

## AB INITIO INTERMOLECULAR POTENTIALS AND PREDICTION OF VAPOR-LIQUID EQUILIBRIA FOR SYSTEMS N<sub>2</sub> AND O<sub>2</sub> USING GIBBS ENSEMBLE MONTE CARLO SIMULATION

Received 6 June 2008

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### ABSTRACT

The vapor-liquid equilibria of diatomic systems N<sub>2</sub> and O<sub>2</sub> were predicted by Gibbs ensemble Monte Carlo simulation techniques using the our new developed site-site intermolecular potential [6] and a Morse-style pair potential [4]. These pair potentials were constructed from *ab initio* intermolecular energies SAPT (symmetry-adapted perturbation theory), using the level of theory equivalent to fourth-order Müller-Plesset perturbation theory [1]. The critical properties, thermodynamic properties and orthobaric densities based on them are found to be in very good agreement with experimental data.

**Keywords:** Gibbs ensemble Monte Carlo simulation, *ab initio* intermolecular potentials.

### I - INTRODUCTION

Computer simulations have become indispensable tools for studying pure fluids and fluid mixtures and for understanding macroscopic phenomena. The most importance in modeling a process involving fluids is vapor-liquid phase behaviour. This creates a need for accurate equilibrium data for multi-component systems and they can be applied for different chemical processes. One of the first attempts Nasrabad and Deiters predicted phase high-pressure vapor-liquid phase equilibria of noble-gas mixtures [1, 2] from the global simulations using the intermolecular potentials. Leonhard and Deiters used a 5-site Morse potential to represent the pair potential of nitrogen [3] and were able to predict vapour pressures and orthobaric densities. Naicker et al. developed the 3-site pair potentials for hydrogen chloride [4]; they predicted successfully the vapor-liquid phase equilibria of hydrogen chloride with GEMC (Gibbs Ensemble Monte Carlo

simulations [5]).

In this work we report the development of 3-site intermolecular pair potentials for nitrogen and oxygen from *ab initio* calculations SAPT and the use of them for the Gibbs ensemble Monte Carlo simulation [5] to find the vapor-liquid equilibrium data for systems N<sub>2</sub> and O<sub>2</sub>. The simulation results obtained by these pair potential functions are compared with experimental data and those from potential Lennard-Jones and Deiters equation of state [12].

### II - COMPUTATIONAL METHOD

#### 1. *Ab initio* potential functions

The potential energy surfaces of nitrogen and oxygen were constructed by selecting 945 configurations. *Ab initio* calculations were carried out on a uniform grid of angular orientations constructed by a permutation  $\alpha = 0 - 180^\circ$ ,  $\beta = 0 - 180^\circ$ ,  $\phi = 0 - 180^\circ$  with increments  $45^\circ$ , and center-of-gravity distances

$r = 2.8 - 15 \text{ \AA}$  with increment  $0.2 \text{ \AA}$ .

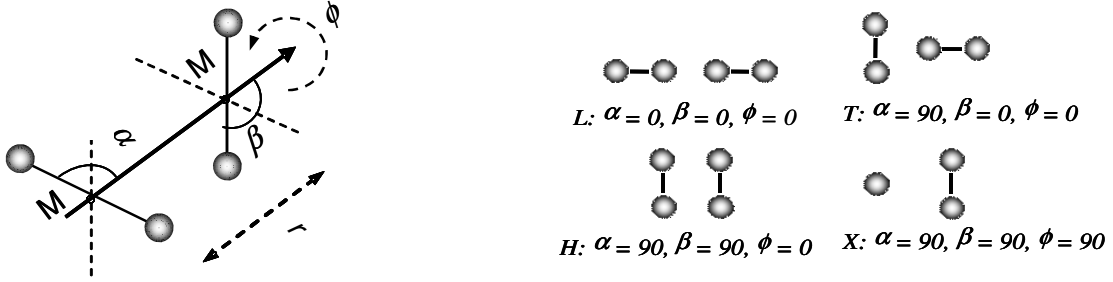


Figure 1: 3-site model of dimers  $N_2-N_2$  and  $O_2-O_2$  and special molecular orientations

