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1        **Excess volume, isothermal compressibility, isentropic compressibility and speed of**  
2        **sound of carbon dioxide + n-heptane binary mixture under pressure up to 70 MPa.**

3        **II. Molecular Simulations**

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13        **Abstract**

14        Molecular simulations have been performed in this work to provide a microscopic  
15        understanding of the experimental results of asymmetric supercritical binary mixtures of carbon  
16        dioxide and n-heptane published in the first article of the series [Bazile *et al.* J. Supercrit. Fluids  
17        140, 218 (2018)]. Interestingly, molecular simulations results compared well with experimental  
18        data on density, isothermal compressibility, speed of sound, isentropic compressibility and the  
19        corresponding excess properties. In addition, using Kirkwood-Buff theory, computed partial  
20        molar volumes are found to be consistent with those obtained indirectly from experimental data.  
21        In particular, the negative value of partial molar volume of n-heptane at infinite dilution close  
22        to CO<sub>2</sub> critical conditions is well captured, confirming the occurrence of a clustering  
23        phenomenon at such conditions. Last, computed properties of the cluster indicates a weak  
24        cluster with a radius of about 3 nm and a residence time of the CO<sub>2</sub> molecules in the cluster of  
25        about 25 ps.

26        **Keywords:** Thermophysical properties, Carbon Dioxide, Clusters, Asymmetric mixture,  
27        Molecular Simulations, Kirkwood-Buff Theory.

## 31 I. Introduction

32 In the first article of the series [1], an experimental investigation of volumetric and  
33 acoustic properties of a simple proxy to carbon dioxide enhanced oil recovery systems  
34 consisting of a binary mixture of carbon dioxide + n-heptane (nC<sub>7</sub>) has been presented. The  
35 measurements were performed for two isotherms (303.35 and 313.25 K) at pressures from 10  
36 to 70 MPa, i.e. including thermodynamic states in the vicinity of the CO<sub>2</sub> critical point. The  
37 experimental results highlighted the highly non-ideal behavior of the mixture in conditions  
38 close to the CO<sub>2</sub> critical point. In particular, the partial molar volume of n-heptane at infinite  
39 dilution, that was computed by fitting the molar volume data at fixed pressure and temperature,  
40 was found to be noticeably negative close to the critical point of CO<sub>2</sub>. However, because of a  
41 lack of data due to experimental limitations [1], the molar volume data used in the fitting process  
42 was not containing the values for mole fractions of nC<sub>7</sub> ranging from 0.00 to 0.10 where the  
43 molar volume significantly varies with mole fraction. This may have led to inaccurate  
44 determination of the partial molar volume as pointed out by various authors [2-3]. Therefore,  
45 and this is one goal of this work, it would be relevant to propose an alternative to compute the  
46 partial molar volume of such systems.

47 The negative value of the nC<sub>7</sub> partial molar volume at infinite dilution was attributed to  
48 a clustering phenomenon occurring in the mixture [4-9]. This phenomenon, usually interpreted  
49 as the organization of solvent molecules (here CO<sub>2</sub>) in “cluster” around the solute (here nC<sub>7</sub>)  
50 molecules, corresponds to an augmentation of the solvent density around solute molecule [8-  
51 9]. To quantify the clustering phenomenon, a quantity, called “cluster size”, could be estimated  
52 from the partial molar volumes [7]. This is what has been done in our previous experimental  
53 work [1], obtaining a value of the cluster size of about 8 CO<sub>2</sub> molecules at an experimental  
54 condition close to the CO<sub>2</sub> critical point ( $T=313\text{K}$  and  $P=10.11\text{MPa}$ ). However, the exact  
55 microscopic nature of the clustering effect and the definition of the “cluster size” has not, to the  
56 best of our knowledge, been explored for molecular fluids such as those studied here [1]. This  
57 is the main goal of the proposed study.

58 Molecular simulation has shown to be a useful tool to provide microscopic insights on  
59 fluid mixtures at the molecular level [10-13]. Among others, this tool has been used to elucidate  
60 microscopic characteristics of clustering in supercritical solutions [14-16]. In addition,  
61 molecular simulation combined with the fluctuation theory allows a direct computation of  
62 thermodynamic derivative properties such as isothermal compressibility and partial molar  
63 volumes, whereas, experimentally, these quantities are usually deduced indirectly from a fitting  
64 procedure on density data. [12, 17-21]. Furthermore, with progresses in the definition of the

force fields used to describe the molecular interactions, molecular simulations are now able to predict thermodynamic properties of fluids in good agreement with the experiments [22-27]. Thus, molecular simulation is fully adapted for the purposes of this work which are to complement experimental data and to provide a microscopic interpretation of the results obtained in [1], in particular those related to the clustering effect.

The article is structured as follows. In Sect. II, details on the molecular simulations are provided. Methods used to compute the thermodynamic properties are introduced in Sect. III. Simulation results on the thermodynamic properties and the microscopic analysis of CO<sub>2</sub> clusters are presented and discussed in Sect. IV. Finally, the main outcomes of this study are summarized in Sect. V, which forms the conclusion.

## II. Molecular Modeling and Simulations

### 2.1. Molecular Modeling

All the molecules of carbon dioxide and n-heptane binary mixture have been modeled by a Mie Chain Coarse Grained (MCCG) force field developed in [27], following the ideas proposed by Mejia *et al.* [28]. This coarse grained force field has been shown to successfully predict the thermophysical properties of these kind of components [27, 29-31] with a reasonable computational cost as it is usually the case with coarse grained force fields [32-33].

The molecular representation with MCCG consists in using homo-nuclear chains composed of  $N$  freely jointed spheres in which two adjacent particles in a chain are linked by a bond with a constant length. Interactions between two non-bonded spheres  $i$  and  $j$  are described by the Mie  $\lambda$ -6 potential [34]:

$$u_{Mie}(r_{ij}) = \left(\frac{\lambda_{ij}}{\lambda_{ij}-6}\right) \left(\frac{\lambda_{ij}}{6}\right)^{6/(\lambda_{ij}-6)} \varepsilon_{ij} \left[ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{\lambda_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right] \quad (1)$$

where  $\varepsilon_{ij}$ ,  $\sigma_{ij}$ ,  $\lambda_{ij}$  and  $r_{ij}$ , are respectively the potential well depth, the collision diameter, the exponent characterizing the repulsive interactions between non-bonded spheres and the distance between two spheres. The MCCG parameters used for both carbon dioxide and n-heptane are reported in Table I. The bond length is fixed to be equal to  $\sigma_{ij}$ .

