

Development of an all-atoms force field from ab initio calculations for alternative refrigerants

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Abstract

A general all-atoms force field (FF) for atomistic simulation of low molecular weight hydrofluorocarbons (HFCs) was developed using state-of-art ab initio calculations and empirical parameterization techniques. The FF is based on ab initio quantum mechanical calculations for the valence parameters and on molecular dynamics (MD) simulations for the tuning of the Lennard-Jones (LJ) parameters describing the dispersion forces.

Validation of the proposed FF 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 for molecules of interest. The reported results show that the present force field enables accurate and simultaneous prediction of structural, conformational, vibrational and thermophysical properties for low molecular weight HFCs in isolation and in condensed phase. Detailed results of the parameterization and validation are reported.

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1. Introduction

The year 2000 has ratified the banning of ozone-damaging substances such as fully chlorinated hydrocarbons used as working fluids in existing refrigeration units. As a consequence, the air-conditioning and refrigeration industry is in the midst of an unprecedented transition, catalyzed by environmental concerns with the impacts of refrigerant emission. In the selection of alternative refrigerant fluids, attention is now focused on ozone depletion and global warming, with a view toward reducing greenhouse gas emissions. Calm and Didion [1], in an extensive investigation on the preferred properties for an ideal refrigerant, drew the following, general conclusions: (i) the number of suitable elements that can be combined at the molecular level is small; (ii) that the probability of finding an ideal refrigerant is practically zero and

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no perfect solution exists; (iii) greater attention is needed in addressing both environmental and safety concerns by containment, particularly for compounds with minimal adverse impact, rather than phase out; (iv) indiscriminate elimination of entire classes of compounds, without regarding to offsetting benefits for those of low concern, may force less desirable compromises later; (v) efforts to address stratospheric ozone depletion and reduce greenhouse gas emissions have spawned numerous secondary benefits, such as increased safety, efficiency, resource conservation, and lowered life-cycle costs.

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 framework of the IUPAC initiative focusing on halocarbons, culminated in the workshops in Pisa and Paris, we have shown [2–6] how it is possible to extract the characteristic parameters of some equation of state (EOS) from computer experiments, thus reducing the experimental efforts necessary to characterize the VLE behavior of pure components as well as their mixtures. This can be basically done by two different methods: (i) one based on the description of the solvation phenomena at a molecular level using the conductor-like screening model for real solvents (COSMO-RS) [7], and the other (ii) based on molecular mechanics/dynamics experiments [2,4]. In both cases, the molecular orbital description was based on available interaction potential.

In this respect, a key point in the molecular simulation of a real system is the availability of an accurate force field (FF). Several authors have developed FF in the last years, particularly for hydrocarbons. But simulation studies and FF developments for HFCs and perfluorinated compounds are limited and poorly advanced.

In the specific area of molecular modeling of HFCs, accurate FFs are of paramount importance, when used in molecular dynamics (MD) and Monte Carlo simulations, to gain insight into the molecular interactions by providing evidence for molecular associations via H–F bonds. Focus point in the molecular simulations in this area for the future is on methane, ethane and propane derivatives [8]. 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.

One of the reasons for developing all-atoms FFs is that the available potentials are usually developed for biosystems at atmospheric pressure, and their applicability to process modeling at high pressure and different temperature is still questionable due to the parameterization procedure based on low pressure, room temperature, solid phase data. In the past years, perfluoroalkanes FFs focused on modeling the solid phase diagram of (poly)tetrafluoroethylene (PTFE) using explicit atoms: Rice et al. [9] developed a united atom model for CF_3 and CF_2 , but obtained poor performances in the liquid state. Sandler and coworkers [10] presented results for quantum chemistry calculations on halocarbons, including hydrogen fluoride treating dispersion forces by empirical method. Fuchs and coworkers [11] developed a transferable potential for chlorofluorocarbons showing good results for liquids at atmospheric pressure and for vapor–liquid equilibria. Deiters and Hloucha [12] reported Monte Carlo calculations by using a Lennard-Jones (LJ) potential with partial charges and polarizability effects applied to substituted methane. Finally, a united-atoms FF for perfluoromethylpropylether [13] gave good results in Monte Carlo Gibbs ensemble calculations.

Table 1
Hydrofluorocarbons (HFCs) considered in this paper

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

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.

