

# Calculation the thermodynamic properties of carbon monoxide gas using Monte Carlo simulation for adsorption researches

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## ABSTRACT

*The vapor-liquid equilibria of pure fluid carbon monoxide was predicted by Gibbs Ensemble Monte Carlo simulation method (GEMC) 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) [1]. These potentials were also used for prediction of thermodynamics properties of vapor-liquid equilibria by GEMC. The coexistence phase diagram and thermodynamic properties based on them are found to be in very good agreement with experimental data.*

**Keywords:** *Gibbs ensemble Monte Carlo simulation (GEMC), ab initio pair potentials, vapor - liquid equilibria*

## 1. INTRODUCTION

Computer simulations have become indispensable tools for studying pure fluids and fluid mixture [2]. One of the first attempts Nasrabad and Deiters predicted high-pressure vapour-liquid phase equilibria of noble-gas mixtures [3 - 4] from the global simulations using the intermolecular potentials. Leonhard and Deiters used a 5 - site Morse potential to represent the pair potential of nitrogen [5] and were able to predict vapour pressures and orthobaric densities successfully with GEMC [6]. The thermodynamic data of vapor - liquid equilibrium states need for adsorption researches.

Adsorption plays an important role in the physical chemistry processes occurring in the body, especially activated carbon, with a high adsorption capacity of many colorants, odors, impurities, ..., which are significant in life and in the pharmaceutical industry. In particular, ion exchange adsorption has very important applications in the processes of separating,

extracting or purifying products of natural origin. In addition, adsorption is also the basis for analytical methods by chromatographic techniques.

In this work we report the simulation results of the vapor - liquid equilibria for fluid carbon monoxide using Gibbs Ensemble Monte Carlo (GEMC) simulation techniques with our new 5 - site intermolecular pair potentials *ab initio* [7] resulting from quantum mechanical calculations of dimer CO-CO. The simulation results density, vapour pressure, enthalpy and entropy of vaporization are compared with experimental data.

## 2. COMPUTATIONAL DETAILS

### 2.1. Ab initio calculation

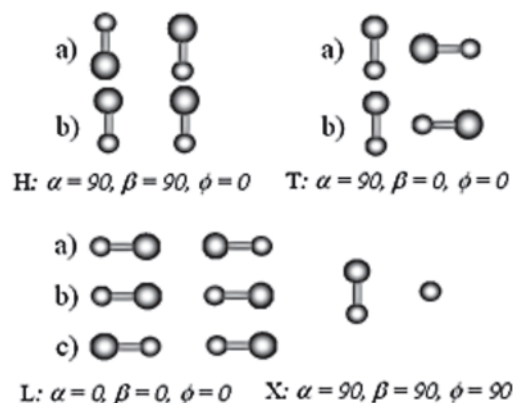
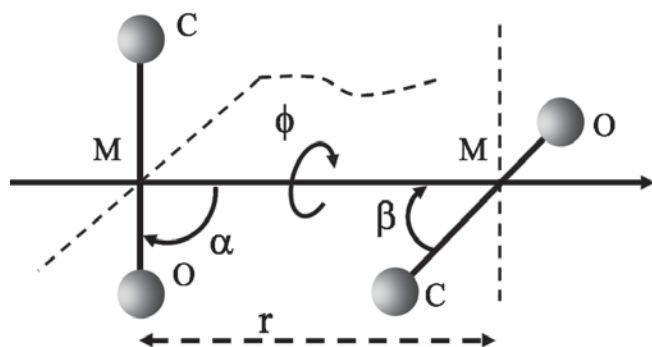
The *ab initio* potential energy surface of dimer CO-CO was constructed by selecting over 1,000 molecular configurations. *Ab initio*

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energy calculations were carried out on a uniform grid of angular orientations constructed by a permutation  $\alpha$  of 0 to 180°,  $\beta$  of 0 to 180°,  $\phi = 0 - 180^\circ$  with increments 45°,

and center-of-gravity distances  $r$  of 2.8 to 15 Å with increment 0.2 Å. The 5-site intermolecular models for this dimer were illustrated in **Figure 1**.



