molecular simulations is limited by the applicability of the forcefield to a particular system.

In this study, we investigated the capabilities of Monte Carlo (MC) simulations to assess several thermodynamic properties of two fluorine-containing refrigerants—perfluoropropane (R-218) and 2,3,3,3-tetrafluoropropene (R-1234yf). The first compound has been very thoroughly studied experimentally, with an accurate established equation of state available [6]. It was also used for validation of the OPLS-AA (Optimized Potentials for Liquid Simulations-All Atoms) [7] forcefield parameters for perfluoroalkanes [8]. The values of the liquid density and vaporization enthalpy at the normal boiling temperature obtained in the MC simulations with the OPLS-AA forcefield [8] were in agreement with experiments, within 0.4 % and $0.2\,\mathrm{kJ \cdot mol^{-1}}$ for the density and vaporization enthalpy, respectively. However, the predictions of critical properties and the saturated vapor pressure for this compound were not tested. Therefore, R-218 is used here primarily as a test target that allows assessing the method's capabilities via a comparison with a well-established collection of experimental data. The second compound, R-1234yf, is a promising next-generation refrigerant that, in addition to a very low environmental impact, exhibits a number of other attractive characteristics (such as low toxicity, low flammability, excellent plastics compatibility, etc.), making it potentially superior to the presently used alternatives [9]. Experimental studies of this compound are starting to appear [10–12], and several equations of state based on empirical estimates [13] and on emerging experimental data [14,15] (E.W. Lemmon, personal communication, 2009) have been proposed.

Fluorinated methanes and ethanes were previously investigated with MC methods [16–19]. The most recent work of Peguin et al. [19] presented an all-atom forcefield model optimized for 1,1,1,2-tetrafluoroethane that was capable of accurately reproducing a wide range of thermopysical properties for this compound, including vapor–liquid equilibrium data. However, only limited MC studies were performed for fluorohydrocarbons beyond C_2. Besides the previously mentioned OPLS-AA development work [8], a series of fluoropropanes was investigated with MC methods in earlier work of Yamamoto et al. [20] where only a fair level of agreement with the experimental data was reported. To the best of our knowledge, no Monte Carlo simulations were reported for fluorinated olefins. Considering the rapidly growing interest in R-1234yf and other potential refrigerants based on fluorinated olefins, investigation of the performance of MC methods based on one of the most widely used forcefields (i.e., OPLS-AA) can be helpful in guiding future molecular simulation efforts that can lead to better equation of state models for these compounds.

2 Simulation Details

In the MC method, configurations of a system are produced from a certain probability distribution for the statistical ensemble. Each configuration is generated by a MC move. The MC moves include translation or rotation of a molecule, change of molecular configuration, change of volume, transfer of a molecule between the simulation boxes, or more complicated transformations. To improve the efficiency of configuration sampling, statistical bias methods are used. The configurational-bias regrowth [21] and aggregation-volume bias [22] methods are often used for simulation of fluids. The MC simulation includes equilibration and production periods. During the former, the MC moves lead the system to the equilibrium state. The latter (production period) is used to get the property ensemble averages.

All MC simulations in this work were carried out with the MCCCS TOWHEE v. 6.2.6 package [23]. The calculations were performed using the OPLS-AA forcefield with the most recent set of the forcefield parameters provided by Prof. W. L. Jorgensen (personal communication, 2009). A non-bond cutoff of 1 nm with analytical tail corrections [24] was applied.

The vapor–liquid equilibrium (VLE) simulations were performed in the Gibbs ensemble [25–27]. Initially, the system contained 280 molecules, 216 of which were placed in the liquid box, and 64 were in the gas box. Each simulation included an equilibration of at least 30000 MC cycles followed by a production of 10000 MC cycles where a cycle was defined as a number of MC moves that is equal to the number of molecules in the system (i.e., 280). The statistical uncertainties reported in the following section are standard deviations of the corresponding values. The property values were sampled by dividing the simulation results into 10 blocks. The following move probabilities were adopted: 0.33 for translation and rotation, 0.32 for configurational-bias regrowth, 0.01 for aggregation-volume bias (in the AVBMC2 implementation [22]) move, 0.008 for interbox swap, and 0.002 for box volume change.