2. Force field methods and parameterization

An underlying issue of all-atomistic simulations is the quality of the FF. A FF consists of a set of analytical function forms and parameters, and provides a detailed description of intra- and intermolecular interactions as functions of molecular structures and relative positions. A FF derived from high-quality ab initio calculations plays a uniquely important role since it builds a bridge between the high-quality ab initio calculations and the large-scale property predictions. In developing a FF several steps should be accomplished. A brief description of each step in the development of the proposed FF is reported below.

The first step in developing a FF 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 [14]:

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

In this work, the following expressions were used for the relevant terms.

Bond stretching and bond bending are described by simple harmonic functions:

$$E_b = \frac{1}{2} K_{ij} (r_{ij} - r_{ij}^0)^2 \quad (2)$$

$$E_a = \frac{1}{2} K_{ijk} (\cos_{ijk} - \cos_j^0)^2 \quad (3)$$

where r_{ij} and \cos_{ijk} are the bond lengths and angles, respectively, and r_{ij}^0 and \cos_j^0 are the corresponding equilibrium values, obtained from geometry optimized molecular conformations resulting from accurate ab initio calculations (vide infra).

The potential energy profile, obtained for each dihedral angle from further quantum mechanics calculations as reported below, was fitted to a seventh order polynomial equation in $\cos \phi$:

$$E_t = \sum_{D_i} \sum_{j=0}^7 a_{D_{ij}} \cos^j \phi \quad (4)$$

Finally, a 9-6 LJ function [15] is used to represent the van der Waals forces, while the electrostatic interaction is written in the form of a standard Coulomb interaction with partial atomic charges:

$$E_{\text{vdW}} = \sum_{i,j} \varepsilon_{ij} \left[2 \left(\frac{r_{ij}^{\text{eq}}}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^{\text{eq}}}{r_{ij}} \right)^6 \right] \quad (5)$$

$$E_{\text{el}} = \sum_{i,j} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \quad (6)$$

The procedure used to parameterize the present FF can be briefly summarized as follows. First, the geometries of all the molecules considered were optimized using density functional theory based electronic calculations. These were performed with DMol³ [16], as implemented in the suite Cerius² (version 4.2) from Accelrys Inc. (San Diego, USA). All optimizations were conducted in full—all degrees of freedom were relaxed, and no constraints were imposed during these calculations. In order to probe the conformational properties for which high-quality ab initio calculations must be employed to obtain reliable information, the BPW91 functional [17–19] and the DNP basis set were used. The geometry optimization convergence threshold for energy change was set to $10^{-7} E_h$ (hartree, which correspond to 4.3598×10^{-25} J), $10^{-5} a_0$ (bohr, which correspond to 5.2918×10^{-16} m) for the displacement and $10^{-5} E_h/a_0$ (which correspond to 0.8239×10^{-7} J/m) for the gradient.

In addition to optimized structures, several methods were used to generate varied configurations of the molecules considered to sample the conformational surface. To ensure that all deformations were sampled, most of the distorted configurations were obtained by displacing the atoms along the directions of their normal modes of vibrations, while randomly selecting the magnitude of the atomic displacements, as discussed in detail elsewhere [20,21]. 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 potential energy surface sampling was completed by calculating the ab initio energy, and the first and second derivatives of the energy with respect to the atomic coordinates. In general, for M configurations of a molecule containing N atoms, there will be $M - 1$ relative energies, $M(3N - 6)$ independent first derivatives, and $M(0.5)(3N - 6)(3N - 5)$ independent second derivatives of the energy [21]. For example, the number of independent quantum observables for 36 distorted fluoroethane structures comprise 35 relative energies, 432 first derivatives, and 2808 second derivatives. The latter two quantities represent the slope and curvature of the potential surface at the particular configuration.

The proposed FF was derived by fitting the parameters of Eqs. (2)–(4) to these quantum mechanical observables, using the least-square fitting proposed by Maple et al. [21].

In the derivation of the atomic partial charges, we adopted the approach recently revisited by Li et al. [13], according to which these parameters are obtained by fitting the ab initio generated electrostatic potential (ESP) energies [22,23], with the Boltzmann factor weighting. During the calculations of the torsional potential energy, ESP charges q_i for each atom were obtained with the Merz–Singh–Kollman [24,25] algorithm at each different conformation.

$$r_{ij}^0 = (\frac{1}{2}((r_i^0)^6 + (r_j^0)^6))^{1/6} \quad (8)$$

All molecular modeling, dynamics simulations and quantum calculations were performed on a Silicon Graphics Origin 200, using the commercial software Cerius² (version 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.