**Figure 1.** 5-site model of dimer CO-CO and special molecular orientations

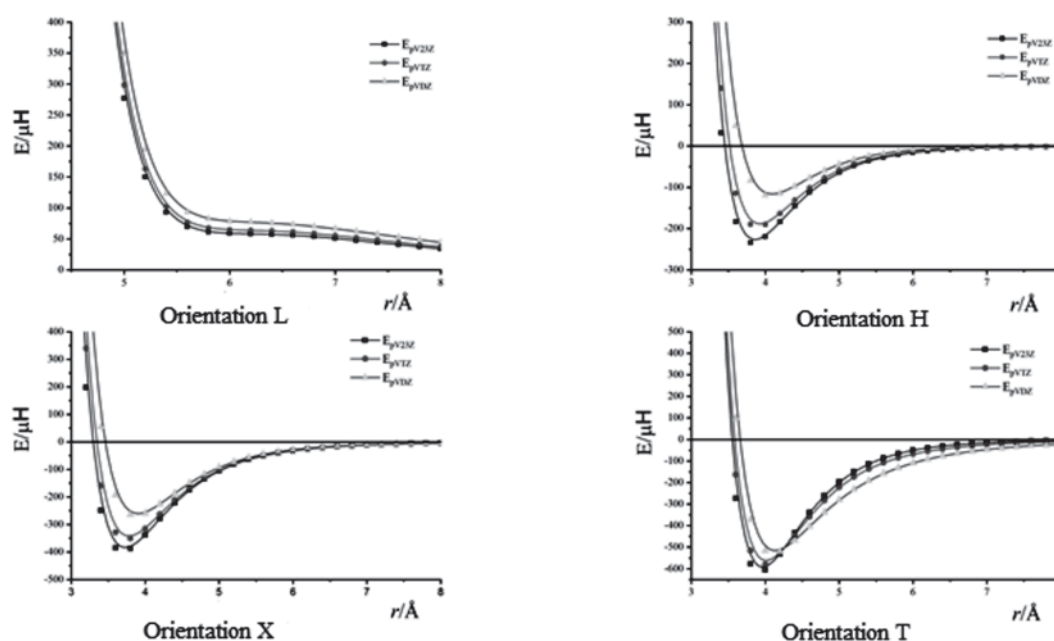
The theoretical level CCSD(T) and the correlation-consistent basis sets proposed by Dunning et al. [8] aug-cc-pVDZ for oxygen 10s5p2d/4s3p2d, carbon: 9s4p1d/3s2p1d and basis set aug-cc-pVTZ for oxygen: 12s6p3d2f/5s4p3d2f, carbon: 15s6p3d1f/9s5p3d1f were used. The *ab initio* energies were corrected for the basis set superposition error (BSSE) [9]:

$$\Delta E_{\text{int}} = E_{AB} - (E_A + E_B) \quad (1)$$

$$\Delta E(m) = \Delta E(\infty) + cm^{-3} \quad (2)$$

where  $E_{AB}$  denotes the total electronic energy of a

dimer AB,  $E_{Ab}$  the energy of a dimer consisting of an A atom and a B ghost atom (an atom without nucleus and electrons, but having its orbitals), and  $E_{aB}$  vice versa. With  $m = 2$  (for the aug-cc-pVDZ basis set) or 3 (for the aug-cc-pVTZ basis set), the complete basis set limit aug-cc-pV23Z was calculated by *ab initio* intermolecular energies  $\Delta E(m)$ . *Ab initio* calculations were carried out with the Gaussian03™ program package [1]. The potential energy surfaces of special orientations were constructed by *ab initio* intermolecular energies, as shown in **Figure 2**.