**Table I.** Mie Chain Coarse Grained (MCCG) parameters of Carbon dioxide and n-heptane [27].

Molecules	$N$	$\sigma_{ii}$ (Å)	$\varepsilon_{ii}/k_B$ [K]	$\lambda_{ii}$
Carbon Dioxide	2	2.861	211.54	16.93
n-Heptane	3	4.049	294.29	14.03

For weakly asymmetric mixtures, Hoang et al. [27] proposed to use the classical Lorentz-Berthelot (LB) combining rules for  $\sigma_{ij}$  and  $\varepsilon_{ij}$  as:

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2} \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (3)$$

And, the repulsion exponent of the cross-interactions,  $\lambda_{ij}$ , is evaluated using an arithmetic average as:

$$\lambda_{ij} = \frac{\lambda_{ii} + \lambda_{jj}}{2} \quad (4)$$

Such combining rules was found to be provide reasonable results for noble gases mixtures as well as normal alkanes mixtures [27, 29-31]. However, when dealing with an asymmetric mixture of CO<sub>2</sub> + nC<sub>7</sub>, in which the CO<sub>2</sub> molecules have a quadrupole moment, the classical LB combining rules, i.e. Eqs. 2 and 3, are usually insufficient to accurately describe the cross interaction mixture parameters [35]. To check this point, we have performed a preliminary study to assess the capability of these combining rules for predicting equilibrium phase composition and Henry's law constant of CO<sub>2</sub> in liquid nC<sub>7</sub>, the latter being defined [36] as:

$$H_{CO_2} = \lim_{x_{CO_2} \rightarrow 0} \left[ \frac{f_{CO_2}^{liq}}{x_{CO_2}} \right] = \rho_{nC_7}^* k_B T \exp\left(\frac{\mu_{CO_2}^{ex}}{k_B T}\right) \quad (5)$$

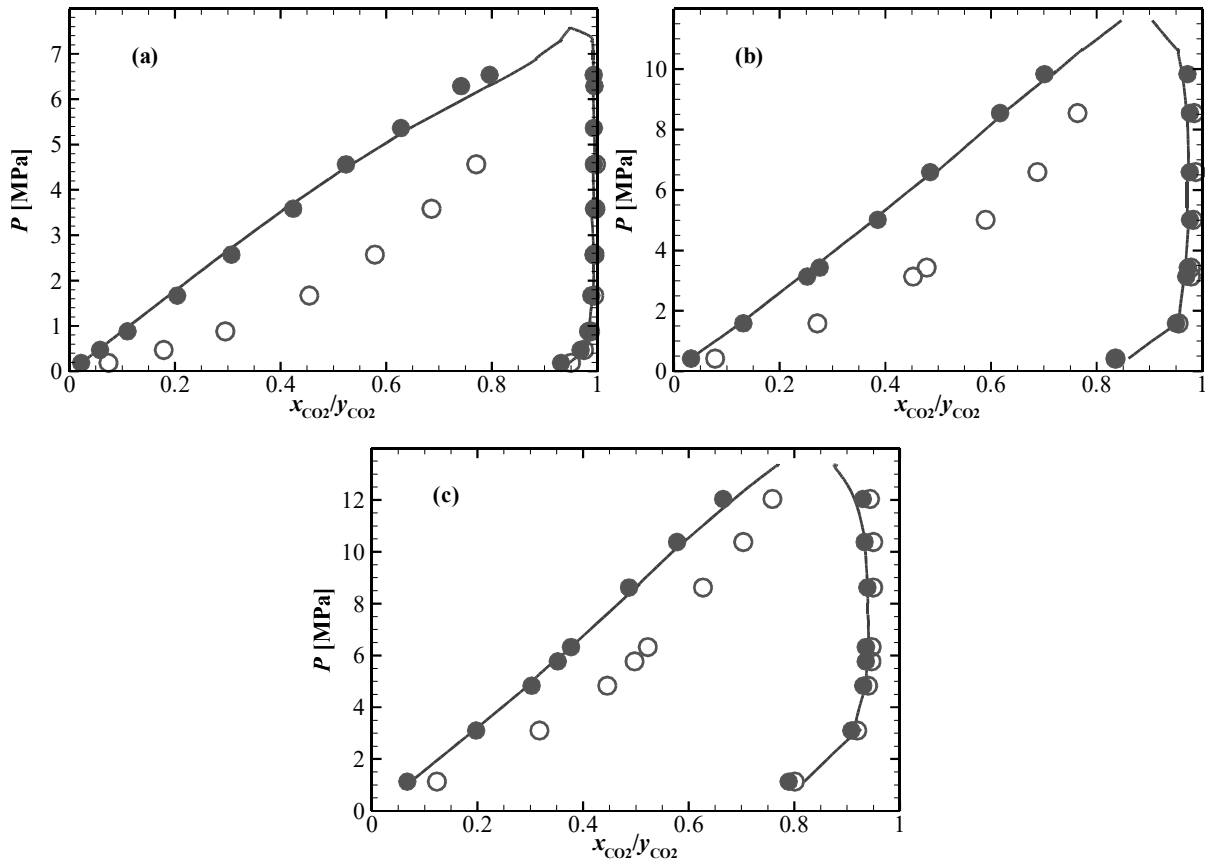
where  $f_{CO_2}^{liq}$  and  $x_{CO_2}$  are respectively the fugacity and the mole fraction of CO<sub>2</sub> in liquid nC<sub>7</sub>,  $\rho_{nC_7}^*$  the number density of the liquid n-heptane and  $\mu_{CO_2}^{ex}$  is the excess chemical potential of CO<sub>2</sub> in the liquid nC<sub>7</sub>. To do so, phase equilibrium properties have been computed by carrying out Gibbs Ensemble Monte Carlo simulations [37-38] during which  $\mu_{CO_2}^{ex}$  has been estimated by using the Widom method [39-40].

Figs. 1 and 2 show comparisons between molecular simulation and experimental results [41]. It appears clearly that the combining rules defined by Eqs. 2-4 do not correctly capture the cross interactions of the studied mixture. To overcome this problem, the potential well depth combining rule given by Eq. 3 was corrected using a binary interaction parameter  $k_{ij}$ :

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (6)$$

assuming that fluid-phase equilibria are dominated by the energetic contributions to the interactions [35, 42-43]. The correction protocol consists in choosing a  $k_{ij}$  value leading to the right prediction of the aforementioned phase equilibrium properties. To determine the appropriate binary coefficient, we have employed a minimization method [44] based on the

123 deviations between experimental and numerical data on phase composition and Henry's law  
 124 constant.

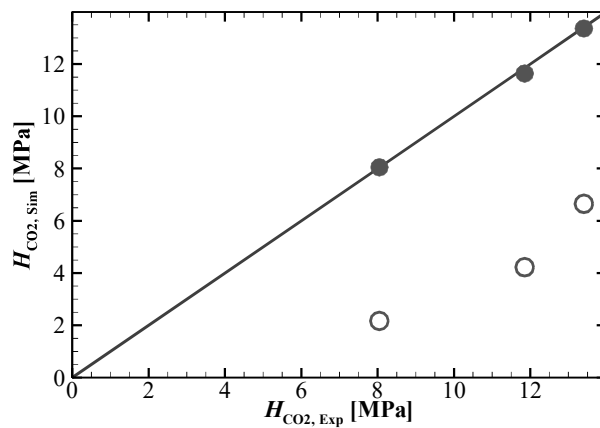


125

126

127 Figure 1. Equilibrium phase compositions for the carbon dioxide + n-heptane binary systems at  
 128 different temperatures. (a):  $T=310.65$  K. (b):  $T=352.60$  K. (c):  $T=394.26$  K. Comparison  
 129 between experimental data (lines) provided by Kalra et al. [41] and GEMC simulation results  
 130 with (solid circles) and without (open circles) binary coefficient correction  $k_{ij}$ .

131



132

133 Figure 2. Henry's law constants obtained from molecular simulation as a function of  
 134 experimental values taken from Kalra et al. [41] for carbon dioxide + n-heptane mixture.

135 Comparison between simulation results with (solid circles) and without (open circles) binary  
136 coefficient correction  $k_{ij}$ .