The liquid densities at a given pressure were obtained from the simulation in the isobaric–isothermal ensemble [28] containing 216 molecules. The ranges of pressures and temperatures were chosen based on availability of experimental data; the pressure range for R-1234yf was extended to 10 MPa to test model extrapolation in comparison with the predictions of the preliminary equation of state [15] (E.W. Lemmon, personal communication, 2009). Each simulation included an equilibration of at least 10000 MC cycles followed by a production of 10000 MC cycles. As for the previous case, the statistical uncertainties were estimated by dividing the simulation results into 10 blocks. The move probabilities adopted for these simulations were as follows:

0.33 for translation and rotation, 0.32 for configurational-bias regrowth, 0.018 for the AVBMC2, and 0.002 for box volume change. In both the types of simulation, the maximum displacements during the moves were adjusted to yield acceptance probabilities of 50 %.

For the compounds considered, the parameters from the original OPLS-AA forcefield can be unambiguously chosen, with the exception of the F atom attached to a double bond in R-1234yf; OPLS-AA does not have parameters for this atom. Therefore, the missing parameters were determined in this study, as described next. The existing parameters for different types of F atoms had the following ranges: from (222 to 255) $\mathrm{J \cdot mol^{-1}}$ for the Lennard–Jones well depth (ε), from (0.285 to 0.295) nm for the Lennard–Jones diameter (σ), and from -0.22 to -0.12 for the atomic partial charge (q). A series of simulations arranged in a 2^3 factorial design with respect to the above parameters was performed to compute the liquid density of R-1234yf at the normal boiling temperature. The combination of parameters that produced the best agreement with the experimental value ($1264\,\mathrm{kg \cdot m^{-3}}$ [10]) was chosen; the resulting values were close to those for the monoalkyl fluoride: $\sigma = 0.294\,\mathrm{nm}$, $q = -0.22$, and $\varepsilon = 255\,\mathrm{J \cdot mol^{-1}}$.

The parameters for the F–C(=)–C–F torsion were assumed equal to those for F–C–C–F in the original forcefield. Use of the parameter for the C=C–C–F torsion as defined in the original forcefield ($V_3 = 2.1\,\mathrm{kJ \cdot mol^{-1}}$), however, yields an incorrect position of the CF_3-top in the stable conformer. Therefore, the new parameter $V_3 = -3.5\,\mathrm{kJ \cdot mol^{-1}}$ was determined following the procedure described in [7] based on the rotational potential of the CF_3-top in R-1234yf computed at the HF/6–31G(d) level. The quantum-chemical calculations were performed using Gaussian 03 [29], and the molecular mechanics calculations for a single molecule were carried out with the TINKER package [30].

The critical parameters were obtained according to the conventional procedure. Specifically, the critical temperature, T_c, and critical density, ρ_c, were determined by simultaneously fitting computed liquid and gas saturated densities with the following equations:

$$\rho_\mathrm{l} - \rho_\mathrm{g} = B(T_\mathrm{c} - T)^\beta \tag{1}$$

and

$$(\rho_\mathrm{l} + \rho_\mathrm{g})/2 = \rho_\mathrm{c} + A(T_\mathrm{c} - T), \tag{2}$$

where ρ_l and ρ_g are the liquid and gas densities, respectively, A and B are fitted parameters, T is the temperature, and $\beta = 0.32$ is the Ising-type critical exponent. The critical pressure was obtained by fitting the calculated saturation pressure P_sat with

$$\log P_\mathrm{sat} = C - D/T, \tag{3}$$

where C and D are fitted parameters; substitution of the previously obtained T_c into Eq. 3 gave the value of the critical pressure.

