

Prediction of thermophysical properties of alternative refrigerants by a novel, ab initio force field

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Abstract

A general all-atoms force field for atomistic simulation of low molecular weight hydro fluoro hydrocarbons (HFCs) was developed using state-of-art ab-initio calculations and empirical parameterization techniques. The force field is based on ab-initio quantum mechanical calculations for the valence parameters and on molecular dynamics simulations for the tuning of the Lennard-Jones parameters describing the dispersion forces. Validation of the proposed force field has been made versus intra-molecular properties of isolated molecules, vibrational spectra, and inter-molecular properties of liquid state molecules such as cohesive energy, enthalpy of vaporization and density for molecules of interest. The reported results show that the present force field enables accurate and simultaneous prediction of structural, conformational, vibrational and thermo physical properties for low molecular weight HFCs in isolation and in condensed phase. Results of the parameterization and validation are reported.

Introduction

Hydrofluorocarbons (HFCs) are among the best fluids for the refrigeration industry [1]: they have almost zero ODP, since they do not contain chlorine; however, if increasing fluorine content decreases flammability, it also increases the atmospheric lifetime and, hence, GWP, which can range from very low to very high. Several HFCs, and particularly their binary and/or ternary mixtures, have been recently reconsidered as promising candidates to replaced (to be) banned refrigerants; therefore it would be of great value to be able to model HFCs with molecular simulation techniques.

In the specific area of molecular modeling of HFCs, accurate force fields are of paramount importance, when used in molecular dynamics and Monte Carlo simulations, to gain insight into the molecular interactions by providing evidence for molecular associations via H-F bonds.

HFC Formula	IUPAC name	ASHRAE name
CH ₂ F ₂	difluoromethane	R32
CH ₃ - CH ₂ F	flouroethane	R161
CH ₃ - CHF ₂	1,1-difluoroethane	R152a
CH ₃ - CF ₃	1,1,1-trifluoroethane	R143
CH ₂ F - CH ₂ F	1,2-difluoroethane	R143a
CHF ₂ - CHF ₂	1,1,2,2-tetrafluoroethane	R134
CH ₂ F - CF ₃	1,1,1,2-tetrafluoroethane	R134a
CHF ₂ - CF ₃	1,1,1,2,2-pentafluoroethane	R125

Table 1: Hydrofluorocarbons (HFCs) considered in this paper.

To perform such calculations, an all atoms ad-hoc potential should be derived, due to the higher accuracy needed in the investigations, even if simulations with an all-atoms force field is undoubtedly computationally more expensive than a united-atom model.

In this paper we propose an all-atom model for HFCs based on ab-initio calculations, which we show to reproduce accurately experimental PVT and phase equilibrium data. The pure components considered in this work are listed in Table 1, in which both the IUPAC and the ASHRAE names are reported.

Force Fields development

The first step in developing a force field is the choice of a simple expression for the total potential energy of a molecule, with contributions from each of the major internal valence coordinates (terms from distortion of bond lengths E_b , bond angles E_a , and torsion angles E_t), and intra- and intermolecular non-bonded interactions (van der Waals forces E_{vdW} , and electrostatic interactions E_{el}). The total potential energy is then given by the contribution of the different terms:

$$E = E_b + E_a + E_t + E_{vdW} + E_{el} \quad (1)$$

Details on the different terms used for the force field are reported elsewhere [2].

The procedure used to parameterize the present force field can be briefly summarized as follows. First, the geometries of all the molecules considered were optimized using density functional theory based electronic calculations. All optimizations were conducted in full – all degrees of freedom were relaxed, and no constraints were imposed during these calculations.

High-quality ab-initio calculations have been used to obtain reliable information on the considered molecules: the BPW91 functional and the DNP basis set were used. Optimized structures for stable conformers, as well as other stationary states (e.g. transition states), were generated to sample conformational energies and rotational barriers.