3. Results and discussion

Table 2 reports, as an example, the parameters of the FF for two systems investigated, as obtained from the procedure described above and used to perform all the calculations presented in this paper. The complete set of parameters in electronic format is available upon request from authors.

The first step in the validation of a FF is the comparison with experimental data on intramolecular geometrical properties on isolated molecules, such as bond lengths and angles. Table 3 reports such comparison for R32, R143a and R152a, in which an excellent agreement is obtained between experimental and calculated geometrical values. In general, the calculated bond lengths agree extremely well with the experimental data, and the root mean square deviation (rmsd) and maximum deviation (md) for all compounds are only 0.0025 and 0.015 Å, respectively. Also for bond angles, the quality of the predicted values is very high, being the rmsd 0.35° and the md 1.4°.

Table 4 shows the comparison between experimental and calculated data of intramolecular energetical properties for molecules in isolation. The comparison is made in terms of absolute energy (Ha), zero point vibrational energy (ZPVE) (kJ/mol), enthalpy of formation (kJ/mol), ionization potential (eV) and dipole moment (D). The first two properties are compared with values calculated by other authors [27], while the remaining quantities are directly compared with experimental data [28,29]. Once again, the agreement obtained is generally very good.

Table 3

Force field validation for intramolecular properties on isolated molecules: bond lengths and angles for R32, R143a and R152a

HFC	Length/angle	Calculated	Experimental
R32	C–F (Å)	1.355	1.357
	C–H (Å)	1.092	1.093
	FCF (°)	108.3	108.3
	HCH (°)	112.5	113.7
R143a	C–F (Å)	1.390	1.389
	C–H (Å)	1.100	1.103
	C–C (Å)	1.503	1.503
	CCF (°)	110.8	110.3
R152a	C–F (Å)	1.360	1.364
	C–H _{av} (Å)	1.099	1.081
	C–C (Å)	1.504	1.498
	CCF (°)	110.2	110.7

Table 4

Force field validation for intramolecular properties on isolated molecules: absolute energy (AE), zero point vibrational energy (ZPVE), enthalpy of formation (ΔH_{form}), ionization potential (IP) and dipole moment (μ)

HFC	AE (Ha)		ZPVE (kJ/mol)		ΔH_{form} (kJ/mol)		IP (eV)		μ (D)	
	Calculated	Literature	Calculated	Literature	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
R32	-138.95	-139.49	96.8	97.4	-443.5	-451.9	12.3	12.7	2.02	1.98
R161	-179.07	-178.70	172.6	168.8	-266.1	-263.6	11.78	11.78	1.99	1.94
R152a	-277.15	-277.82	151.0	150.4	-501.8	-502.1	11.95	11.87	2.27	2.27
R143	-377.67	-376.94	130.5	130.0	-738.9	-748.9	13.1	13.3	235	2.35
R143a	-278.99	-277.79	150.9	152.3	-448.4	-447.7	13.0	12.9	2.59	2.67
R134	-475.55	-476.02	113.8	114.6	-871.8	-878.6	11.68	-	0.00	-
R134a	-476.94	-475.36	112.7	112.9	-890.0	-895.4	12.8	-	2.04	2.05
R125	-576.23	-575.14	93.8	93.5	-1099.1	-1104.6	12.7	-	1.48	1.56

Table 5
Force field validation for vibrational spectrum of R161

n_{calc} (cm^{-1})	n_{exp} (cm^{-1})
409	415
878	880
1055	1048
1123	1108
1168	1171
1275	1277
1372	1365
1408	1395
1454	1449
1470	1456
1499	1479
2916	2915
2931	2941
2957	2967
3015	3012

The average and maximum deviation between calculated and experimental data are 8 cm^{-1} and 20 cm^{-1} respectively.

In addition to structural and energetical properties, it is important to test FF's ability to account for dynamic properties. Vibrational spectra are a sensitive probe of this property, and thus we have explored the ability of the FF to account for HCFs dynamics. Table 5 reports a comparison between predicted and experimental [30] normal modes for R161, in which an average deviation of 8 cm^{-1} and a maximum deviation of 20 cm^{-1} is obtained. Similar results are achieved for the other systems.

NVT MD simulations of molecular liquids were used primarily to derive the van der Waals parameters in light of efficiency. The final results of the NVT simulations of three liquid HFCs, taken as representative of the entire set, are summarized in Table 6, where the experimental densities, temperatures and heat of vaporization are listed for comparison.

