MONTE CARLO SIMULATION OF VAPOR-LIQUID EQUILIBRIA OF LIQUID FLUORINE USING NEW *AB INITIO* INTERMOLECULAR INTERACTION POTENTIALS

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ABSTRACT

This paper presents vapor-liquid equilibria of pure fluid fluorine which were predicted by Gibbs Ensemble Monte Carlo (GEMC) simulation techniques using our two new 5-site intermolecular pair potentials ab initio. The ab initio pair potentials were established from coupled-cluster calculations, using the CCSD(T) level of theory and Dunning's correlation consistent basis sets aug-cc-pVmZ (m =2, 3) [8]. The coexistence phase diagram, and the resulting critical properties, thermodynamic properties, vapor pressures and orthobaric densities are found to correspond well with the experimental data.

Keywords: *Gibbs Ensemble Monte Carlo simulation, vapor - liquid equilibria, ab initio potentials*

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1. INTRODUCTION

Computer simulations have become indispensable tools for studying pure fluids and fluid mixture [1]. One of the first attempts Nasrabad and Deiters predicted phase high-pressure vapour-liquid phase equilibria of noble-gas mixtures [2,3] from the global simulations using the intermolecular potentials. Leonhard and Deiters used a 5-site Morse potential to represent the pair potential of nitrogen [4] and were able to predict vapour pressures and orthobaric densities successfully with Gibbs Ensemble Monte Carlo simulation, GEMC [5].

In this work we report the simulation results of the vapor-liquid equilibria for fluid fluorine using Gibbs Ensemble Monte Carlo (GEMC) simulation techniques with our new 5-site intermolecular pair potentials ab initio resulting from quantum mechanical calculations of dimer F_2-F_2. The simulation results density, vapour pressure and enthalpy of vaporization are compared with experimental data and with those from literature data.

2. COMPUTATIONAL DETAILS

2.1. Simulation technique

The GEMC-NPT simulation was used to examine the accuracy of the pair potentials. This simulation was investigated on isobars at 1.0 MPa and 10.0 MPa in the range 90.0 K to 270 K. GEMC-NVT simulations were performed to obtain coexisting liquid and vapor densities and vapor pressures in the range 60.0 K to 140.0 K with an increment 10.0 K.

The 5-site potentials for fluorine were used for both simulation cases:

$$u_1 = \sum_{i=1}^{5}\sum_{i=1}^{5}\left[D_e^{ij}((1-e^{-\alpha_{ij}(r_{ij}-\beta_{ij})})^2 - 1) + f_{1a}(r_{ij})\left(\sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij})\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) \right] \quad (1)$$

$$u_2 = \sum_{i=1}^{5}\sum_{i=1}^{5}\left[D_e^{ij}((1-e^{-\alpha_{ij}(r_{ij}-\beta_{ij})})^2 - 1) + f_{1b}(r_{ij})\left(\sum_{n=6,8,10,12} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij})\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right) \right] \quad (2)$$

with $f_{1a}(r_{ij}) = (1 + e^{-2(\delta_{ij} r_{ij} - 2)})^{-15}$ and $f_{1b}(r_{ij}) = 1 - e^{-\delta_{ij} r_{ij}} \sum_{k=0}^{10} \frac{(\delta_{ij} r_{ij})^k}{k!}$

Total number of particles N = 512 were used in both GEMC simulations with the standard periodic boundary conditions and the minimum image convention. For GEMC-NVT simulation runs the equilibration between two phase required 1-2 x 106 cycles. All movements were performed randomly with defined probabilities. The simulation data were exported using block averages with 1000 cycles per block. The simulations were started with equal densities in two phases. The simulation systems were equilibrated for about 1.0 x 106 cycles. The cut-off radius rc was set to 8.5 Å for fluorine.

2.2. Phase coexistence properties

The critical temperature T_c/K, density ρ_c/g.cm^{-3} and volume Vc/ cm^3.mol^{-1} of the pure fluid fluorine were derived from least-squares fits to the densities of coexisting phase using the relations of the rectilinear diameter law:

$$\frac{\rho_1 - \rho_2}{2} = \rho_c + A(T_c - T) \quad (3)$$

$$\rho_1 - \rho_2 = B(T - T_c)^{\beta}$$

where ρ_l and ρ_v are the coexistence liquid density and vapor density, β is the critical exponent ($\beta = 0.325$). A and B are adjustable constants. The critical pressure P_c/ MPa was calculated with the Antoine equation. Vapor pressure and heat of vaporization $\Delta_{vap}H$ were calculated by the Clausius-Clapeyron equation.

3. RESULTS AND DISCUSSIONS

3.1. Structural properties

The site-site pair distribution functions resulting from two GEMC-NVT and -NPT simulation techniques for the pure fluid fluorine are shown in Figure 1 and Figure 2. The *ab initio* pair potentials Eq. 1 and Eq. 2 of fluorine, respectively, were used for those simulations.
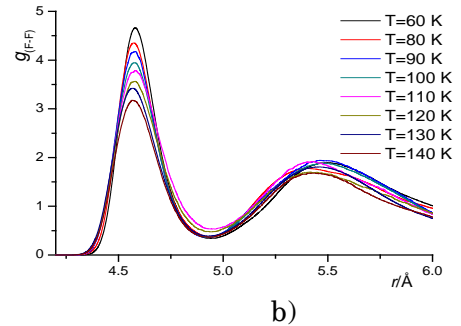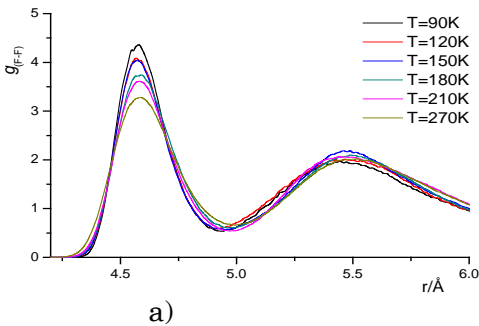

a)

b)

Figure 1: *Temperature dependence of g_{F-F} at P = 1.0 Mpa - a) simulation GEMC-NPT and, b) simulation GEMC-NVT, in both cases; using intermolecular pair potential Eq.1).*

All first peaks of the site-site correlation functions for fluorine are located between 3.98 Å and 4.88 Å. The second peaks are located between 5.256 Å and 5.717 Å.