Table 1 Two-phase coexistence properties of R-218 obtained from MC simulations

T (K)	ρ_l (kg · m^{-3})	ρ_g (kg · m^{-3})	P_{sat} (MPa)	$\Delta_{vap}H$/(kJ · mol^{-1})
236.4[a]	1593 ± 10	11.0 ± 0.2	0.108 ± 0.004	19.4 ± 0.3
275	1407 ± 27	49 ± 4	0.53 ± 0.05	16.0 ± 0.5
295	1331 ± 19	109 ± 7	1.03 ± 0.07	14.0 ± 0.4
305	1247 ± 46	127 ± 9	1.24 ± 0.11	12.9 ± 0.8
315	1231 ± 22	173 ± 10	1.59 ± 0.13	11.8 ± 0.5
325	1076 ± 70	196 ± 19	1.81 ± 0.21	10.0 ± 1.3
335	821 ± 136	290 ± 24	2.42 ± 0.25	6.0 ± 1.4

[a] Normal boiling temperature

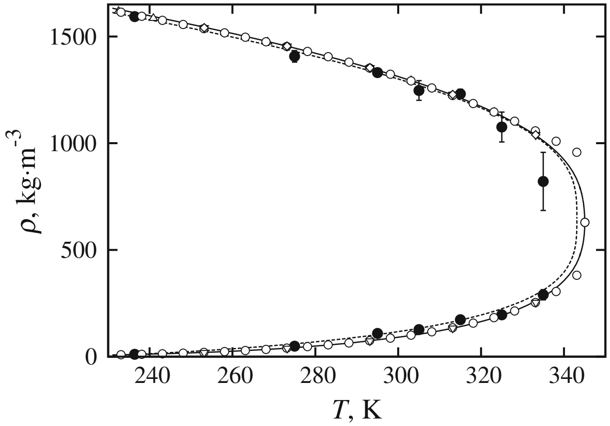

Fig. 1 Saturated density of R-218. *Symbols*: *solid* MC simulations, *open* experimental data (△ Ref. [31], o Ref. [39], ∇ Ref. [40], ◇ Ref. [41]). *Lines*: *solid* computed from the REFPROP [6] equation of state, *dotted* fit of Monte Carlo results with Eqs. 1 and 2

The reported uncertainties in the critical parameters are of 95 % confidence intervals.

3 Results and Discussion

3.1 R-218

The results of the VLE simulations for R-218 are presented in Table 1 and Fig. 1. As seen, saturation densities obtained from the simulations are in very good agreement with the experimental data. The derived critical parameters listed in Table 2 also agree very well with the experimental measurements, i.e., T_c is predicted within the statistical uncertainty of 2 K, and ρ_c and p_c are predicted within 3 % and 11 %, respectively. Liquid densities of R-218 are compared with those computed from the REFPROP equation of state [6] in Fig. 2. Although the results of the simulations slightly

Table 2 Critical parameters of R-218 and R-1234yf

	R-218	R-1234yf
T_c (K)	343 ± 2^a $345.0^{b,c,d,e}$	357 ± 4^a 367.85^f 419^h, $388^{i,j,k}$
ρ_c (kg·m^{-3})	647 ± 13^a $628^{b,e}$ 603^c	495 ± 10^a 478^f 487^h, 462^i, 480^j
p_c (MPa)	2.98 ± 0.15^a $2.68^{b,d}$ 2.66^c 2.67^e	3.74 ± 0.14^a 3.382^f 3.390^g $3.18^{h,j}$, $3.81^{i,k}$

[a] Present simulations
[b] Ref. [31]
[c] Ref. [32]
[d] Ref. [33]
[e] Ref. [34]
[f] Ref. [12]
[g] Ref. [11]
[h] Predicted with Constantinou–Gani method [35]
[i] Predicted with Joback method [36]
[j] Predicted with Marrero–Pardillo method [37]
[k] Predicted with Wilson–Jasperson method [38]