Table 6
Cohesive energy density, evaporation enthalpy and liquid density at different temperature for R32, R143 and R152a

HFC	T (K)	Property	Unit	Calculated	Experimental	Deviation (%)
R32	260	C.E.D.	J/cm^3	335.5	–	–
		ΔH_{vap}	kJ/mol	18.08	17.80	+1.6
		Density	kg/m^3	1108.7	1096.6	+1.1
R143	259	C.E.D.	J/cm^3	193.5	–	–
		ΔH_{vap}	kJ/mol	17.19	16.94	+1.5
		Density	kg/m^3	1106.5	1081.6	+2.3
R152a	261	C.E.D.	J/cm^3	254.3	–	–
		ΔH_{vap}	kJ/mol	19.21	19.83	–3.1
		Density	kg/m^3	968.1	985.8	–1.8

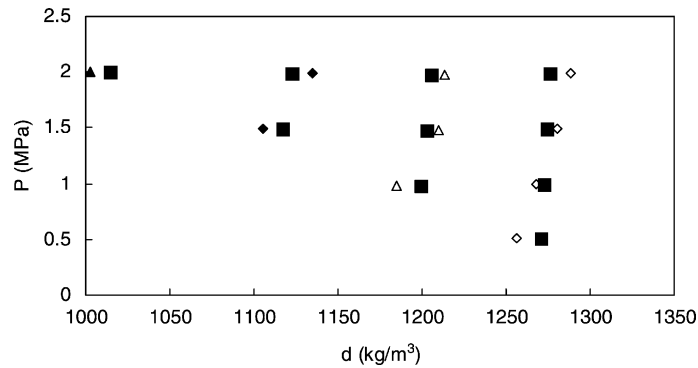


Fig. 1. Density of R134a as a function of pressure for different isotherms: (▲) $T = 340$ K; (◆) $T = 320$ K; (△) $T = 300$ K; (◇) $T = 280$ K; (■) calculated.

Direct comparison of the compressed liquid densities was made at the end of the FF parameterization using NPT simulations. Two illustrative examples are reported in Figs. 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 percent.

The FF developed according to the procedure described above was implemented in a Gibbs ensemble Monte Carlo simulation code, in order to calculate saturated liquid and vapor densities and phase equilibrium. In the Gibbs ensemble Monte Carlo simulation, equilibration of temperature, pressure and chemical potential is achieved by means of different trial configurations [31].

The results obtained using the FF developed in this work are shown in Figs. 3–6, and reported in terms of relative absolute deviation (RAD) in saturated liquid density and saturated vapor density in Table 7. 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.

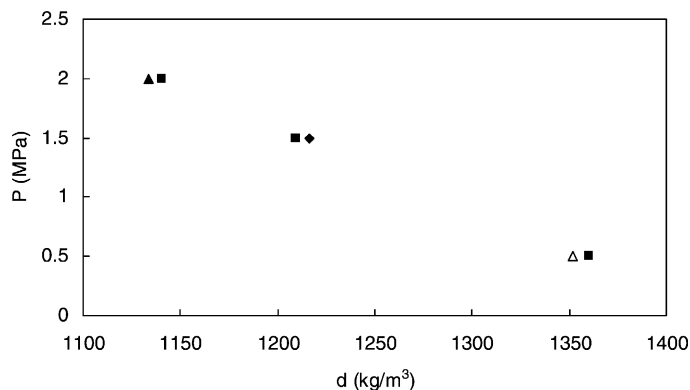


Fig. 2. Density of R134 as a function of pressure for different isotherms: (▲) $T = 340$ K; (◆) $T = 320.02$ K; (△) $T = 280$ K; (■) calculated.

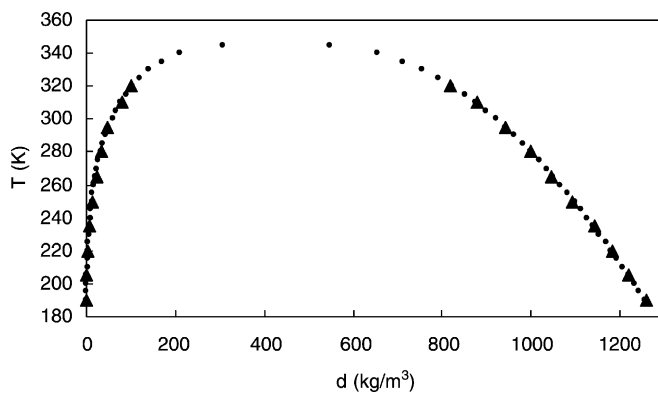


Fig. 3. Phase diagram of R143a from simulation (●) and experiment (▲).