**Figure 2.** *Ab initio* potential surface of CO-CO dimer for special molecular orientations

## 2.2. *Ab initio* pair potentials

In this work two new 5 - site pair intermolecular potentials were developed from Lennard-Jones potential and Morse potential

for dimer CO-CO as [5 - 6, 10].

The *ab initio* Morse - style pair potential proposed by Naiker [10] is developed to use for dimer CO:

$$u = \sum_{i=1}^5 \sum_{j=1}^5 \left[ D_e^{ij} e^{-\alpha_{ij} r_{ij}} + f_n(r_{ij}) \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + f_1(r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (3)$$

$$\text{With } f_n(\delta_{ij} r_{ij}) = 1 - e^{-\delta_{ij} r_{ij}} \sum_{k=0}^n \frac{(\delta_{ij} r_{ij})^k}{k!}, \text{ and } f_1(r_{ij}) = 1 - e^{-\beta_{ij} r_{ij}}$$

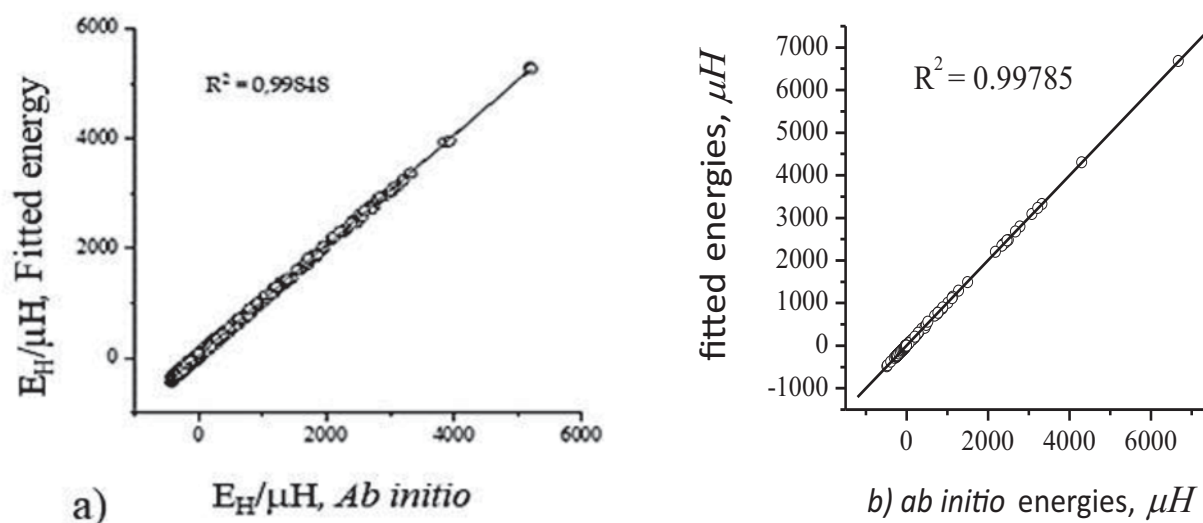
In this work the *ab initio* Lennard - Jones - style intermolecular pair potential is also constructed to apply for dimer CO-CO:

$$u = \sum_{i=1}^5 \sum_{j=1}^5 \left[ 4\epsilon_{ij} \left( \frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) + f_1(r_{ij}) \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (4)$$

$$\text{With } f_1(r_{ij}) = 1 - e^{-\beta_{ij} r_{ij}}$$

Where  $D_e^{ij}$  the well-depth parameter;  $\alpha_{ij}$  the potential well width parameter;  $\delta_{ij}, \beta_{ij}$  the position parameters of the potential energy well, for all the interactions between site  $i$  on molecule A and site  $j$  on molecule B;  $r_{ij}$  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  $r$ ;  $f_n(\delta_{ij} r_{ij})$  and  $f_1(r_{ij})$  the Tang - Toennies damping function [8].