The Morse-style pair potential proposed by Naiker [4] is used for  $N_2$  and  $O_2$ :

$$u = \sum_{i=1}^3 \sum_{j=1}^3 \left[ -\beta_{ij} \{1 - (1 - \exp[-\alpha_{ij}(r_{ij} - r_{\min}^{ij})])^2\} + f_{10}(\delta_{ij} r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (1)$$

With:  $f_{10}(\delta_{ij} r_{ij}) = 1 - e^{-\delta_{ij} r_{ij}} \sum_{k=0}^{10} \frac{(\delta_{ij} r_{ij})^k}{k!}$

where  $\beta_{ij}$  the well-depth parameter,  $\alpha_{ij}$  the potential well width parameter, and  $r_{\min}^{ij}$  the position of the potential energy well, for all the interactions between site  $i$  on molecule  $a$  and site  $j$  on molecule  $b$ ;  $f_{10}(\delta_{ij} r_{ij})$  the Tang-Toennies damping function [7].

In this work our new developed intermolecular pair potential in [6] is used for  $N_2$  and  $O_2$ :

$$u = \sum_{i=1}^3 \sum_{j=1}^3 \left[ D_{ij} e^{-\alpha_{ij} r_{ij}} + f_1(r_{ij}) \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (2)$$

With:  $f_1(r_{ij}) = (1 + e^{-2(\delta_{ij} r_{ij} - 2)})^{-15}$ , and  $f_2(r_{ij}) = 1 - e^{-\beta_{ij} r_{ij}}$

Where the  $r_{ij}$  site-site distances, the  $q_i, q_j$  electric charges of sites, and the  $C_n^{ij}$  dispersion coefficients; the leading dispersion term is always proportional to  $r$ .

The *ab initio* intermolecular energies were computed by symmetry-adapted perturbation theory SAPT proposed by Szalewicz and et al. [8]. For SAPT method the *ab initio* energy points are the sum of various contributions (dispersion, induction, exchange and electrostatics) to the interaction energy. These determined directly from the perturbed monomer wave functions, unlike the supermolecular approach, as shown in [6]. The highest level of theory used for this work is

equivalent to fourth-order Møller-Plesset perturbation theory.

All the optimal adjustable parameters of the potentials Eq. 1 and Eq. 2 were drawn out by nonlinear least-square fitting to the *ab initio* energy points. This fit process has to be carried out by two steps, as used in [6]. The global minima are coarsely located by means of the Genetic algorithm, and the parameters resulting from the Genetic algorithm are used as initial values for the Marquardt-Levenberg algorithm.

## 2. Second virial coefficients

The second virial coefficient is an important property for assessing two-body interactions, so it is a good way for testing any pair potential.

The second virial coefficient proposed by Gray and Gubbins [9], is defined as the sum of the contributions from the classical virial coefficient Eq. 4 and the first-order translational and rotational quantum corrections Eq. 3..

$$B_{QM}^1(T) = \frac{\hbar^2}{24(k_B T)^3} \left[ \frac{\langle F^2 \rangle_0}{2M_r} + \sum_{x,y,z} \frac{\langle T_\alpha^2 \rangle_0}{I_\alpha} \right] \quad (3)$$

Where  $\hbar$  planck's constant,  $M_r$  is the reduced mass of the system, and  $T_\alpha$  is the torque about the local molecular axis  $\alpha$  with moment of inertia  $I_\alpha$ . The notations  $\langle F^2 \rangle_0$  and  $\langle T_\alpha^2 \rangle_0$  represent integrations weighted with the zero-density pair distribution function.

The classical virial coefficient relates to the pair potential function:

$$B_{cl}^0 = -\frac{N_A}{4} \int_0^{2\pi} d\phi \int_0^\pi \sin\beta d\beta \int_0^\pi \sin\alpha d\alpha \int_0^\infty \left( \exp\left(-\frac{u(\alpha, \beta, \phi, r)}{k_B T}\right) - 1 \right) r^2 dr \quad (4)$$

Where  $u(\alpha, \beta, \phi, r)$  the pair potential function. A Monte Carlo integration was used for evaluating this 4D integral over the molecular orientation vectors  $r$ ,  $\alpha$ ,  $\beta$  and  $\phi$ .