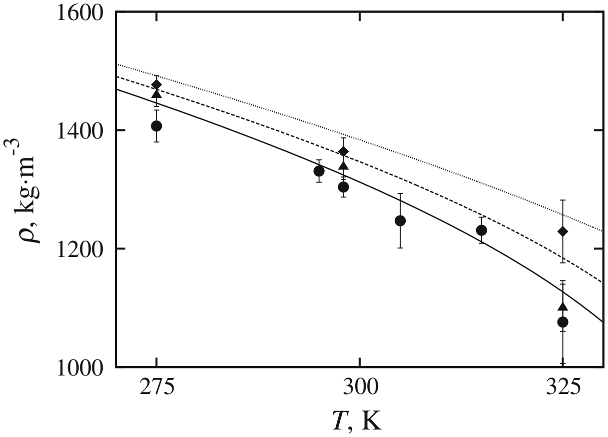

Fig. 2 Liquid density of R-218. *Symbols* are the results of MC simulations (● saturation, ▲ $p = 3$ MPa, ♦ $p = 6$ MPa). *Lines* are computed with the REFPROP [6] equation of state (*solid* saturation, *dashed* $p = 3$ MPa, *dotted* $p = 6$ MPa)

underpredict the REFPROP values, the deviations are within the statistical uncertainties, and the overall temperature dependence is reproduced very well.

The saturated vapor pressure is the most expensive property from the computational standpoint, and further, it has the largest statistical uncertainty ranging from 4 % to 12 %. The calculated values are between 7 % and 29 % higher than the experimental

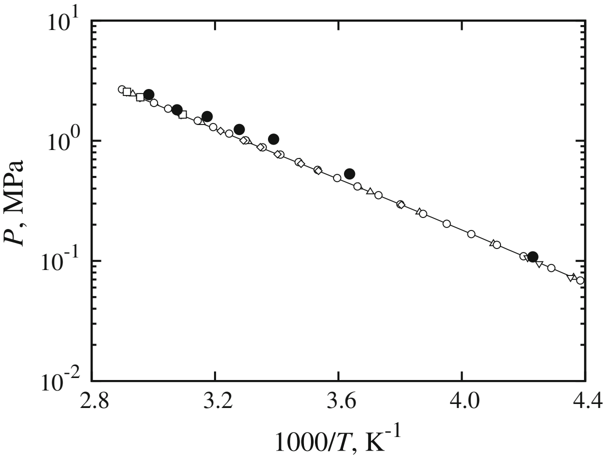

Fig. 3 Saturated vapor pressure of R-218. *Symbols*: *solid* MC simulations, *open* experimental data (△ Ref. [31], o Ref. [39], ▽ Ref. [42], ◇ Ref. [43]). *Line* was computed with the REFPROP [6] equation of state

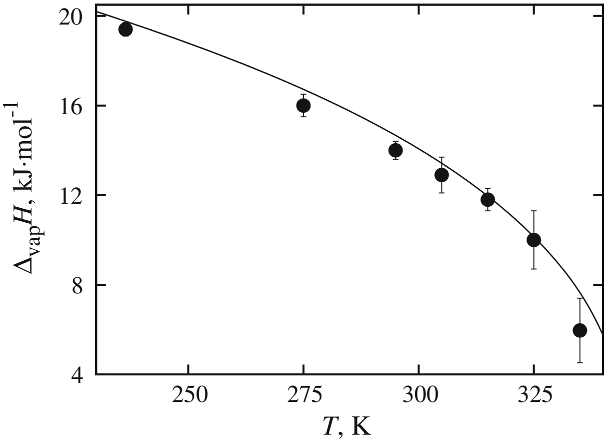

Fig. 4 Vaporization enthalpy of R-218 at saturation. *Symbols* MC simulations, *line* computed with the REFPROP [6] equation of state

data (Fig. 3), however, the temperature dependence is reproduced well. Because the slope of the saturation pressure curve is well predicted, and saturation densities also exhibit good agreement with the values derived from the equation of state [6], the calculated vaporization enthalpy also agrees with REFPROP, with deviations ranging between $0.2\,\text{kJ}\cdot\text{mol}^{-1}$ and $1.7\,\text{kJ}\cdot\text{mol}^{-1}$ (Fig. 4). As noted earlier, Watkins and Jorgensen [8] calculated the liquid density and vaporization enthalpy of R-218 at the normal boiling temperature using the same forcefield, and the present values agree with their results.