All the optimal adjustable parameters of the potentials Eq.3 and Eq.4 were drawn out by nonlinear least - square fitting to the *ab initio* energy points, as in **Figure 3**. This fit process has to be carried out by two steps, as used in [7]. The global minima are coarsely located by means of the differential evolution algorithm, and the parameters resulting from this algorithm are used as initial values for the Marquardt - Levenberg algorithm.



**Figure 3.** Correlation of *ab initio* vs. fitted energies resulting from potential: a) Eq.3 and b) Eq.4.

### 2.3. Simulation runs

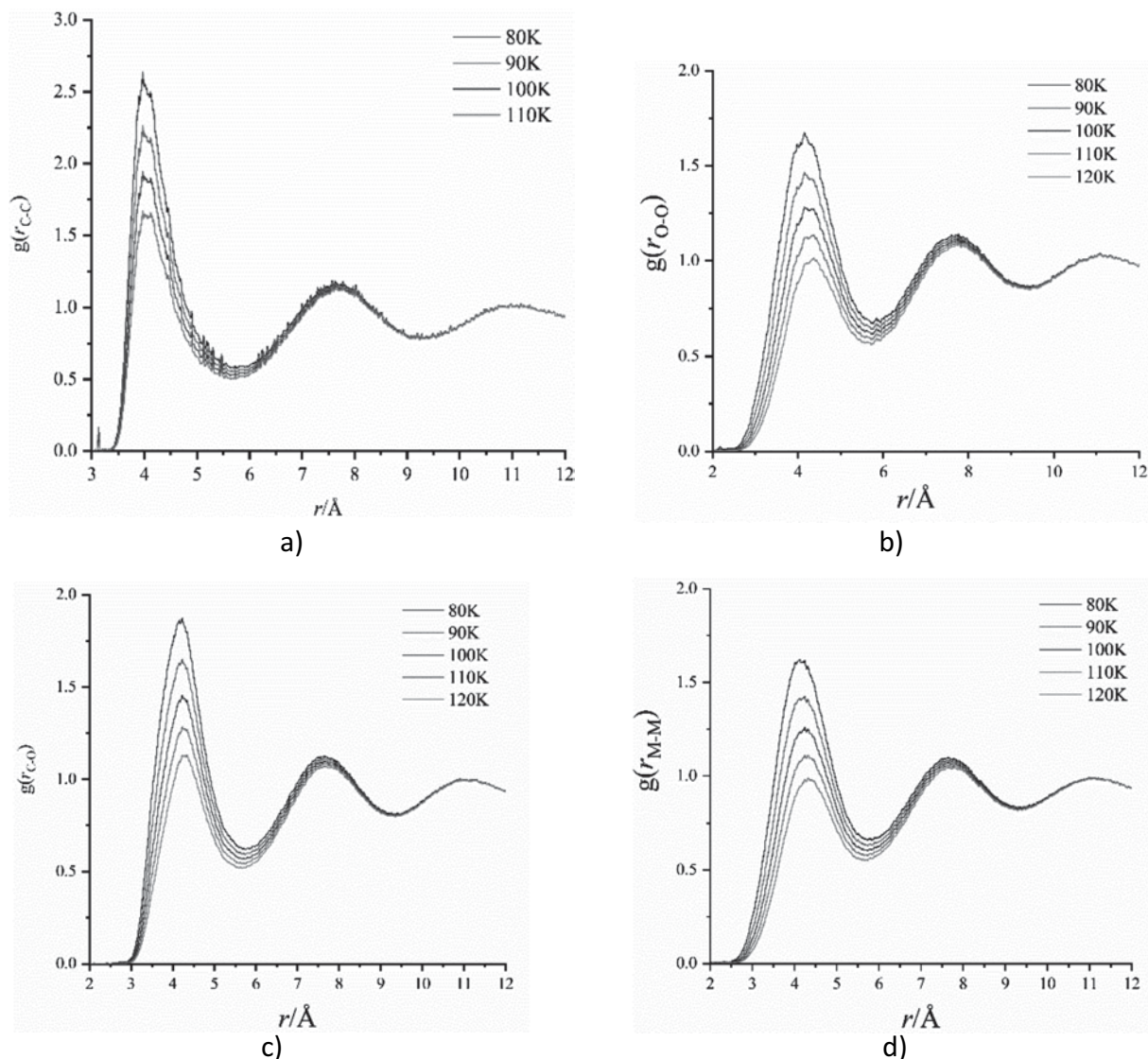
The *ab initio* pair potentials Eq.3 and Eq.4 were used in Gibbs ensemble Monte Carlo (GEMC) simulations to predict the vapor-liquid equilibria of pure fluid carbon monoxide. The GEMC simulations in this study were performed under conditions of number of particles (N), volume (V) and temperature (T) constant (GEMC - NVT) with  $N = 512$  molecules [2, 14]. The temperatures used for all the simulation runs were less than the critical points of pure fluid carbon monoxide. 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 1,000 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.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Structural properties