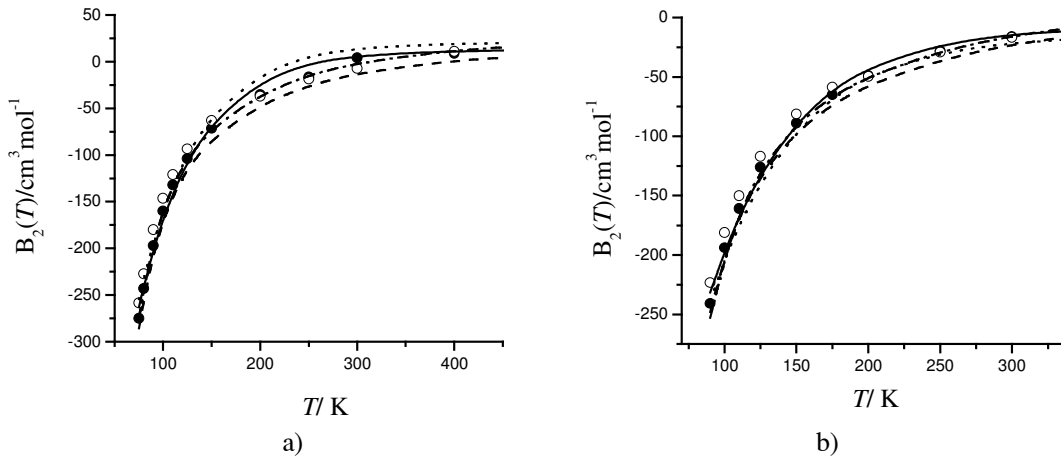


Figure 2: Second virial coefficient of pure fluid: a) nitrogen and b) oxygen; —, ----: *ab initio* pair potentials Eq. 1 and Eq. 2; ····, -·-·: first-order quantum correction based on Eq.1 and Eq.2 (this work); ○: Deiters equation of state EOS-D1 [12]; ●: experimental data [11].

## 3. Simulation runs

The *ab initio* pair potentials Eq. 1 and Eq. 2 were used in Gibbs ensemble Monte Carlo (GEMC) simulations to predict the vapor-liquid equilibria of pure fluids nitrogen and oxygen. The GEMC simulations were carried out in the

NVT ensemble (GEMC-NVT) with 512 molecules. The temperatures used for all the simulation runs were less than the critical points of pure fluids nitrogen and oxygen. The simulation equilibration between two phases required  $2.0 \times 10^5$  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  $1.0 \times 10^5$  cycles.

### III - RESULTS AND DISCUSSION

#### 1. Structural properties

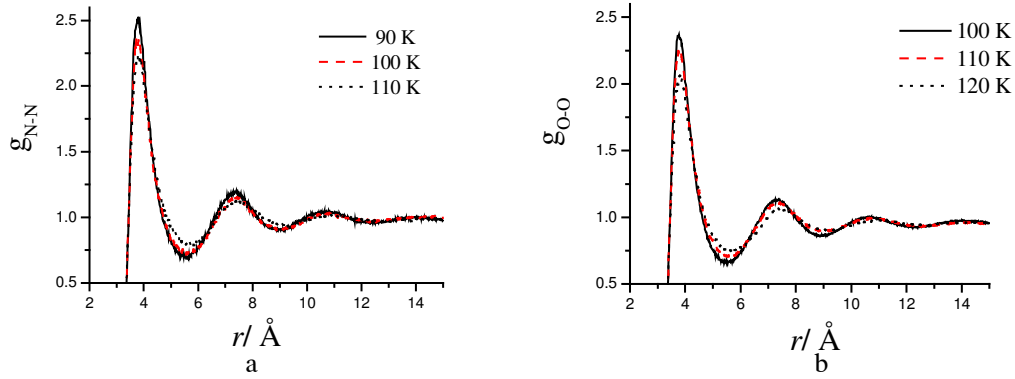


Figure 3: Temperature dependence: a) of  $g_{N-N}$  for nitrogen and b) of  $g_{O-O}$  for oxygen at different temperatures using simulation GEMC-NVT by using pair potential Eq.2