Table 3 Two-phase coexistence properties of R-1234yf obtained from simulations

T (K)	ρ_l $(\mathrm{kg \cdot m^{-3}})$	ρ_g $(\mathrm{kg \cdot m^{-3}})$	P_{sat} (MPa)	$\Delta_{vap}H$ $(\mathrm{kJ \cdot mol^{-1}})$
243.7[a]	1263 ± 12	9.0 ± 0.3	0.152 ± 0.004	20.3± 0.3
310	1038 ± 20	66 ± 8	1.21 ± 0.14	15.0 ± 0.3
320	981 ± 17	115 ± 6	1.79 ± 0.15	12.8 ± 0.3
330	919 ± 18	131 ± 11	2.08 ± 0.13	11.7 ± 0.6
340	859 ± 39	152 ± 3	2.44 ± 0.17	10.4 ± 0.5

[a] Normal boiling temperature

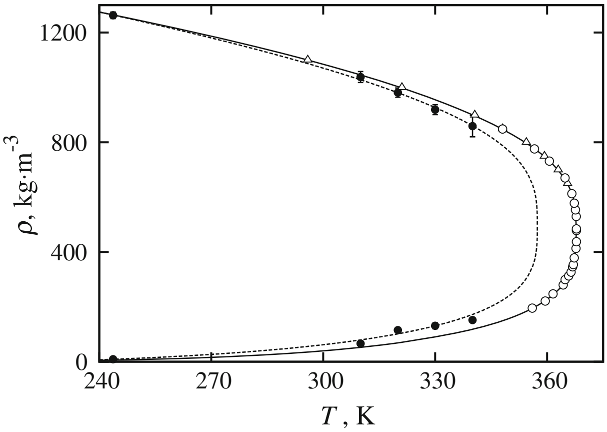

Fig. 5 Saturated density of R-1234yf. *Symbols*: *solid* Monte Carlo simulations, *open* experimental data (△ Ref. [10], o Ref. [12]). *Line* markings are the same as in Fig. 1

3.2 R-1234yf

The results of the vapor–liquid equilibrium simulations for R-1234yf are presented in Table 3 and Fig. 5. As seen, the saturated liquid densities are slightly underpredicted for temperatures above 310 K. Consequently, the derived value of the critical temperature is also underpredicted by about 11 K (Table 2). The critical density and the critical pressure are overpredicted by 4 % and 10 %, respectively; these deviations are similar to those observed for R-218. The liquid densities calculated as a function of pressure are compared with those computed using the preliminary REFPROP equation of state [15] in Fig. 6. As in the case of saturated densities (Fig. 5), REFPROP values are slightly underpedicted; below 340 K, the differences range from −3.9 % to 0.2 %. Of note, however, is that the calculated values cover wider temperature and pressure ranges as compared to limited available experimental data.

The calculated saturated vapor pressures are presented in Fig. 7. As previously seen in the case of R-218, MC simulations overpredict saturated pressures observed experimentally. The deviations in this case range from 29 % to 50 %. Nevertheless, the slope of the vapor pressure curve is reproduced well. As a result, the predicted vaporization enthalpy also shows a reasonable agreement with the values computed using the