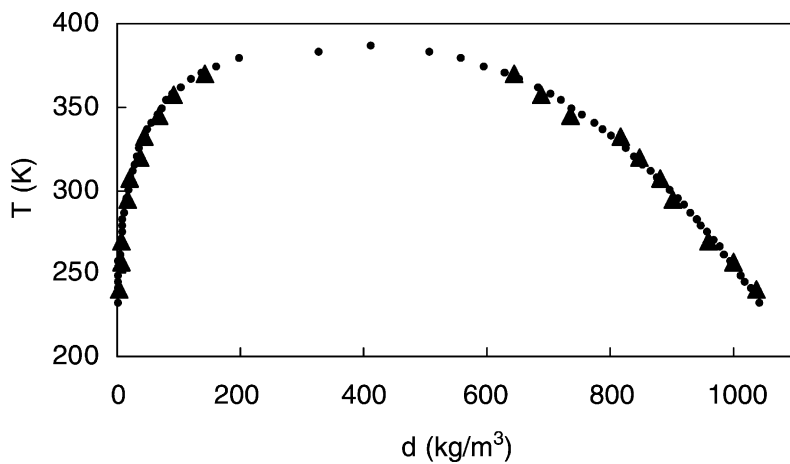


Fig. 4. Phase diagram of R152a from simulation (●) and experiment (▲).

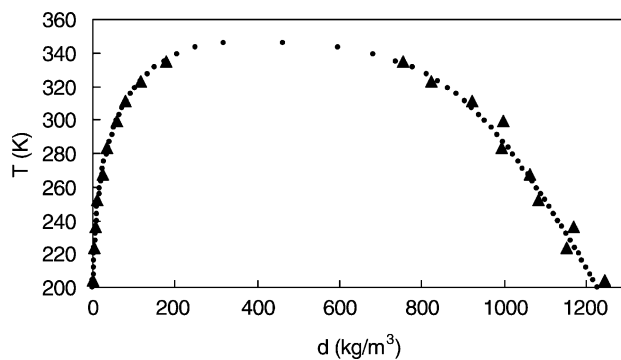


Fig. 5. Phase diagram of R143 from simulation (●) and experiment (▲).

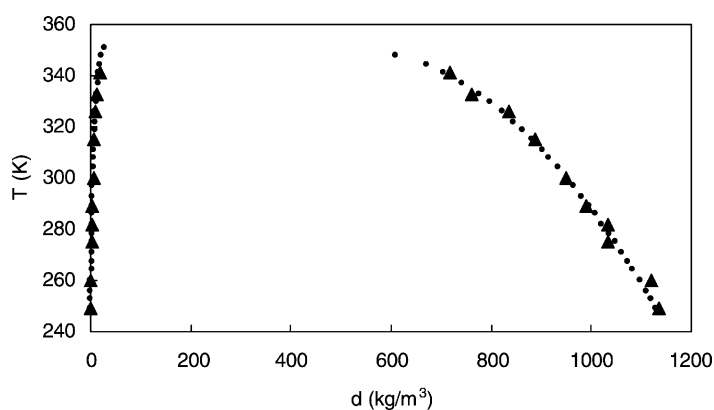


Fig. 6. Phase diagram of R32 from simulation (●) and experiment (▲).

Table 7

Phase equilibrium prediction for all the systems investigated: relative average deviation in percent of saturated liquid and saturated vapor density

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

4. Conclusions

In this paper, the description of the development of all-atom FF for HFCs is reported. The FF is based on ab initio quantum mechanical calculations and on MD simulations for the tuning of the LJ parameters.

Validation of the proposed FF 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.

Finally, 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 present paper reports the first attempt to develop an all-atom FF from ab initio calculations for low molecular weight HFCs specifically designed for the prediction of phase equilibria. Such FF derived from high-quality ab initio calculations plays a uniquely important role since it builds a bridge between

the high-quality ab initio calculations and the large-scale property predictions. The results reported in this paper may be used to implement the FF 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. Work is in progress to extend the FF development to propane derived HFCs and to oxygen and sulfur containing molecules.