The proposed force field was derived by fitting the geometrical parameters to these quantum mechanical observables, using the least-square fitting proposed by Maple et al.. The van der Waals parameters for the potential energy were initially guessed and subsequently refined using molecular dynamics (MD) simulations of molecules in condensed phases. In all cases, this was done by calculating and comparing two physical properties of the molecular liquids – densities and cohesive energies at given temperature and pressures.

All molecular modeling, dynamics simulations and quantum calculations were performed on a Silicon Graphics Origin 200, using the commercial software *Cerius²* (v. 4.2) from Accelrys Inc.. (for both QM and MD simulations) and in-house developed computer programs (stand-alone and add-on to the commercial package) for the phase equilibria prediction by the Monte Carlo Gibbs ensemble method.

Results and Discussion

Table 2 reports, as an example, the parameters of the force field for two systems investigated, as obtained from the procedure described above and used to perform all the calculations presented in this paper.

R32			R134a		
	Bond length (Å)	Force constant (kJ/mol/Å ²)		Bond length (Å)	Force constant (kJ/mol/Å ²)
C-F	1.355	4150.5	C-F	1.369	3734.6
C-H	1.092	2850.3	C-C	1.511	3022.8
	Bond angle (°)	Force constant (kJ/mol/rad ²)		Bond angle (°)	Force constant (kJ/mol/rad ²)
FCF	108.3	602.2	FCF	107.7	640.1
HCH	112.5	331.7	CCF	109.3	572.1
FCH	108.9	481.8	FCH	108.7	499.2
	LJ σ (Å)	LJ ϵ (kJ/mol)		LJ σ (Å)	LJ ϵ (kJ/mol)
F	3.538	0.0883	F	3.248	0.103
C	3.884	0.353	C	3.450	0.0209
H	2.995	0.0837	H	2.940	0.0962

R32	Partial charges	R134a	Partial charges
C	-0.18	C	-0.23
F	-0.076	C	0.78
F	-0.076	F	-0.33
H	0.17	F	-0.29
H	0.17	F	-0.27
		F	-0.27
		H	0.31
		H	0.31

Table 2: Intra and inter molecular potential model parameters for R32 and for R134a.

The first step in the validation of a force field is the comparison with experimental data on intramolecular geometrical properties on isolated molecules, such as bond lengths and angles. For all the molecules considered in this work, the calculated bond lengths agree extremely well with the experimental data, and the root-mean-square (rmsd) and maximum deviations (md) for all compounds are only 0.0025 and 0.015, respectively. Also for bond angles, the quality of the predicted values is very high, being the rmsd 0.35 and the md 1.4.

The comparison between experimental and calculated data of intramolecular energetical properties for molecules in isolation is made in terms of absolute energy, zero point vibrational energy, enthalpy of formation, ionization potential and dipole moment. Once again, the agreement obtained is generally very good.

Direct comparison of the compressed liquid densities was made at the end of the FF parameterization using NPT simulations.

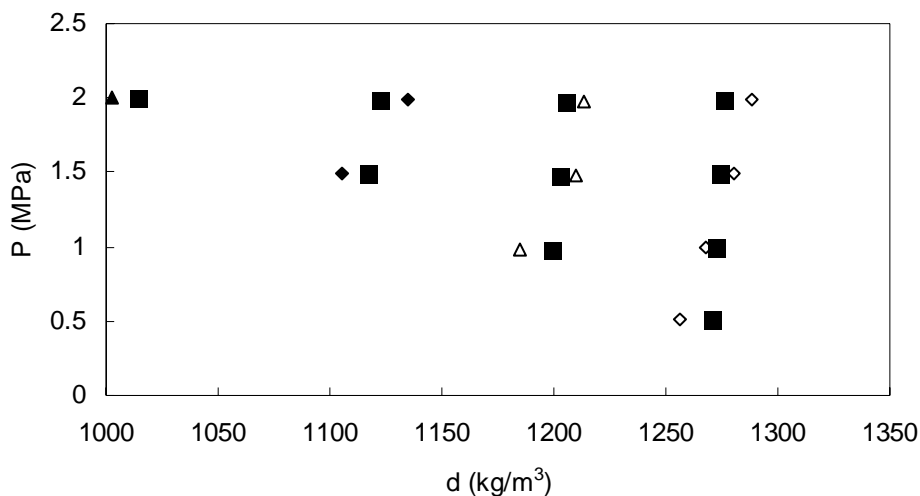


Figure 1: density of R134a as a function of pressure for different isotherms: ▲ T= 340 K; ◆T= 320; △T= 300; ◇T= 280; ■= calculated.