137 Results shown in Figs. 1 and 2 indicate that  $k_{ij}$  equals 0.138, 0.128 and 0.113 at  
138  $T=310.6, 352.6$  and  $394.3\text{K}$ , respectively, provides both VLE and Henry's law constant in good  
139 agreement with experimental data [41]. Then, these values were fitted as a linear function of  
140 temperature [45] to determine  $k_{ij}$  at the temperatures of interest, i.e.  $T=303.35$  and  $313.25\text{K}$ .  
141 This has led to  $k_{ij}$  equal to 0.140 and 0.138 for  $T=303.35$  and  $313.25\text{K}$ , respectively.

## 142 2.2. Molecular Simulations.

### 143 A. Monte-Carlo simulations.

144 To compute equilibrium thermodynamic properties such as density, isothermal  
145 compressibility, speed of sound and isentropic compressibility, we performed Monte Carlo  
146 simulations in the isobaric isothermal ensemble ( $NPT$ ) [10-12] using an in-house code. The  
147 simulation systems were composed of cubic boxes containing at least 500 molecules for  
148 conditions far from the critical point of  $\text{CO}_2$  (i.e.  $x_{\text{CO}_2} \leq 60$  mol% and  $P \geq 40.23$  MPa) and 1000  
149 molecules for other systems. The periodic boundary conditions were applied in all the  
150 directions. The Mie  $\lambda$ -6 potential was truncated at a cut-off radius  $r_c$  and the long range  
151 corrections were included [10-12]. Details about chosen  $r_c$  values are provided in the following  
152 section.

153 To generate new configurations, four MC moves were implemented: volume change,  
154 molecular translation, molecular rotation and configurational-bias MC partial regrowth [10-12].  
155 In these simulations, the system was first equilibrated by carrying out at least  $3 \cdot 10^7$  MC moves  
156 followed by a period of more than  $2 \times 10^8$  moves during which the sampling was carried out  
157 to determine the thermodynamic properties. During the equilibration stage, the maximum  
158 amplitudes of the three first MC moves were adjusted so that their acceptance rates are  
159 approximately equal to 50% [10-12]. Error bars have been computed from the sub-block  
160 method [10].

### 161 B. Molecular Dynamics Simulations.

162 To compute additional microscopic properties such as the radial distribution functions  
163 and residence times of  $\text{CO}_2$  molecules around the n-heptane molecule, Molecular Dynamics  
164 (MD) simulations in  $NPT$  ensemble [10-12] have been performed by using an in-house code.  
165 For that purpose, the simulation systems were made up of cubic boxes composed of at least  
166 3000 molecules for conditions far from the critical point of pure  $\text{CO}_2$  (i.e.  $x_{\text{CO}_2} \leq 60$  mol% and

170 P  $\geq$  40.23 MPa) and at least 5000 molecules for other mixtures. In particular, for the MD  
171 simulations performed at “infinite dilution” of nC<sub>7</sub>, the system was composed of at least 5000  
172 molecules of CO<sub>2</sub> and 1 molecule of n-heptane. Classical periodic boundary conditions were  
173 applied in all directions.

174 During MD simulations, the equations of motion were integrated using the velocity-  
175 Verlet algorithm [46]. The temperature and pressure were kept constant using a Berendsen  
176 thermostat and barostat, respectively [47]. The classical RATTLE algorithm was employed to  
177 constrain the bond length [48]. All MD simulations consist of two steps. First, the systems were  
178 equilibrated for 2.10<sup>6</sup> time steps. Then, the samplings were carried out during at least 6.10<sup>6</sup> time  
179 steps. Error bars have been computed from the sub-block method, except for the infinite dilution  
180 systems for which they were calculated from at least 10 independent MD simulations to  
181 improve the statistical uncertainties [10].

182 Similarly to MC simulations, the non-bonded Mie  $\lambda$ -6 potential was truncated at a cut-  
183 off radius  $r_c$  and long range corrections were included [10-12]. It should be noticed that, even  
184 if the long range corrections are included, the cut-off radius has a strong effect on  
185 thermodynamic properties of the mixtures close to the critical point [49]. This is because the  
186 correlation lengths of the near-critical fluctuations are known to diverge when approaching the  
187 critical point [49-50]. Therefore, to choose adequate values of  $r_c$ , we have investigated its effect  
188 on the simulation of density. Results have shown that a  $r_c$  value higher or equal to  $7\sigma_{ij}$  was  
189 sufficient for the thermodynamic condition that is the most impacted by the critical point  
190 vicinity, i.e. the one corresponding to the highest value of the isothermal compressibility which  
191 is at  $x_{CO_2}=1.0$ ,  $T=313.25K$ ,  $P=10.11MPa$  [1]. Then, we have evaluated the range of conditions  
192 (both in pressure and in composition) for which a usual lower cut-off radius ( $r_c = 4\sigma_{ij}$ ) could  
193 yield results consistent with those provided with ( $r_c = 7\sigma_{ij}$ ). It has been obtained that  $r_c =$   
194  $4\sigma_{ij}$  is sufficient to provide consistent densities for the following thermodynamic conditions  
195  $T=313.25K$ ,  $P=10.11MPa$ ,  $x_{CO_2}\leq 0.6$  and  $T=313.25K$ ,  $P\geq 40.23 MPa$ ,  $x_{CO_2}=1.0$ . To sum up, for  
196 both  $T=303.35 K$  and  $313.25 K$ , we have used  $r_c = 7\sigma_{ij}$  for thermodynamic conditions  
197 respecting  $10.11\leq P < 40.23$  and  $0.6 < x_{CO_2} \leq 1.0$ , so-called conditions close to the critical  
198 point, and  $r_c = 4\sigma_{ij}$  for the other thermodynamic conditions, so-called conditions far from the critical  
199 point. Such values of  $r_c$  have been used in both MC and MD simulations to compute both the  
200 thermodynamic and the structural properties.

### 199 III. Thermodynamics Properties Computations

#### 200 3.1. Classical computations

201 Density was directly computed by taking the average of its values during the MC  
202 simulations as [10, 12]:

$$203 \rho = \left\langle \frac{\sum_i N_i \times M_i}{V} \right\rangle \quad (7)$$

204 where,  $N_i$  and  $M_i$  are number of molecules and molecular mass of the  $i^{th}$  compound,  
205 respectively,  $V$  is the volume, and  $\langle \dots \rangle$  denotes an ensemble average over MC moves.

206 The isothermal compressibility was also directly estimated from the MC simulations  
207 thanks to the fluctuation theory [10, 12, 17, 51] using:

$$208 \kappa_T = -\frac{1}{\langle V \rangle} \left( \frac{\partial \langle V \rangle}{\partial P} \right)_T = \frac{1}{\langle V \rangle k_B T} (\langle V^2 \rangle - \langle V \rangle^2) \quad (8)$$

209 where,  $k_B$  is the Boltzman constant.