3.2. Phase coexistence properties

The simulation results are shown in Table 1 and Table 2. The vapor-liquid coexisting phase curve of the fluid fluorine is illustrated in Figure 2. Experimental data [8,9], values from the Deiters equation of state [7] as well as from LJ potential [6] are also included.
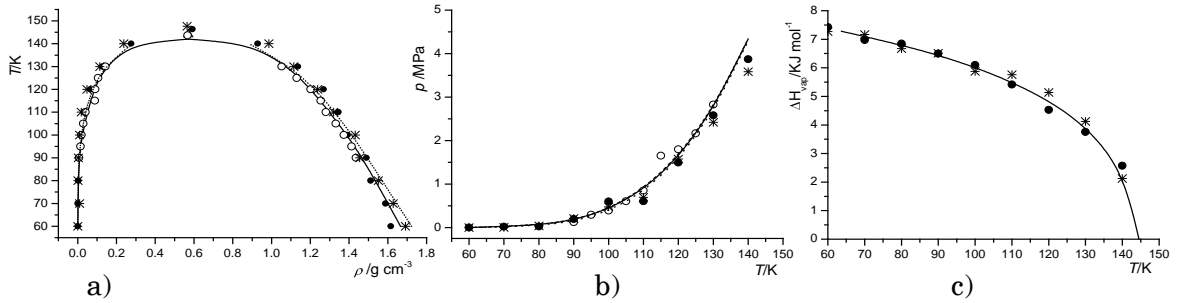

Figure 2: *a) vapor-liquid coexistence diagram; b) vapor pressure, c) vaporization enthalpy.*

Symbols: —, experimental Data [8,9]; o, Lennard-Jones potential; ----, Deiters equation of state D1-EOS [7]; •, ∗, pair potentials Eq. 1 and Eq. 2.

These vapor pressures differ on absolute average from the experimental data typically by about 1.4% and 5.8%. These differences are small within statistical uncertainties of experimental resources [8,9].

Table 1: Critical properties resulting from the GEMC-NVT simulation using equations Eq. 1 and Eq. 2; D1-EOS: Deiters equation; LJ: Lennard-Jones potential; Exp.: experimental values.

Method	T_c/ K	ρ_c/ g.cm^{-3}	P_c /Mpa	V_c/ cm^{3}mol^{-1}	ref.
Eq. 1	146.41	0.592	4.911	64.207	this work
Eq. 2	147.65	0.565	5.380	67.298	this work
LJ	143.63	0.567	5.039	66.996	[6]
D1-EOS	144.16	0.568	5.050	66.954	[7]
Exp.	144.30	0.574	5.215	66.200	[8]
Exp.	144.12	0.571	5.172	66.545	[9]

The critical properties of the pure fluid fluorine could be obtained from the orthobaric densities of vapor-liquid equilibria by the least-square fit to the relation (3),

as shown in Table 2. The critical pressure of fluorine agreed reasonable well with experimental data.

Table 2: Enthalpy of vaporization $\Delta_{vap}H$, entropy of vaporization $\Delta_{vap}S$ and boiling temperature T_b at P = 101.3 kPa predicted from simulation vapor pressures.

Method	$\Delta_{vap}H$/ kJ mol^{-1}	$\Delta_{vap}S$/ kJ.mol^{-1}.K^{-1}	T_b/ K	ref.
Eq. 1	6.805	0.0791	85.978	this work
Eq. 2	7.160	0.0821	87.181	this work
LJ	7.646	0.0871	87.768	[6]
D1-EOS	7.131	0.0821	86.835	[7]
Exp.	6.921	0.0809	85.597	[8]
Exp.	6.941	0.0811	85.570	[9]

The discrepancies between predicted results and experimental data are insignificant.

4. CONCLUSION

The vapour-liquid phase equilibria and thermodynamic properties of the fluid fluorine were calculated successfully with our developed simulation programs GEMC-NVT and GEMC-NPT using new ab initio intermolecular pair potentials. The simulation results turn out to be in very good agreement with experimental data.

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MÔ PHỎNG MONTE CARLO CÂN BẰNG LỎNG HƠI CỦA FLO LỎNG SỬ DỤNG CÁC THẾ TƯƠNG TÁC PHÂN TỬ *AB INITIO* MỚI

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TÓM TẮT

Cân bằng lỏng hơi của flo lỏng được dự đoán bằng kĩ thuật mô phỏng Monte Carlo (GEMC) sử dụng hai thế cặp tương tác phân tử 5 vị trí ab initio mới của chúng tôi. Các thế cặp ab initio đã được xây dựng từ các tính toán sử dụng mức lí thuyết CCSD(T) với các tập cơ sở của Dunning aug-cc-pVmZ (m = 2, 3) [8]. Giản đồ pha, các tính chất tới hạn, tính chất nhiệt động, áp suất hơi và tỉ trọng các pha nhận được phù hợp rất tốt với các số liệu thực nghiệm.

Từ khóa: *Mô phỏng Monte Carlo, cân bằng lỏng hơi, thế ab initio*

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