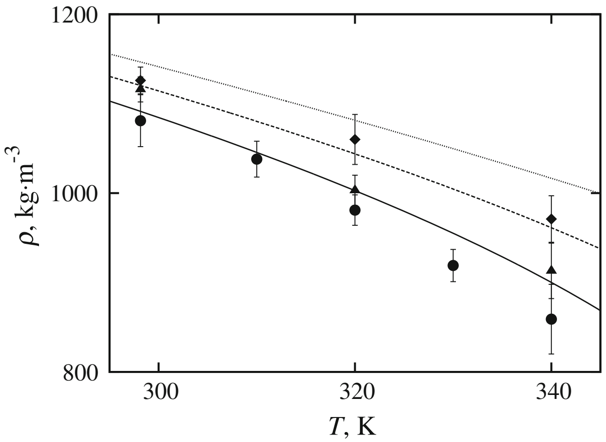

Fig. 6 Liquid density of R-1234yf. *Symbols* are the results of Monte Carlo simulations (● - saturation, ▲ $p = 5\,\text{MPa}$, ♦ $p = 10\,\text{MPa}$). *Lines* are computed with the REFPROP [6,15] equation of state (*solid* saturation, *dashed* $p = 5\,\text{MPa}$, *dotted* $p = 10\,\text{MPa}$)

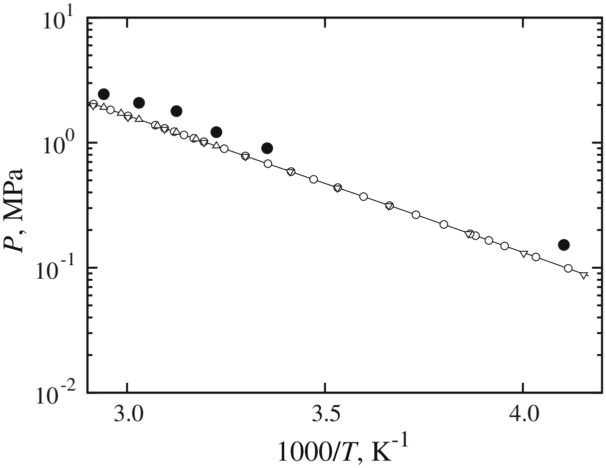

Fig. 7 Saturated vapor pressure of R-1234yf. *Symbols*: *solid* MC simulations, *open* experimental data (▽ Ref. [10], o Ref. [11], △ Ref. [12]). *Line* was computed with the REFPROP [6,15] equation of state

preliminary equation of state [15] (Fig. 8); the differences are between $0.4\,\text{kJ}\cdot\text{mol}^{-1}$ and $2.4\,\text{kJ}\cdot\text{mol}^{-1}$.

4 Discussion

The results presented in the previous sections demonstrate that MC simulations based on the OPLS-AA forcefield are capable of describing VLE behavior for two fluorinated refrigerants. This is especially promising considering the fact that this forcefield was

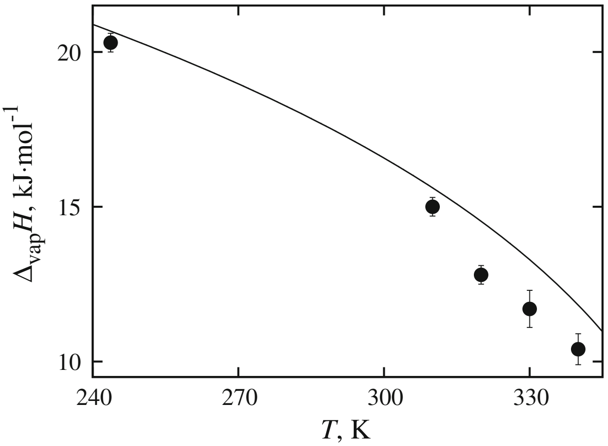

Fig. 8 Vaporization enthalpy of R-1234yf at saturation. *Symbols* MC simulations, *line* computed with the REFPROP [6,15] equation of state

Table 4 Summary of MC statistical uncertainties and absolute deviations between the results of simulations and REFPROP calculations

	R-128		R-1234yf	
Property	MC	REFPROP	MC	REFPROP
ρ_l	3.4 (16.6)	3.4 (18.8)	2.2 (4.5)	2.5 (5.0)[a]
ρ_g	6.7 (9.7)	16.1 (39.6)	6.2 (12.1)	43.6 (67.5)[b]
P_{sat}	8.4 (11.6)	15.8 (29.4)	7.2 (11.6)	38.2 (54.9)
$\Delta_{vap}H$	0.7 (1.4)[c]	0.6 (1.7)[c]	0.4 (0.6)[c]	1.1 (1.7)[c]
T_c	2[d]	4[d]	2[d]	11[d]
p_c	2	11.6	2.0	10.7
ρ_c	5	3	3.7	3.6