210 The isentropic compressibility and the speed of sound, whose direct calculation during  
211 the simulations is not straightforward for molecular fluids, were deduced from other  
212 thermodynamic properties via classical thermodynamic relations [52] as:

$$213 k_s = \kappa_T - \frac{T M \alpha_p^2}{\rho c_p} \quad (9)$$

$$214 w = \frac{1}{\sqrt{\rho \left( \kappa_T - \frac{T M \alpha_p^2}{\rho c_p} \right)}} \quad (10)$$

215 where,  $\alpha_p$  is the isobaric thermal expansion and  $c_p$  is the molar isobaric heat capacity. These  
216 two last quantities were obtained from the simulations by using the fluctuation theory [17]. The  
217 isobaric thermal expansion was computed by:

$$218 \alpha_p = \frac{1}{\langle V \rangle} \left( \frac{\partial \langle V \rangle}{\partial P} \right)_T = \frac{1}{\langle V \rangle k_B T^2} (\langle V \hat{H} \rangle - \langle V \rangle \langle \hat{H} \rangle) \quad (11)$$

219 where,  $\hat{H}$  is the configurational enthalpy:  $\hat{H} = U^{ext} + U^{int} + PV$ ,  $U^{ext}$  and  $U^{int}$  are the  
220 intermolecular and intramolecular potential energy, respectively. Regarding the molar isobaric  
221 heat capacity  $c_p$ , since the kinetic energy is not considered in MC simulations, it is decomposed  
222 in an ideal and residual isobaric heat capacities as follows [17]:

$$223 c_p = c_p^{id} + c_p^{res} \quad (12)$$

224 where  $c_p^{id}$  is the ideal molar heat capacity obtained from the NIST database [53] and  $c_p^{res}$  is the  
225 residual heat capacity estimated from the simulations [17] as:

$$226 c_p^{res} = \frac{N_a}{k_B N T^2} (\langle U^{ext} \hat{H} \rangle - \langle U^{ext} \rangle \langle \hat{H} \rangle) + \frac{N_a P}{k_B N T^2} (\langle V \hat{H} \rangle - \langle V \rangle \langle \hat{H} \rangle) - N_a k_B \quad (13)$$

227 where  $N_a$  is the Avogadro number.

228 The radial distribution functions (RDF), which provide information on the structure of  
 229 the studied fluid, were directly computed from the MD simulations [10] as:

$$230 \quad g_{\alpha\beta}(r) = \left\langle \frac{V}{N_\alpha} \times \frac{1}{N_\beta} \sum_{i \in \alpha} \sum_{j \in \beta} \frac{\delta(r_{ij}-r)}{4\pi r^2} \right\rangle \quad (14)$$

231 where,  $g_{\alpha\beta}$  is the RDF of species  $\beta$  around species  $\alpha$ ,  $\delta$  is the Dirac distribution function,  $N_\alpha$   
 232 and  $N_\beta$  are the numbers of molecules of species  $\alpha$  and  $\beta$ , respectively.

### 233 3.2. Computations from the Kirkwood-Buff Theory

234 Interestingly, in addition to the usual approach, Eq. 8, the isothermal compressibility  
 235 can be alternatively computed from the microscopic structure thanks to the Kirkwood-Buff  
 236 theory [54] using:

$$237 \quad \kappa_T = \frac{1+c_\alpha G_{\alpha\alpha}+c_\beta G_{\beta\beta}+c_\alpha c_\beta (G_{\alpha\alpha}G_{\beta\beta}-G_{\alpha\beta})^2}{k_B T (c_\alpha+c_\beta+c_\alpha c_\beta (G_{\alpha\alpha}+G_{\beta\beta}-2G_{\alpha\beta}))} \quad (15)$$

238 where  $c_\alpha$  and  $c_\beta$  are the molar concentration of species  $\alpha$  and  $\beta$ , respectively, and  $G_{\alpha\beta}$  is the  
 239 Kirkwood-Buff Integral (KBI) between species  $\alpha$  and  $\beta$  that is defined as:

$$240 \quad G_{\alpha\beta} = 4\pi \int_0^\infty [g_{\alpha\beta}^{\mu VT}(r) - 1] r^2 dr \quad (16)$$

241 where  $g_{\alpha\beta}^{\mu VT}$  is the RDF of species  $\beta$  around  $\alpha$  in the grand canonical  $\mu VT$  ensemble. As can be  
 242 seen from this expression, Eq. 16, KBI has unit of volume per molecule and quantifies the  
 243 excess (or deficiency) of species  $\alpha$  around species  $\beta$  relatively to a homogenous (random)  
 244 distribution, i.e. when  $g_{\alpha\beta}^{\mu VT}(r) = 1$ .

245 The Kirkwood-Buff theory also provides a formula to directly calculate the partial molar  
 246 volume  $v_\alpha$  from the KBI as [54]:

$$247 \quad v_\alpha = \frac{1+(G_{\beta\beta}-G_{\alpha\beta})c_\beta}{c_\alpha+c_\beta+c_\alpha c_\beta (G_{\alpha\alpha}+G_{\beta\beta}-2G_{\alpha\beta})} \quad (17)$$

248 This direct way to compute the partial molar volume is of great interest, as it is often indirectly  
 249 obtained from a fitting procedure of volumetric data, which may induce important errors [55-  
 250 57].

251 However, it is worth pointing out that the calculation of KBI, Eq. 16, from the RDFs  
 252 obtained from molecular simulations is not straightforward and this explains why Kirkwood-  
 253 Buff theory is not yet widely employed in the molecular simulations community. The  
 254 difficulties in computing Eq. (16) are due to two main reasons. First,  $g_{\alpha\beta}^{\mu VT}(r)$  of a molecular  
 255 mixture in a dense state, as studied in this work, is often not accurately computed because of  
 256 the difficulties in performing molecular simulations in the grand canonical ensemble, in  
 257 particular when dealing with mixtures [10-11]. Second, the molecular simulations are carried

258 out on finite systems [10-11] and so the integral in Eq. 16 cannot be computed over an infinite  
 259 volume as it should.

260 In this work, instead of determining  $g_{\alpha\beta}^{\mu VT}(r)$  directly from molecular simulations in the  
 261 grand canonical ensemble, we have first computed the RDF in the NPT (or NVT) ensemble,  
 262 i.e.  $g_{\alpha\beta}^{NPT}(r)$ , and then corrected it to obtain an approximation of  $g_{\alpha\beta}^{\mu VT}(r)$ , as proposed in ref.  
 263 [58], i.e.:

$$264 \quad g_{\alpha\beta}^{\mu VT}(r) \approx g_{\alpha\beta}^{NPT}(r) \frac{N_{\alpha} \left(1 - \frac{(4/3)\pi r^3}{V}\right)}{N_{\alpha} \left(1 - \frac{(4/3)\pi r^3}{V}\right) - \Delta N_{\alpha\beta}(r) - \delta_{\alpha\beta}} \quad (18)$$

265 with

$$266 \quad \Delta N_{\alpha\beta}(r) = 4\pi \int_0^r \rho_{\beta} [g_{\alpha\beta}^{NPT}(r') - 1] r'^2 dr' \quad (19)$$

267 where  $\Delta N_{\alpha\beta}(r)$  is the excess or depletion number of particles of type  $\alpha$  within a sphere of radius  
 268  $r$  around particles of type  $\beta$  and  $\rho_{\beta}$  the number density of particle of type  $\beta$ .