References

- [1] J.M. Calm, D.A. Didion, *Int. J. Refrig.* 21 (1998) 308.
- [2] M. Fermeglia, S. Pricl, *Fluid Phase Equilib.* 166 (1999) 21.
- [3] M. Fermeglia, S. Pricl, *AIChE J.* 45 (1999) 2619.
- [4] F. Belloni, M. Fermeglia, S. Pricl, *Mol. Simul.* 25 (2000) 53.
- [5] M. Fermeglia, S. Pricl, A. Klamt, *Proceedings of the 1st International Conference on Foundations of Molecular Modeling and Simulations*, Keystone Resort, Colorado, USA, 2000, p. A20.1, *AIChE Simp. Ser.* 97 (2001) 191.
- [6] O. Milocco, M. Fermeglia, S. Pricl, *Fluid Phase Equilib.* 199 (2002) 15.
- [7] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* (1993) 799.
- [8] J. Dymond, *Panel Discussion on 3rd International Workshop on Thermochemical, Thermodynamic and Transport Properties of Halogenated Hydrocarbons and Mixtures*, IUPAC Conference on Chemical Thermodynamics, Rostock, 2002.
- [9] S.A. Rice, N. Collazo, S. Shin, *J. Chem. Phys.* 96 (1992) 4735.
- [10] A.K. Sum, S.I. Sandler, P.K. Naicker, *Fluid Phase Equilib.* 199 (2002) 5.
- [11] A. Boutin, B. Levy, C. Beauvais, J. Ridard, A.H. Fuchs, A.K. Cheetham, *Proceedings of the 2nd Workshop on Thermochemical, Thermodynamic and Transport Properties of Halogenated Hydrocarbons and Mixtures*, Paris, France, 9–11 April 2001, p. 52.
- [12] U.K. Deiters, M. Hloucha, *Proceedings of the 2nd Workshop on Thermochemical, Thermodynamic and Transport Properties of Halogenated Hydrocarbons and Mixtures*, Paris, France, 9–11 April 2001, p. 59.
- [13] H.-C. Li, C. McCabe, S.T. Cui, P.T. Cummings, H.D. Cochran, *Mol. Phys.* 100 (2002) 265.
- [14] H. Sun, *Macromolecules* 28 (1995) 701.
- [15] A.T. Hagler, S. Lifson, P. Dauber, *J. Am. Chem. Soc.* 101 (1979) 5122.
- [16] B. Delley, *J. Chem. Phys.* 92 (1990) 508.
- [17] J.P. Perdew, Y. Wang, *Phys. Rev. B* 33 (1986) 12.
- [18] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [19] J.P. Perdew, J.A. Chevari, H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Phys. Rev. B* 46 (1992) 6671.
- [20] D.H. Kitson, F. Avbelj, J. Moulton, D.T. Nguyen, J.E. Mertz, D. Hadzi, T.A. Hagler, *Proc. Natl. Acad. Sci. U.S.A.* 90 (1993) 8920.
- [21] J.R. Maple, M.-J. Hwang, T.P. Stockfish, U. Dinur, M. Waldman, C.S. Ewig, A.T. Hagler, *J. Comput. Chem.* 15 (1994) 162.
- [22] D.E. Williams, *J. Comput. Chem.* 9 (1988) 745.
- [23] D.E. Williams, *Biopolymers* 29 (1990) 1367.
- [24] U.C. Singh, P.A. Kollman, *J. Comput. Chem.* 5 (1984) 129.
- [25] B.H. Besler, K.M. Merz Jr., P.A. Kollman, *J. Comput. Chem.* 11 (1990) 431.
- [26] M. Waldman, A.T. Hagler, *J. Comput. Chem.* 14 (1993) 1077.
- [27] Y.G. Lazarou, P. Papagiannacopoulos, *Chem. Phys. Lett.* 301 (1999) 19.
- [28] *CRC Handbook of Chemistry and Physics*, 79th ed., CRC press, Boca Raton, USA, 1998.
- [29] B.D. Smith, R. Srivastava, *Thermodynamic Data for Pure Compounds*, Elsevier, Amsterdam, The Netherlands, 1986.
- [30] D.C. Smith, R.A. Saunders, J.R. Nielsen, E.E. Ferguson, *J. Chem. Phys.* 20 (1952) 847.
- [31] A.Z. Panagiotopoulos, *Mol. Phys.* 61 (1987) 813.