

# MONTE CARLO SIMULATION OF SUPERCRITICAL FLUIDS. A PARTIAL MOLAR VOLUME STUDY

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Partial molar volumes for methane in supercritical carbon dioxide were computed running Monte Carlo simulations (MCS) in the canonical (NVT) ensemble at  $T_r=1.02$  critical isotherm. Simulation radial distribution functions are used to examine the structure of the solution at the molecular level. The results are analysed in terms of Kirkwood-Buff theory. Partial molar volumes are found to be strongly dependent on pressure reaching their maximum value at  $p \approx 7.9$  MPa, which is in good agreement with theory. The addition of a methane molecule into supercritical carbon dioxide gives positive partial molar volumes. The used method of prediction- Kirkwood-Buff formalism combined with molecular simulations - gives reasonable accuracy establishing it as a method of choice for further predictions at supercritical conditions.

## 1 INTRODUCTION

Partial molar volume is one of the important properties of a fluid, which gives very strong indication of the unusual behaviour at supercritical conditions. Furthermore, being able to predict partial molar volumes of components in supercritical solutions - and therewith the activation volume of chemical reactions- should lead to prediction of the pressure dependence of chemical reactions. Over the years, many experimental data on partial molar volumes have been collected for a large variety of solutes in different solvents [1-4]. So far the main focus of supercritical research on solution thermodynamics regarding property predictions is the use of equations of states (EoS). However, they fail at so-called 'difficult systems', binary mixtures of molecules with a large difference in size as well as systems in the vicinity of their critical point. The combination of both of the above makes the applicability of EoS even more problematic. In that case, special binary interaction parameters have to be introduced to correct deviations from classical mixing rules in order to improve accuracy.

Molecular simulation techniques should bring an improved understanding of fluid structure and molecular interactions between various components in supercritical fluid mixtures. They allow access to these 'difficult systems' without any additional scaling as a lot of parameters, like different size or shape of the molecules, are implicitly taken into account in the model. Moreover, they give us an insight to the systems on an atomic scale, which can be used to establish a relationship between intermolecular potential and thermodynamic behaviour. When solutes are introduced into supercritical fluids, substantial solvent density enhancement (clustering) or depletion (cavitation) is often observed around solute molecules. Debenedetti and co-workers identified three solute behaviours: repulsive, weakly attractive, and attractive [5]. Zhang et al. [3] reported new data that the partial molar volumes of the solutes in dilute supercritical solution have positive value. The mixture of methane in supercritical carbon dioxide at infinite dilution is one of them and belongs to the mixtures with repulsive behaviour.

Molecular dynamics and Monte Carlo (MC) simulation have been used for estimation of properties of supercritical fluids in the past decade [6-9]. Particle-based simulations are an ideal tool to investigate SCF systems in microscopic detail.

## 2 COMPUTATIONALLY METHODOLOGY

### 2.1 Theory

For a solute (u) in solvent (v), the partial molar volume is defined as

$$\bar{V}_u = \left( \frac{\partial V}{\partial n_u} \right)_{p,T,n_v} \quad (1.1)$$

with  $n_u$  and  $n_v$  being the numbers of moles of the solute and solvent, respectively. At infinite dilution  $\bar{V}_u^\infty = \lim_{n_u \rightarrow 0} (\partial/\partial n_u)_{p,T,n_v} \approx V(n_u=1, n_u, T, P) - V(n_u=0, n_u, T, P)$ , so  $\bar{V}_u^\infty$  can be computed in isothermal-isobaric ensemble (NPT) from Monte Carlo simulations [10]. Partial molar volume studies have been reported on this method [1] for naphthalene carbon dioxide mixture near the critical point. An alternative approach is to use the Kirkwood-Buff (KB) fluctuation theory [9, 10]. In this formalism, the partial molar volume at infinite dilution can be calculated as

$$\rho \bar{V}_u^\infty = 1 - \rho (G_{uv}^\infty - G_{vv}^o) \quad (1.2)$$

where  $G_{uv}$  and  $G_{vv}$  are solute-solvent and solvent-solvent fluctuation integral, respectively. The subscript u refers to the solute and v to the solvent. The superscript o and  $\infty$  refer to the pure solvent or infinitely dilute co solvent, respectively. These fluctuation integrals are a function of pair correlation functions  $g_{ij}(r)$ :

$$G_{ij} = 4\pi \int_0^\infty [g_{ij}(r) - 1] r^2 dr \quad (1.3)$$

The KB theory relates fluctuations in particle densities in the grand canonical ensemble to thermodynamic properties of mixtures. The pair correlation function or radial distribution function (RDF) calculated through Monte Carlo simulations in canonical ensemble. The values of  $G_{uv}^\infty$  and  $G_{vv}^\infty$  can be obtained from the RDFs between cosolvent in pure solvent from a single cosolvent in pure solvent and between a pair of solvent molecules in a pure solvent. The isothermal compressibility can be calculated from radial distribution functions through the equation

$$\rho_v RT \kappa_T = 1 + \rho_v G_{vv}^o \quad (1.4)$$

For our study, methane has been dissolved in the supercritical carbon dioxide in order to observe the effect made by solute over solvent at infinite dilution. And this effect is analyzed using the partial molar volume of solute in solvent. Only 1 molecules of CH<sub>4</sub> is dissolved in 999 molecules of CO<sub>2</sub>, in order to obtain same specifications of 0.1 mol % of solute in solvent that has been used by Zhang et al. [3].