269 For the estimation of the integral in Eq. 16, we have first computed the KBI for different  
 270 finite volumes, and then extrapolated it to the infinite volume limit [58-60]. The KBI for the  
 271 finite volumes proposed by Krüger et al. [60] is defined as:

$$272 \quad G_{\alpha\beta}^V(V) = \int_V \int_V [g_{\alpha\beta}^{\mu VT}(r) - 1] dr_1 dr_2 \quad (20)$$

273 This double integral can be reduced to a single one by introducing a weighting function  $w(r)$   
 274 that is defined as:

$$275 \quad w(r) = \frac{1}{V} \int_V \int_V \delta(r - r_{12}) dr_1 dr_2 \quad (21)$$

276 where  $\delta(r - r_{12})$  is the Dirac delta function and  $r_{12} = |r_1 - r_2|$  is the pair distance. The  
 277 weighting function  $w(r)$  is the one that is proportional to the probability of having two points  
 278 inside the sub volume  $V$  separated by a distance  $r$  [60]. Then,  $G_{\alpha\beta}^V$  is given by:

$$279 \quad G_{\alpha\beta}^V(V) = G_{\alpha\beta}^V(R) = \int_0^{2R} w(r) [g_{\alpha\beta}^{\mu VT}(r) - 1] dr \quad (22)$$

280 For a spherical volume, the weighting function is defined [60] as:

$$281 \quad w(r) = 4\pi r^2 (1 - 3r/4R + r^3/4R) \quad (23)$$

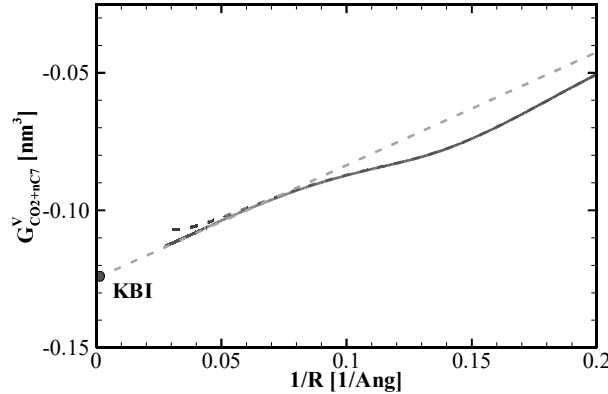
282 Given the variation in  $G_{\alpha\beta}^V(R)$  with  $R$ ,  $G_{\alpha\beta}$  is approximated as:

$$283 \quad G_{\alpha\beta} = \lim_{R \rightarrow \infty} G_{\alpha\beta}^V(R) = \lim_{1/R \rightarrow 0} G_{\alpha\beta}^V(R) \quad (24)$$

284 It has been shown that  $G_{\alpha\beta}^V(R)$  linearly varies with  $1/R$  for small values of  $1/R$  [21, 60]. This  
 285 enables a linear extrapolation of  $G_{\alpha\beta}^V(R)$  with  $1/R$  to finally compute KBI as shown in Fig. 3.

286 It should be noted that the direct replacement of  $g_{\alpha\beta}^{\mu VT}(r)$  by  $g_{\alpha\beta}^{NPT}(r)$  does not provide good

287 values for the KBI, whereas the corrected  $g_{\alpha\beta}^{NPT}(r)$ , using Eq. 18, is able to yield good results,  
 288 as shown in Fig. 3.



289  
 290 Figure 3: Dependence of  $G_{CO_2+nC_7}^V$  with  $1/R$  for the binary mixture of  $CO_2+nC_7$  at  $x_{CO_2}=0.40$   
 291  $T=303.35K$  and  $P=10.12$  MPa. (Red color) solid line corresponds to the use of  $g_{CO_2+nC_7}^{\mu VT}(r)$   
 292 given by Eq. 18. (Blue color) dashed-dotted line corresponds to the use of  $g_{CO_2+nC_7}^{NPT}(r)$ . (Green  
 293 color) short-dashed line corresponds to the linear extrapolation used to deduce the KBI.

## 294 IV. Results and discussions

### 295 4.1. Thermodynamic Properties

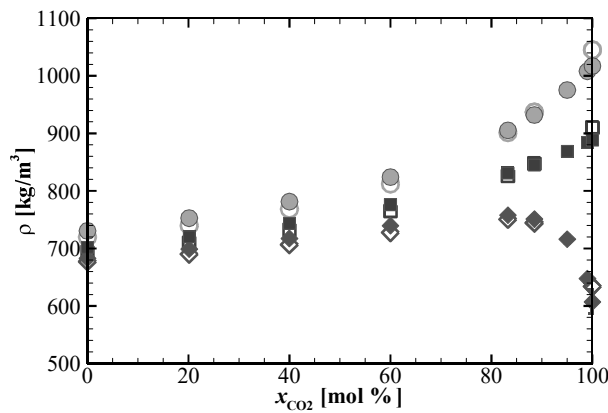
296 In this section, we compare thermodynamic properties obtained from the molecular  
 297 simulations and those provided from the experiments published in Ref. 1. To do so, MC  
 298 simulations on pure carbon dioxide, n-heptane and their mixtures with  $CO_2$  mole fractions of  
 299 20, 40, 60, 83.26, 88.49 mol% were carried out at the same conditions as experimental  
 300 measurements, i.e. pressures ranging from 10 to 70 MPa and for two isotherms corresponding  
 301 to 303.35 and 313.25 K. For further investigations, molecular simulations were also performed  
 302 for two additional compositions (95 and 99 mol%) where experimental measurements on the  
 303 speed of sound were not possible to achieve with our experimental devices [1, 61].

#### 304 A. Density and derivative properties

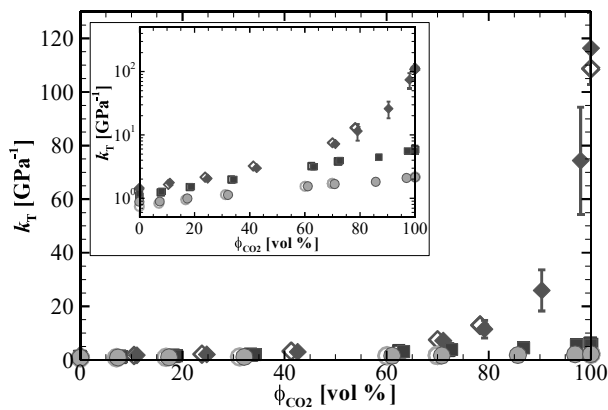
305 Densities obtained from the MC simulations are reported in Table A. 1 of the Appendix.  
 306 Compared to experimental results reported in the previous work [1], they are globally in good  
 307 agreement with the experimental densities, see Fig. 4. In more details, simulation results  
 308 remarkably matches experimental ones with absolute deviations (AD) that are not greater than  
 309 1% for conditions far from the critical point (i.e.  $x_{CO_2} \leq 60$  mol% and  $P \geq 30$  MPa), whereas the  
 310 deviations from experimental data are much more pronounced for the conditions near the  $CO_2$   
 311 critical point, reaching up to 4% for the pure  $CO_2$  at  $T=313.15$  K and  $P=10.11$  MPa, see Fig. 4.

312 These observations indicate that the deviations mostly arise from the proximity to the CO<sub>2</sub>  
 313 critical point, which is probably due to the difficulties to accurately describe this region with  
 314 molecular simulations combined with the intrinsic limitations of the MCCG force field [12, 27].

315 Experimental results have shown a non-monotonic variation in the density with CO<sub>2</sub>  
 316 content at  $P=10.11$  MPa [1], which is well captured by the molecular simulations, as shown in  
 317 Fig. 4. However, due to difficulties in experimental measurements [1], the experimental data  
 318 do not include the values for CO<sub>2</sub> contents in the range of 88.49 to 100 mol% [1], where the  
 319 variation of the density with the CO<sub>2</sub> content is the largest at  $P=10.11$  MPa, see Fig. 4. Hence,  
 320 to better describe this variation, we have performed MC simulations to compute the density at  
 321 two additional CO<sub>2</sub> contents (95 and 99 mol%).



322  
 323 Figure 4. Comparison between variations in density with the CO<sub>2</sub> mole fraction obtained from  
 324 experiments [1] (open symbols) and molecular simulations (solid symbols) at  $T=313.25$  K and  
 325  $P=10.11$  MPa (diamonds),  $P=30.16$  MPa (squares) and  $P=70.54$  MPa (circles).