#### 2. Phase coexistence properties

The critical temperature  $T_c/K$  and density  $\rho_c/g.cm^{-3}$  of the pure fluids nitrogen and oxygen were derived from least-squares fits to the orthobaric densities using the relations of the rectilinear diameter law [10]:

$$\frac{\rho_1 - \rho_2}{2} = \rho_c + A(T_c - T) \quad (5)$$

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

Where  $\rho_l$  and  $\rho_v$  are the coexistence liquid density and vapor density,  $\beta$  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:

$$\log P = A - \frac{B}{T - C} \quad (6)$$

Where  $A$ ,  $B$  and  $C$  are Antoine constants.

In this simulation case the temperature dependence is shown by site-site pair distribution function  $g_r$ . Because of the 3-site model of dimers  $N_2-N_2$  and  $O_2-O_2$  were constructed with two sites placed on the atoms N and O, one site in the center of gravity M [8]. Consequently, the pair distribution functions also consisted of the interactions N-N, M-M and N-M for the nitrogen, and O-O, M-M and O-M for fluid oxygen. The structural properties of these fluids were shown in Figs 3a and 3b.

The relation between vapor pressure, heat of vaporization  $\Delta_{vap}H$  and temperature at the standard state  $P^0 = 0.101$  MPa is given by the Clausius-Clapeyron equation

$$\ln \frac{P}{P^0} = -\frac{\Delta_{vap}H}{R} \frac{1}{T} + \frac{\Delta_{vap}S}{R} \quad (7)$$

Here the slope and the intercept of  $\ln P$  are proportional to  $\Delta_{vap}H$  and  $\Delta_{vap}S$ .

The critical properties of the pure fluids nitrogen and oxygen could not be calculated directly from the simulation, but they could be obtained from the orthobaric densities of vapor-liquid equilibria by the least-square fit to the relations (5), as shown in table 1. The critical pressures of nitrogen and oxygen were calculated from the Antoine equation Eq. 6. The results agreed reasonable well with experimental data. The thermodynamic properties of these fluids are also shown in table 2.

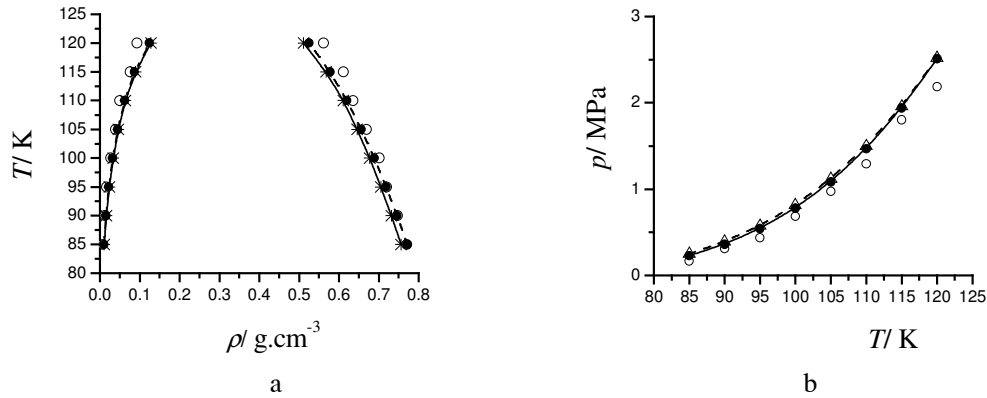


Figure 4: a) Vapor-liquid coexistence diagram of nitrogen; b) Vapor pressure of nitrogen; Symbols: •, experimental Data [13]; o, Deiters equation of state EOS-D1 [12]; \*, Lennard-Jones [14]; —, --- : *ab initio* pair potentials Eq. 1 and Eq. 2.