### 2.2 Simulation

The standard canonical ensemble (NVT) Monte Carlo (MC) simulations are carried out in this work using the Metropolis algorithm in order to estimate the RDF of the system as a function

of pressure at temperature  $T=308.15$ . In any MC calculation, the spherical cut-off length was set to be one-half of the box length. The long-range corrections were made for the internal energy by assuming that the radial distribution function  $g(r) \approx 1$  for  $r \geq r_c$ . For this study, we used the molecular model for  $\text{CO}_2$  developed by Harris and Yung [11] and is referred to as EPM2 model. The potential model used for methane was Optimized Potential for Liquid Simulations (OPLS-AA) proposed by Jorgensen et al [12]. The interaction between two molecules I and J is assumed to be given by the sum of site-site terms of the Lennard-Jones plus Coulomb form

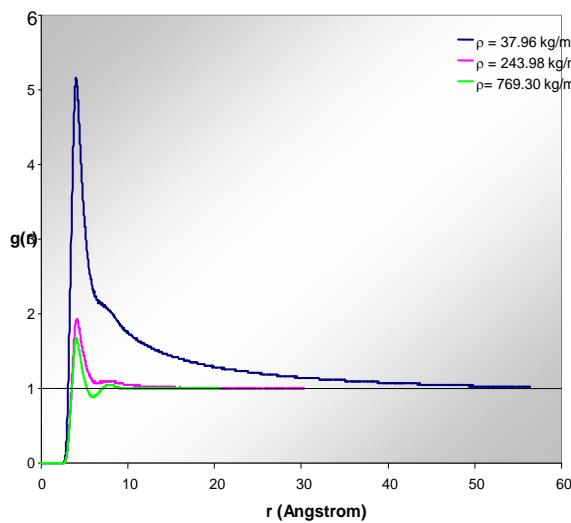
$$U = \sum_{i \in I} \sum_{j \in J} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1.5)$$

where  $\epsilon_0=8.8541910^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2}$  is the dielectric constant of the vacuum,  $q_i$  is the charge on site  $i$  of the molecule I,  $r_{ij}$  is the distance between sites  $i$  and  $j$ , and  $\sigma_{ij}$  and  $\epsilon_{ij}$  are Lennard-Jones interaction parameters between sites  $i$  and  $j$  located at molecules I and J. For the Lennard-Jones interactions between unlike atoms, the Lorentz-Berhelot combining rules were used. In each run, more than  $10^6$  Monte Carlo configurations were generated to reach equilibrium and the structural and thermodynamic properties were obtained from the following  $20 \times 10^6$  MC moves

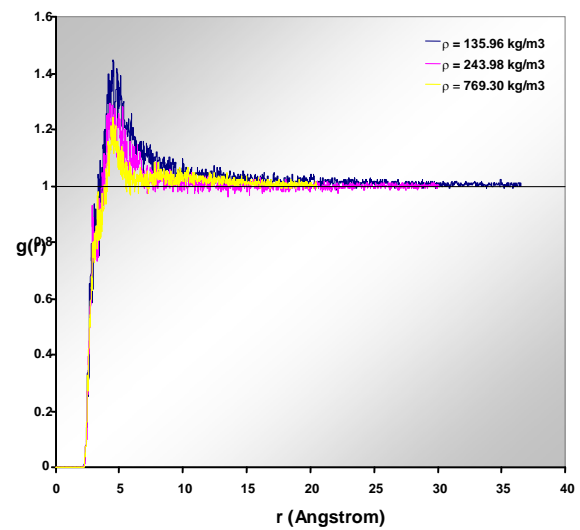
### 3 RESULTS

#### 3.1 Structural properties

Figures 1-3 show the solute- solvent and solvent-solvent radial distribution functions for  $\text{CO}_2$ - $\text{CH}_4$  and  $\text{CO}_2$ - $\text{CO}_2$  pairs. The correlation functions were determined using the centre of each species, the carbon atom. A sampling from the distribution of local-environment specific pair correlation functions for  $T_c = 308.15$  K over the densities ranging from  $37.96 \text{ kg/m}^3$  to  $769.3 \text{ kg/m}^3$  (critical density of  $\text{CO}_2$  is  $468 \text{ kg/m}^3$ ) is shown in the Figure 1, while Figure 2 corresponds to the solute-centred functions from the infinitely dilute SCF solution. We sampled the radial distribution function every 1000 configurations during Monte Carlo simulations.