326  
 327 Figure 5. Comparison between variations in isothermal compressibility with CO<sub>2</sub> volume  
 328 fraction obtained from experiments [1] (open symbols) and molecular simulations (solid

symbols) at  $T=313.25$  K and  $P=10.11$ MPa (diamonds),  $P=30.16$ MPa (squares) and  $P=70.54$ MPa (circles). The inserted figure displays  $k_T$  in a logarithm scale.

In addition to density, MC simulations provide the isothermal compressibility values of the system by analyzing volume fluctuations thanks to Eq. 8. These data are given in Table A. 2 of the Appendix. This derivative property is rather well predicted by the MC simulations in comparison with the experiments. The AD varies between 0.5% for the pure n-heptane and 10% for the mixture with the highest CO<sub>2</sub> content at  $T=313.25$ K and  $P=10.11$  MPa, see Fig. 5. These deviations are consistent with those on the density and are probably related to the limitations of the chosen force fields in the region around the CO<sub>2</sub> critical point and the difficulties in capturing accurately the density fluctuations in near critical conditions [49].

Despite the non-monotonic behavior of density with composition at  $T=313.25$  K and  $P=10.11$  MPa, isothermal compressibility deduced from experiments monotonously increases with the CO<sub>2</sub> content [1], see Fig. 5, as for all thermodynamic conditions studied in this work. Interestingly, this behavior is well captured by molecular simulations as shown in Fig. 5 in which the volume fraction of CO<sub>2</sub> used in x-axis corresponds to the ideal volume fraction defined [1] as:

$$\phi_{CO_2} = \frac{x_{CO_2} M_{CO_2}}{\rho_{CO_2} \sum_i x_i \frac{M_i}{\rho_i}} \quad (25)$$

where the subscript  $i$  denotes carbon dioxide and n-heptane. The use of the volume fraction as abscissa has been chosen because the isothermal compressibility of an ideal mixture is a linear function of the volume fraction [1]. It is also interesting to notice that the significant departure of  $k_T$  to linearity for the mixtures with a high CO<sub>2</sub> content, indicating non ideality, is well captured by the molecular simulations, see Fig.5.

In addition, the isentropic compressibility  $k_s$  and the speed of sound  $w$  were indirectly calculated from the standard thermodynamic relationships (Eqs. 9 and 10) using density, isothermal compressibility, isobaric thermal expansion and molar heat capacity directly taken from MC simulations. The computed data of  $k_s$  and  $w$  are provided in Tables A. 3 and A. 4 of the Appendix. Although this indirect method can lead to important expanded uncertainties [31], it provides the isentropic compressibility and the speed of sound in quantitative agreement with experimental results as shown in Figs 6 and 7. The AD is smaller than 20% for the isentropic compressibility, and it is of the order of 10% for the speed of sound. The largest deviations correspond to the mixture with the high CO<sub>2</sub> content. Furthermore, the simulation data of the two additional CO<sub>2</sub> contents of 95 and 99 mol%, where experiments were not possible to

361 perform with the pulse echoes technique used, emphasizes the interest of molecular simulations  
 362 to explore conditions for which experiments are difficult to achieve [1, 61].

### 363 B. Excess Properties

364 To go further in our investigations using the simulation results, we have calculated  
 365 excess volumetric and acoustic properties of the studied mixtures that are defined as:

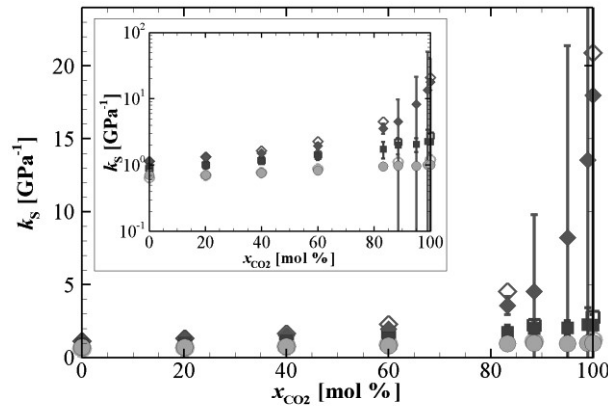
$$366 \quad y^E = y - y^{id} \quad (26)$$

367 where  $y$  denotes either  $V_m$ ,  $\kappa_T$ ,  $\kappa_S$  or  $w$  and the superscript  $id$  the corresponding ideal mixture  
 368 properties estimated using the following equations :

$$369 \quad V^{id} = \sum_i x_i \frac{M_i}{\rho_i} \quad (27)$$

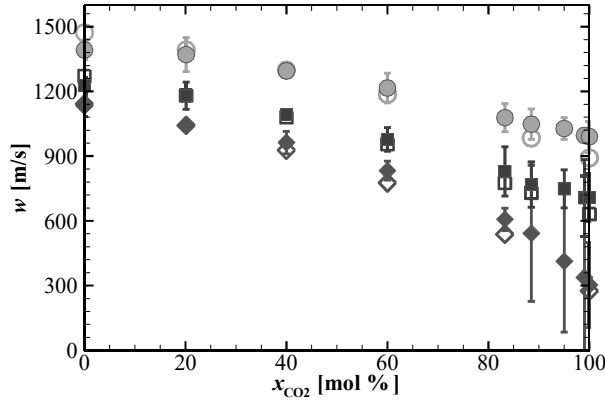
$$370 \quad \kappa_T^{id} = \sum_i \phi_i \kappa_{T,i} \quad (28)$$

371



372

373 Figure 6. Comparison between variations in isentropic compressibility with  $\text{CO}_2$  volume  
 374 fraction obtained from experiments [1] (open symbols) and molecular simulations (solid  
 375 symbols) at  $T=313.25\text{K}$  and  $P=10.11\text{MPa}$  (diamonds),  $P=30.16\text{MPa}$  (squares) and  
 376  $P=70.54\text{MPa}$  (circles). The inserted figure displays  $k_s$  in the logarithm scale.



377

378 Figure 7. Comparison between variations in speed of sound with CO<sub>2</sub> mole fraction obtained  
 379 from experiments [1] (open symbols) and molecular simulations (solid symbols) at  $T=313.25$   
 380 K and  $P=10.11$ MPa (diamonds),  $P=30.16$ MPa (squares) and  $P=70.54$ MPa (circles).

$$381 \quad \kappa_S^{id} = \sum_i \phi_i \kappa_{T,i} - \frac{\left(\sum_i x_i \frac{M_i}{\rho_i}\right) \left(\sum_i \phi_i \alpha_{p,i}\right)^2}{\sum_i x_i \frac{M_i T \alpha_{p,i}^2}{\rho_i (\kappa_{T,i} - \kappa_{S,i})}} \quad (29)$$

$$382 \quad w^{id} = \frac{\sum_i x_i \frac{M_i}{\rho_i}}{M \kappa_S^{id}} \quad (30)$$

383 where the subscript  $i$  denotes either CO<sub>2</sub> or nC<sub>7</sub>.

384 Evaluation of these excess properties is very important because they quantify the non-  
 385 idealities of an asymmetric mixture [2]. Thus, this allows one to deeply check the capability of  
 386 the molecular simulations to deal with the studied mixtures, from the mixing point of view  
 387 alone. However, it is worth noticing that the excess properties determinations either from  
 388 experiment and simulation may be affected by large errors bars, especially for properties such  
 389 as  $\kappa_S^E$  and  $w^E$ .