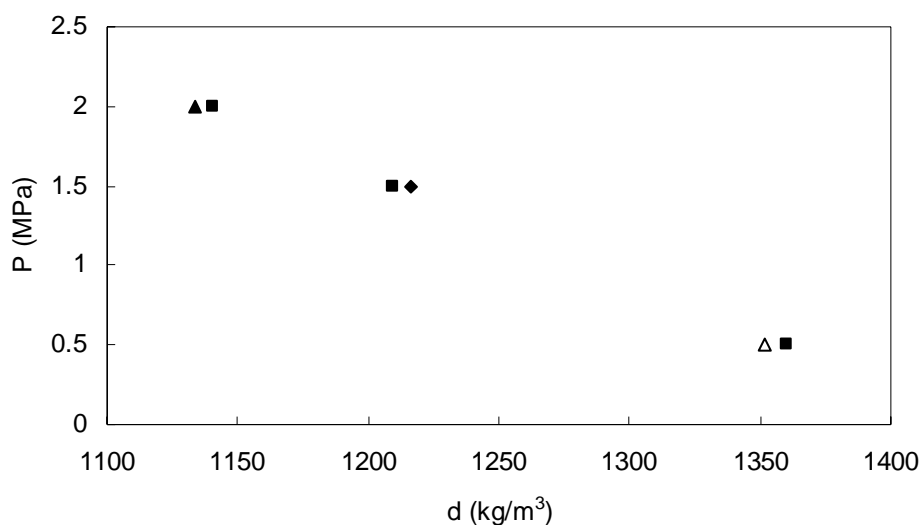


Figure 2: density of R134 as a function of pressure for different isotherms: ▲ T= 340 K; ◆T= 320.02; △T= 280; ■= calculated.

Two illustrative examples are reported in Figures 1 and 2 for R134 and R134a, respectively. As can be seen from these graphs, the average densities obtained agree well with the experimental information, the percent errors of the calculated data with respect to the experimental ones being of the order of few per cent.

The results obtained using the FF developed in this work are shown in Figures 3 and 4 for selected systems, and reported in terms of relative absolute deviation (RAD) in saturated liquid density and saturated vapor density in Table 3. The agreement obtained between calculated and experimental data is generally very good. The deviation never exceeds 2.35% and is, in the average, around 2 % for both liquid and vapor saturated density.

Conclusions

The force field presented in this paper is based on ab initio quantum mechanical calculations and on molecular dynamics simulations for the tuning of the Lennard-Jones parameters.