In this simulation case the temperature dependence is shown by site-site pair distribution function  $g_r$ . Because of the 5-site model of dimer CO-CO was constructed with two sites placed on the atoms C and O, one site in the center of gravity M and A placed between M and C or O [9]. Consequently, the pair distribution functions also consisted of the interaction C-C, O-O, M-M, A-A, A-C and O-M for fluid carbon monoxide. The structural properties of this fluid were shown in **Figure 4**.

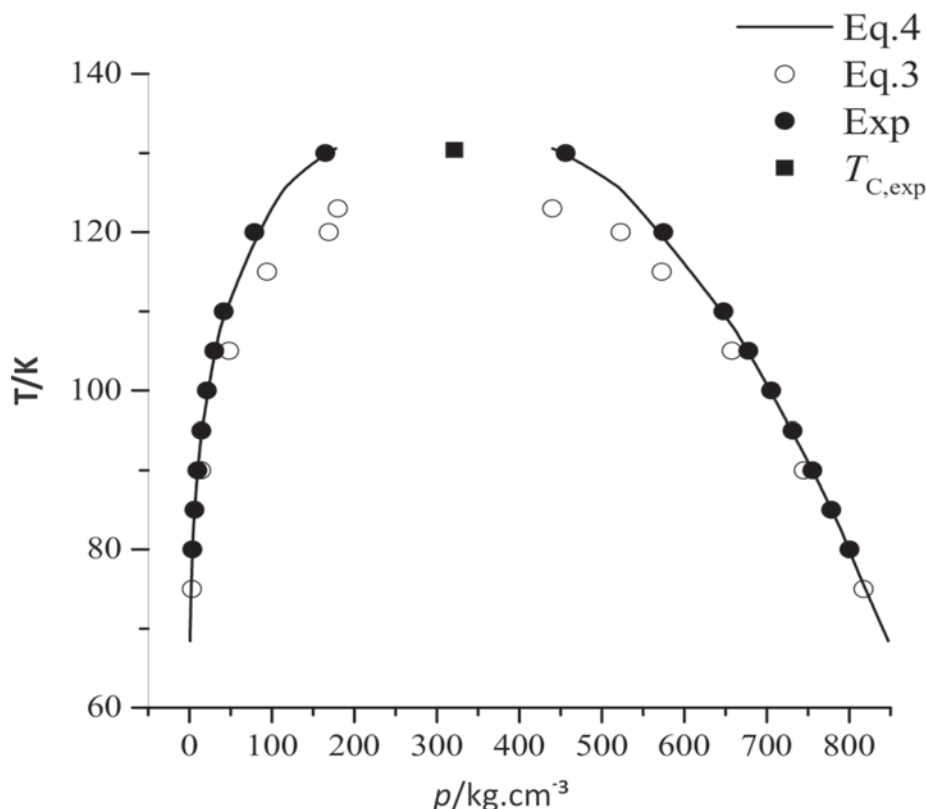


**Figure 4.** Dependence of the distribution functions  $g(r_{C-C})$ ,  $g(r_{O-O})$ ,  $g(r_{C-O})$  and  $g(r_{M-M})$  on temperature during GEMC-NVT simulation on CO

### 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 carbon monoxide is illustrated in Figure 5 that was derived from least - squares fits to the

orthobaric densities using the relations Eq.5 of the rectilinear diameter law [2]. The orthobaric diagrams of them at various temperatures resulting from the intermolecular potentials Eq.3 and Eq.4 were pointed out in **Figure 5**.