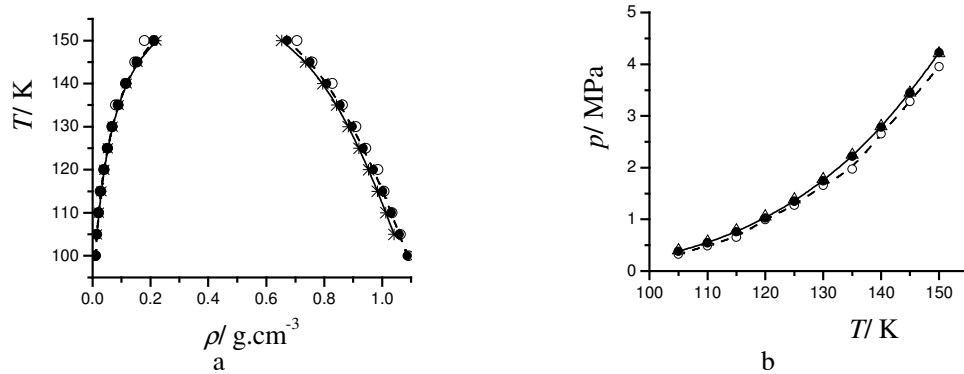


Figure 5: a) Vapor-liquid coexistence diagram of oxygen; b) Vapor pressure of oxygen; for an explanation see Fig. 4

Table 1: Critical properties of nitrogen and oxygen resulting from the GEMC-NVT simulation results using equation Eq. 1; EOS-D1: Deiters equation of state [12]; LJ: Lennard-Jones potential (6-12) [14]; Exp.: experimental values

Method	Nitrogen				Method	Oxygen			
	$T_c$ , K	$\rho_c$ , g.cm <sup>-3</sup>	$P_c$ , MPa	Ref.		$T_c$ , K	$\rho_c$ , g.cm <sup>-3</sup>	$P_c$ , MPa	Ref.
Eq. 1	131.102	0.315	3.431	this work	Eq. 1	157.324	0.437	5.192	this work
Eq. 2	129.572	0.310	3.389		Eq. 2	154.035	0.435	4.987	
LJ	130.034	0.317	3.481	[14]	LJ	156.271	0.423	6.693	[14]
EOS-D1	125.374	0.310	3.190	[12]	EOS-D1	153.520	0.429	4.970	[12]
Exp.	126.192	0.313	3.396	[13]	Exp.	154.581	0.436	5.043	[13]

Table 2: Enthalpy of vaporization  $\Delta_{\text{vap}}H$ , entropy of vaporization  $\Delta_{\text{vap}}S$  at  $P = 0.1013$  MPa for pure fluids nitrogen and oxygen predicted from simulation vapor pressures

Method	Nitrogen			Method	Oxygen		
	$\Delta_{\text{vap}}H$ , KJ mol <sup>-1</sup>	$\Delta_{\text{vap}}S$ , kJ.mol <sup>-1</sup> .K <sup>-1</sup>	Ref.		$\Delta_{\text{vap}}H$ , kJ mol <sup>-1</sup>	$\Delta_{\text{vap}}S$ , kJ.mol <sup>-1</sup> .K <sup>-1</sup>	Ref.
Eq. 1	6.025	0.079	this work	Eq. 1	7.090	0.081	this work
Eq. 2	5.659	0.071		Eq. 2	6.986	0.074	
LJ	6.199	0.077	[14]	LJ	7.231	0.079	[14]
EOS-D1	5.571	0.073	[12]	EOS-D1	6.837	0.076	[12]
Exp.	5.794	0.075	[13]	Exp.	6.993	0.078	[13]

The discrepancies between predicted results and experimental data are insignificant.

#### IV - CONCLUSION

The vapour-liquid coexisting phase and thermodynamic properties of the pure fluids oxygen and nitrogen were calculated successfully with the developed computer simulation program GEMC-NVT using 3-site intermolecular potentials Eq. 1 and Eq. 2 resulting from *ab initio* energies SAPT. The simulation results agree well with experimental data and those from the Lennard-Jones potential and the Deiters equation of state (EOS-D1).

**Acknowledgments:** *We would like to thank Prof. Dr. Szalewicz, Prof. Dr. A. K. Sum (University of Delaware, USA) and Dr. P. K. Naicker for providing the program SAPT2006 and for making available their computer programs.*

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