**Figure 1. Carbon dioxide-carbon dioxide radial distribution function at  $T_r=1.02$  and  $\rho_r=0.08, 0.52, 1.64$**

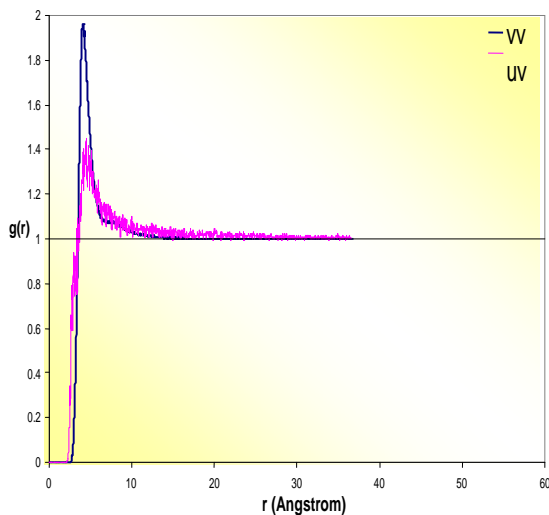


**Figure 2. Carbon dioxide-methane radial distribution function at  $T_r=1.02$  and  $\rho_r=0.29, 0.52, 1.64$**

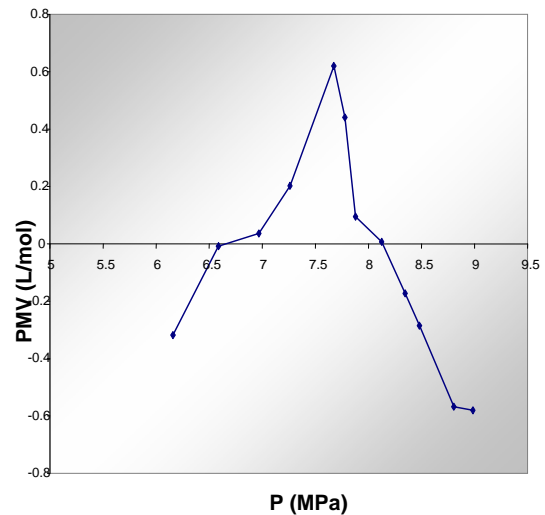
The choppy appearance of the solute-solvent radial distribution function is common and has been observed in other infinite dilute solute mixtures simulations [13]. The figures show that the radial distributions functions exhibit a clear difference at subcritical and supercritical densities

The peak height decreases with increasing density and a second shell appears which is in agreement with theory [14]. As we can see from the two figures the trend of the RDF for carbon dioxide is strongly dependent on carbon dioxide bulk density compare to carbon dioxide methane interaction. Also the height of the peaks and the contrasting trends demonstrate that the strengths of methane-carbon dioxide interactions relatively to carbon dioxide-carbon dioxide interactions are lower. When we compare the RDFs of solute-solvent and solvent-solvent in the same graph (Fig. 3) it is obvious that the number  $N_{ex}$ , which gives the amount of excess molecules around a solute molecule is negative.

$$N_{ex} = \rho_v (G_{uv}^{\infty} - G_{vv}^o) \quad (1.6)$$



**Figure 3. Comparison of RDFs of  $\text{CO}_2\text{-CO}_2$  (vv) and  $\text{CH}_4\text{-CO}_2$  (uv)**



**Figure 4. Calculated partial molar volumes for  $\text{CH}_4$  in supercritical  $\text{CO}_2$  at infinite dilution ( $T_r=1.02$ )**

The negative of value of  $N_{ex}$  indicates that there is a depletion of carbon dioxide molecules around the methane molecule. According to the classification of Debenedetti this is a repulsive mixture and should give positives values of partial molar volumes.

### 3.2 Partial Molar Volumes

Figure 4 shows the solute partial molar volumes versus pressure. MCS predicts positive partial molar volumes as found also in the experiments of Zhang et al. [3]. Furthermore, as the pressure approaches the critical value ( $p \approx 7.9$  MPa), PMV reaches a maximum that is in excellent agreement with theory. For a single component system there is a direct relationship between the average excess number  $\rho G_{vv}$  and the fluid's compressibility. The partial molar volume of methane in carbon dioxide reflects the compressible nature of carbon dioxide. The behaviour of PMV follows this of isothermal compressibility differing only at its magnitude. However, our calculated values are about a factor of two in magnitude smaller than the

reported experimental values. The cause of this discrepancy, albeit not dramatic, is currently investigated. Discrepancies of the same magnitude have also been observed at similar works [2].

#### **4 CONCLUSION AND FUTURE WORK**

In this work, we have successfully employed Monte-Carlo Simulation using the KB theory to study the behaviour of methane in carbon dioxide at infinite dilution. The computational method is not limited to Monte Carlo simulation. Molecular Dynamics is equally applicable, since only radial distribution functions are required. The purpose of the present study was to bring together available data of partial molar volumes at supercritical solutions with the potential of MCS. However, further work has to be done to improve the outcome of our method and to test with Molecular Dynamics simulations. Furthermore, a systematic study of the dependency of the system upon various simulation parameters (e.g. number of molecules-different techniques long range corrections-sampling) has to be carried out in order to improve the accuracy of the method. Overall, the simulation results for partial volumes agree reasonably well with experimental and theoretical studies, giving confidence for using it for structural analysis.

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