**Figure 5.** Vapor-liquid coexistence diagram of carbon monoxide; experimental data and critical temperature [13]

The experimental - critical densities and temperatures of pure fluid carbon monoxide were also shown in there, respectively.

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

$$\rho_l - \rho_v = B(T - T_c)^\beta$$

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 properties of the pure fluid carbon monoxide 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 Eq.5.

The relation between vapor pressure, heat of vaporization  $\Delta H_v$  and temperature is given by the Clausius - Clapeyron equation.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_v}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

For the standard state  $P^0 = 0.101$  MPa this relation is rewritten as

$$\ln \frac{P}{P^0} = -\frac{\Delta H_v}{R} \frac{1}{T} + \frac{\Delta S_v}{R} \quad (7)$$

Here the slope and the intercept of  $\ln P$  are proportional to  $\Delta H_v$  and  $\Delta S_v$ .

The vapour-liquid coexisting phase and thermodynamic properties (such as  $\rho_v$ ,  $\rho_l$ ,  $H_v$ ,  $H_l$ ,  $P_v$ ,  $\Delta H_v$ ,  $\Delta S_v$ ) of the pure fluid carbon monoxide that were calculated from Eq.6 and Eq.7 are also shown in **Table 1** and **Table 2**. The results agreed reasonable well with experimental data.



**Table 1.** Thermodynamic properties of vapor-liquid equilibria of carbon monoxide resulting from the GEMC - NVT simulation results using equations Eq.3 and Eq.4; Exp.: experimental values

T/K	$\rho_v/\text{g.cm}^{-3}$	Exp.	$\rho_l/\text{g.cm}^{-3}$	Exp.	$H_v/\text{J.mol}^{-1}$	$H_l/\text{J.mol}^{-1}$
80	0.006	0.005	0.792	0.791	560.62	-5,276.30
85	0.010	0.008	0.766	0.769	518.79	-5,083.20
90	0.017	0.014	0.740	0.754	210.26	-5,168.33
100	0.040	0.037	0.687	0.700	-189.93	-5,002.35
110	0.087	0.082	0.625	0.653	-959.24	-4,818.83
120	0.180	0.116	0.515	0.566	-879.59	-3,160.00

**Table 2.** Thermodynamic properties of carbon monoxide resulting from the GEMC-NVT simulation results using equations Eq.3 and Eq.4; Exp.: experimental values

T/K	$P_v/\text{bar}$	Exp.	$\Delta H_v/\text{J.mol}^{-1}$	Exp.	$\Delta S_v/\text{J.mol}^{-1}.\text{K}^{-1}$
80	1.021	0.811	5,836.918	6,038	72.961
85	1.631	1.013	5,601.989	5,719	65.906
90	2.536	2.026	5,378.592	5,298	59.762
100	5.726	6.079	4,812.418	4,965	48.124
110	11.960	10.132	3,859.594	4,304	35.087
120	23.430	20.264	2,280.411	3,741	19.003

The discrepancies between predicted results and experimental data are insignificant

#### 4. CONCLUSION

We conclude that our new *ab initio* inter-molecular Lennard - Jones and Morse potentials developed for the dimer CO-CO is reliable. Therefore the parameters obtained from the fitting of the potential functions are used to simulate GEMC - NVT. The vapour-liquid coexisting phase and thermodynamic

properties of the pure fluid carbon monoxide were calculated successfully with the developed computer simulation program GEMC-NVT using 5 - site intermolecular potential functions Eq.3 and Eq.4 resulting from *ab initio* energy calculations. The simulation results agree well with experimental data.