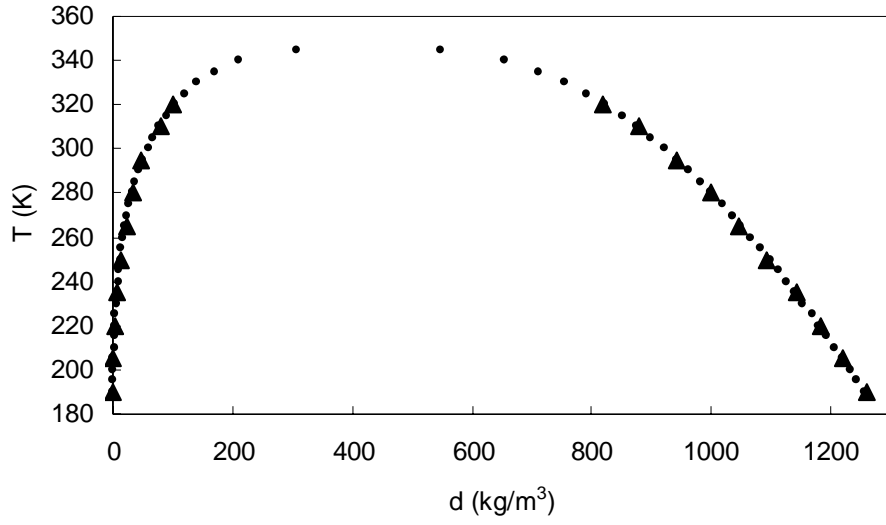


Figure 3: phase diagram of R143a from simulation (●) and experiment (▲).

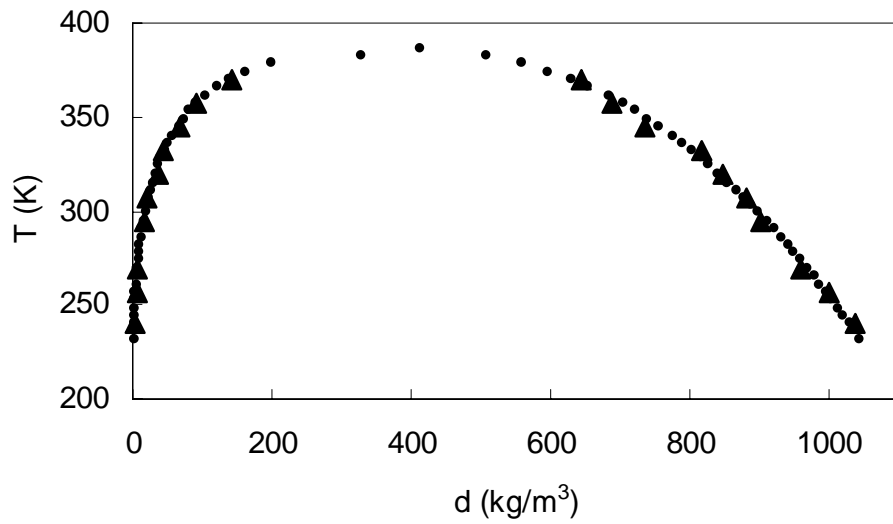


Figure 4: phase diagram of R152a from simulation (●) and experiment (▲).

<i>HFC</i>	<i>T range (K)</i>	<i>Sat Liq. Density RAD</i>	<i>Sat Vap. Density RAD</i>
<i>R32</i>	249 - 351	1.13	1.29
<i>R161</i>	296 - 346	1.22	1.65
<i>R152a</i>	282 - 386	1.49	1.69
<i>R143</i>	200 - 346	2.06	1.70
<i>R143a</i>	190 - 345	2.24	2.51
<i>R134</i>	280 - 340	2.27	2.29
<i>R134a</i>	280 - 340	2.35	2.15
<i>R125</i>	220 - 335	2.11	1.98

Table 3: phase equilibrium prediction for all the systems investigated: relative average deviation in per cent of saturated liquid and saturated vapor density.

Validation of the proposed force field has been made versus intramolecular properties of isolated molecules, vibrational spectra, and intermolecular properties of liquid state molecules such as cohesive energy, enthalpy of vaporization and density.

In general, the calculated geometrical properties (bond lengths and bond angles) and the energetical properties of isolated molecules agree extremely well with the experimental data. Also the agreement of calculated vibrational spectra and compressed PVT data with experimental data is very good.

Gibbs Ensemble Monte Carlo simulations phase behavior prediction with about 2% error in liquid density and in vapor density is obtained for the systems investigated.

The results reported in this paper may be used to implement the force field and calculate physical properties via MD or MC directly or for estimating parameters of accurate EOS (PHSCT and SAFT) to be used in process simulation.

References

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- [2] Fermeglia, M., Ferrone M., Priol, S., *Proceedings of ECTP 2002, Rostock, Germany, August 2002.*

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