Unless indicated otherwise, the reported values are averaged (maxima in *parentheses*) percentages

[a] Limited experimental validation

[b] No direct experimental validation

[c] Absolute deviations in kJ · mol^{-1}

[d] Absolute deviations in K

optimized and tested for prediction of liquid-phase properties, without explicit consideration of two-phase system behavior. The differences between R-218 and R-1234yf for all considered properties are also described well; this suggests that MC methods with OPLS-AA can be used for comparative screening of potential fluorine-containing refrigerants.

Summary of MC statistical uncertainties and the deviations between the results of the simulations and those computed with the REFPROP equations of state [6,15] for both the compounds is presented in Table 4. REFPROP results were chosen for the comparison because, for the majority of cases, they closely describe available experimental data (with the exception of all ρ_g and several ρ_l points for R-1234yf, for which no experimental validation was available). Critical parameters of R-218 are predicted very well based on forcefield parameters that were optimized to predict liquid densities and enthalpies of vaporization. Use of OPLS-AA also yields good a priori predictions for the critical parameters of the fluorinated olefin, R-1234yf. For comparison, a number of group contribution-based prediction methods as implemented in the NIST ThermoData Engine software [44–47] yield estimates of the critical temperature for R-1234yf that deviate from the experimental value by 20 K or more, as opposed to 11 K for the present MC result (see Table 2). For both compounds, liquid densities computed as a function of pressure are slightly underestimated, and saturated vapor pressures are overestimated. However, in both the cases, the deviations appear systematic, suggesting that, if higher accuracy is needed, the agreement between the predictions and the experimental data may be improved by adjustment of forcefield parameters. Ketko and Potoff [48] recently demonstrated that liquid phase data alone do not sufficiently constrain the balance between the short-range Lennard–Jones terms and the long-range Coulombic terms in the forcefield formulation; additional consideration of saturated pressure data (or the acentric factor) during forcefield development produces parameters with wider applicability ranges. Similar arguments are expected to apply to the compounds from the present study.

5 Summary

Thermophysical properties of two fluorine-containing refrigerants, R-218 and R-1234yf, were simulated with MC methods using the OPLS-AA forcefield. The original forcefield formulation was modified to include missing parameters and to correct the erroneous ones using methods consistent with those used in the original forcefield development. Vapor–liquid equilibrium was simulated with the Gibbs ensemble, and liquid-phase simulations were performed with the isobaric–isothermal ensemble. Predictions for saturated densities, saturated pressure, critical parameters, liquid densities, and vaporization enthalpies were reported. The results of the simulations exhibited good agreement with available experimental data. Systematic deviations between the experimental data and the predicted values were observed for liquid densities and saturated pressures, suggesting that further refinement of forcefield parameters is possible if higher accuracy of predictions is needed. Based on the results presented, MC simulations with the OPLS-AA forcefield can be suggested for modeling fluorinated refrigerants, either for exploratory studies or for generation of supplementary data for equation of state model development.

Note added in proof After acceptance of this manuscript, we became aware of the publication by Raabe and Maginn (J. Phys. Chem. Lett. 1, 93 (2010)) that presented Monte Carlo simulations for R-1234yf using a forcefield specifically developed by the authors for fluorinated propenes. The results of Raabe and Maginn support our suggestion that the adjustment of forcefield parameters produces an excellent agreement with the VLE data for R-1234yf.

Acknowledgments The authors thank Prof. W. L. Jorgensen of Yale University and Dr. E.W. Lemmon of NIST for providing the latest set of the OPLS-AA forcefield parameters and the preliminary equation of state for R-1234yf, respectively.

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