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**REFERENCES**

- [1] C. G. Gray, K.E. Gubbins, "Theory of Molecular Fluids," vol. 1: Fundamentals. *Oxford University Press*, Oxford, (1984) 230-350.
- [2] M. P. Allen, D. J. Tildesley, "Computer Simulation of Liquids.," *Clarendon Press*, Oxford, (1991) 210-300.
- [3] A. E. Nasrabad, U. K. Deiters, "Prediction of thermodynamic properties of krypton by Monte Carlo simulation using *ab initio* interaction potentials." *J. Chem. Phys.* 119, (2003) 947–952.
- [4] A. E. Nasrabad, R. Laghaei, U. K. Deiters, "Prediction of the thermophysical properties of pure neon, pure argon, and the binary mixtures neon-argon and argon-krypton by Monte Carlo simulation using *ab initio* potentials." *J. Chem. Phys.* 121, (2004) 6423–6434.
- [5] K. Leonhard, U. K. Deiters, "Monte Carlo simulations of nitrogen using an *ab initio* potential." *Mol. Phys.* 100, (2002) 2571–2585.
- [6] A. Z. Panagiotopoulos, "Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble.," *Mol. Phys.*, 61, (1987) 813-826.
- [7] Pham V. T., U. K. Deiters, "Ab initio calculation of the intermolecular potential and prediction of second virial coefficients for dimer  $H_2-H_2$ ," *Journal of Chemistry*, vol. 5, No. 5, (2007) P. 656-660.
- [8] K. T. Tang, J. P. Toennies, "An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients.," *J. Chem. Phys.*, 80, (1984) 3726-3741.
- [9] S. Rybak, B. Jeziorski, K. Szalewicz, "Symmetry - Adapted Perturbation Theory of Intermolecular Interactions.  $H_2O$  and  $HF$  Dimers," *J. Chem. Phys.* 95, (1991) 6576-6601.
- [10] P. K. Naicker, A. K. Sum, S. I. Sandler, "Ab initio pair potential and phase equilibria predictions for hydrogen chloride.," *J. Chem. Phys.*, 118, (2003) 4086-4093.
- [11] J. H. Dymond, E. B. Smith, "The Virial Coefficients of Pure Gases and Mixtures." *Clarendon Press*, Oxford, (1980) 100-300.
- [12] U. K. Deiters, ThermoC project homepage: <http://thermoc.uni-koeln.de/index.html>
- [13] Database of National Institute of Standards and Technology NIST, <http://webbook.nist.gov/>
- [14] A. Z. Panagiotopoulos, P. Baranello, <http://kea.princeton.edu/ppe/old/>

## Tính toán các tính chất nhiệt động của khí CO bằng mô phỏng Monte Carlo cho các nghiên cứu về hấp phụ

Nguyễn Thành Được

**TÓM TẮT**

Cân bằng lỏng - hơi của chất lỏng CO được dự đoán bằng kỹ thuật mô phỏng Monte Carlo sử dụng cặp hàm thế *ab initio* tương tác 5 - vị trí. Cặp hàm thế *ab initio* được tính toán từ lý thuyết bó cặp, sử dụng ở mức CCSD(T) và các hàm cơ sở tương quan thích hợp của Dunning aug-cc-pV $m$ Z ( $m = 2, 3$ ) [1]. Những hàm thế này được dùng để dự đoán các tính chất nhiệt động của cân bằng lỏng - hơi bằng kỹ thuật mô

*phổ Monte Carlo. Giảm đồ pha cân bằng và các tính chất nhiệt động của chúng được tính toán so với các giá trị thực nghiệm đều đáng tin cậy.*

**Từ khóa:** mô phỏng toàn cục Monte Carlo, hàm thế cặp *ab initio*, cân bằng lỏng - hơi

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