390 Interestingly, it has been found that all excess properties are qualitatively and  
 391 quantitatively well estimated by molecular simulations when compared to experimental data,  
 392 as displayed in Fig. 8. These observations provide further evidence of the good capability of  
 393 the MCCG force fields combined with modified Lorentz-Berthelot rule to describe the  
 394 asymmetric mixture studied in this work, even close to critical conditions.

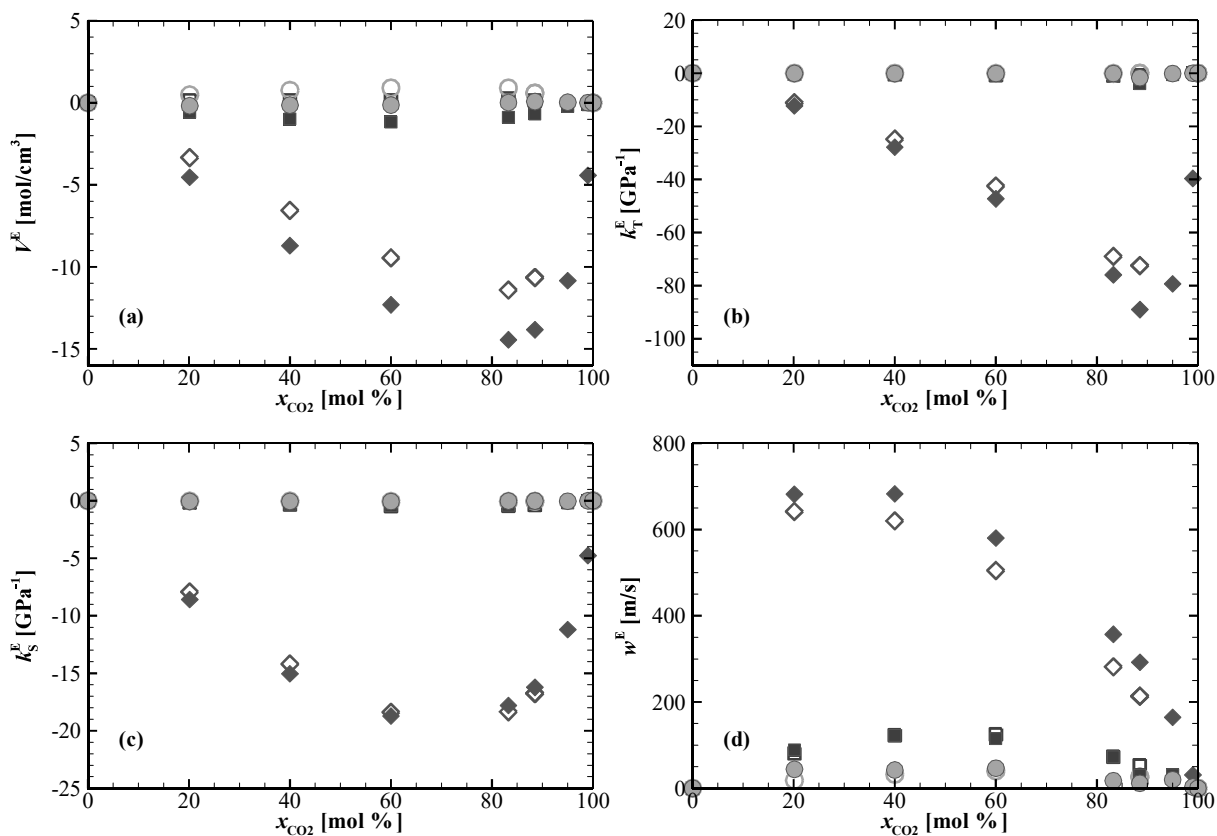


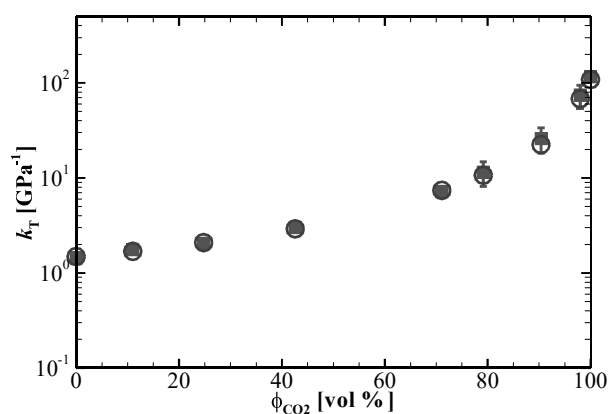
Figure 8. Comparison between variations in excess properties with CO<sub>2</sub> mole fraction deduced from experiments [1] (open symbols) and molecular simulations (solid symbols) at  $T=313.25$  K and  $P=10.11$  MPa (diamonds),  $P=30.16$  MPa (squares) and  $P=70.54$  MPa (circles). (a): Excess molar volume. (b): Excess isothermal compressibility. (c): Excess isentropic compressibility. (d) Excess speed of sound. For sake of clarity, the error bars have not been plotted.

## 4.2. Kirkwood Buff Integrals and partial molar volumes

To investigate more deeply the non-idealities of a mixture, the partial molar volumes of components are very informative regarding the fluid behavior at the microscopic level [7]. To compute this quantity, the simplest method is to first fit the molar volume data at fixed pressure and temperature and then to analytically differentiate the fitted functions with respect to mole fraction [2-3], as done on our experimental data [1]. Nevertheless, this method is subject to high uncertainties due to the choice of the fitting functions and the number of mixture compositions close to the boundary conditions ( $x_{CO_2} = 0$  and 100 mol%). In particular, when applying the fitting method to data that may have large errors [55-57], e.g. systems near the critical point, it can result in inaccurate values of the partial molar volumes. During molecular simulations, partial molar volume can be directly computed from the Kirkwood and Buff Integrals (KBI), as described in Sect. 3.2, avoiding so the problem of the fitting procedure. Thus, we have

414 considered the latter method to determine the partial molar volumes of the two components in  
1 415 the studied mixtures.

3 416 To obtain the partial molar volumes from the Kirkwood-Buff theory [54], the KBI have  
4 417 been first computed by using the approach described in Sect. 3.2. Computed values of KBI are  
5 418 listed in Tables A. 5 - A. 7 of the Appendix. To validate these data, the isothermal  
6 419 compressibilities have been calculated from the Kirkwood-Buff theory by using these KBIs and  
7 420 compared to those obtained from the fluctuation theory, Eq. 8. Figure 9 displays such a  
8 421 comparison at the condition where  $\kappa_T$  varies the most strongly with the mole fraction ( $T=313.25$   
9 422 K,  $P=10.11$  MPa). Results indicate that the two methods provide results consistent with each  
10 423 other, i.e. within error bars, which confirms the accuracy of KBI data.



24 424 Figure 9. Comparison of molecular simulations results of isothermal compressibility of CO<sub>2</sub> +  
25 425 nC<sub>7</sub> mixtures at 313.25 K and 10.11 MPa computed from volume fluctuations (Solid squares)  
26 426 and the KB theory (Open circles).  
27 427

28 428 Then, these KBI were used to calculate the partial molar volumes of CO<sub>2</sub> and n-heptane  
29 429 of the studied mixture at  $T=313.25$  K and  $P=10.11$  MPa thanks to the procedure described in  
30 430 section 3.2. For comparison, results of Kirkwood-Buff theory and experiments are together  
31 431 displayed in Fig. 10, showing a good agreement with each other. It appears clearly that the  
32 432 variations in the experimental partial molar volumes with mole fraction are fully consistent with  
33 433 those deduced from molecular simulations. In particular, the negative value of partial molar  
34 434 volume of n-heptane at infinite dilution is also predicted by the molecular simulations. These  
35 435 observations confirm the consistency in the partial molar volumes computed from experimental  
36 436 data and the chosen fitting procedure [1].

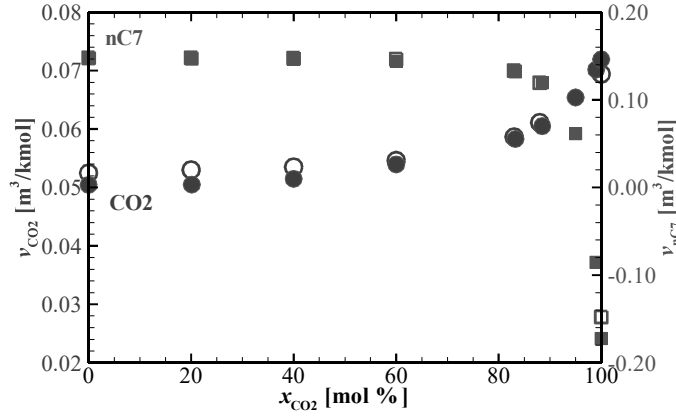


Figure 10. Partial molar volume of carbon dioxide (circles) and n-heptane (square) as a function of CO<sub>2</sub> mole fraction at  $T=313.25$  K and  $P=10.11$  MPa obtained from the fitting procedure on the experimental data (open symbols) and the Kirkwood-Buff theory combined with the molecular simulations (solid symbols).

#### 4.3. Microscopic analysis of the cluster at infinite dilution of nC<sub>7</sub>

Molecular simulations and experiments have both shown that the partial molar volume of n-heptane at infinite dilution is noticeably negative at  $T=313.25$  K and  $P=10.11$  MPa. Such unusual result has been interpreted as due to the formation of a cluster of CO<sub>2</sub> molecules around the nC<sub>7</sub> molecule, the so-called clustering effect [8-9]. This clustering phenomenon is often characterized and quantified by means of the excess number of CO<sub>2</sub> molecules surrounding the nC<sub>7</sub> molecule with respect to a uniform distribution at bulk density as [7]:

$$N_{CO_2}^{excess} = \rho_{CO_2}^* 4\pi \int_0^\infty [g_{CO_2-nC_7}^\infty(r) - 1] r^2 dr = \rho_{CO_2}^* \cdot G_{CO_2-nC_7}^\infty \quad (31)$$

where the superscript  $\infty$  refers to the infinite dilution and  $\rho_{CO_2}^*$  is the density of pure CO<sub>2</sub>. This excess number is also sometimes referred in the literature as the “cluster size”.

Using the density  $\rho_{CO_2}^*$  and the KBIs  $G_{CO_2-nC_7}^\infty$  obtained from molecular simulation,  $N_{CO_2}^{excess}$  is equal to  $6.3 \pm 1.6$ . Such a positive value is the signature of an increase of the CO<sub>2</sub> density around the n-heptane molecule [8-9]. This value is in qualitative agreement with the value of 8 [1] that was computed from the experimental volumetric properties following the fluctuation theory developed in Ref. [7] as:

$$N_{CO_2}^{excess} = \frac{RTk_{T,CO_2} - v_{nC_7}^\infty}{v_{CO_2}} \quad (32)$$

The cluster size defined by Eq. 31 and Eq. 32 provides only an overall property of the cluster related to the excess number CO<sub>2</sub> molecules surrounding a nC<sub>7</sub> molecule relatively to a random distribution. Thus, to gain further microscopic insights on the cluster nature, MD simulations on mixtures close to the infinite dilution of nC<sub>7</sub> have been performed to estimate

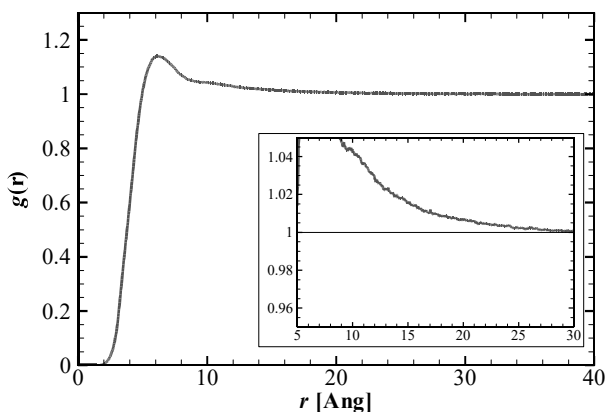
462 the properties of the CO<sub>2</sub> molecules located in the region around the nC<sub>7</sub> where there is an  
463 excess of CO<sub>2</sub> molecules compared to a random distribution, as presented in the following  
464 sections.

#### 465 **A. Determination of the CO<sub>2</sub> molecules belonging to the cluster.**

466 There exist many possible definitions to determine which molecules belong to a cluster  
467 [14, 16, 62-65]. The essence of these definitions is that the cluster is constituted of CO<sub>2</sub>  
468 molecules directly and indirectly “bonded” to the central nC<sub>7</sub> molecule [14, 62-63]. In this  
469 work, two molecules separated by a distance less than the radius of the first minimum of the  
470 corresponding RDF are considered to be directly bonded [64-65], whereas a molecule is  
471 considered to be indirectly bonded to a given molecule, if it is bonded to at least one molecule  
472 bonded to the given molecule [14].

473 In details, we have defined the molecules belonging to a cluster by two successive  
474 conditions. (i) All CO<sub>2</sub> molecules that are bonded directly and indirectly to the central nC<sub>7</sub>  
475 molecule, using the criteria defined above, are collected. (ii) Then, are selected only those that  
476 are located within a spherical region surrounding the central nC<sub>7</sub> molecule [16], with a radius  
477  $R_{cluster}$  for which the RDF between nC<sub>7</sub> and CO<sub>2</sub> is nearly constant and equal to 1.0. Results  
478 shown in Fig. 11 indicate that this distance is around 30Å (i.e. nearly ten CO<sub>2</sub> molecular sizes).  
479 Hence, we have chosen  $R_{cluster}$  to be equal to this value, i.e.  $R_{clust} = 30\text{\AA}$ .

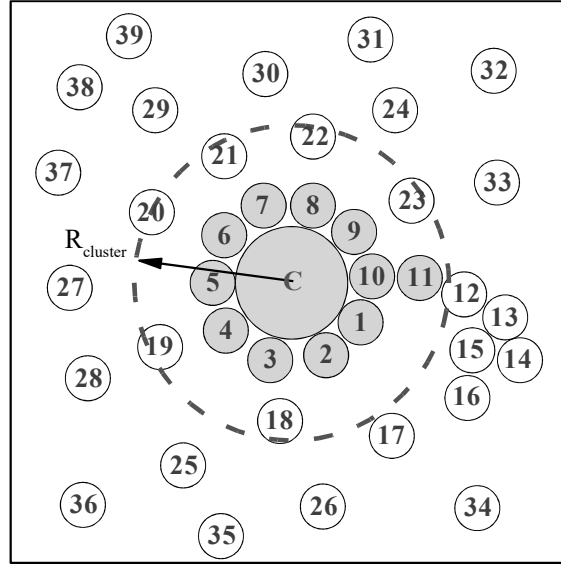
480 An illustration of this two-steps definition is shown in Fig. 12. The 1<sup>st</sup> to 10<sup>th</sup> CO<sub>2</sub>  
481 molecules are directly connected to the nC<sub>7</sub> molecule and so they are accounted for as belonging  
482 to the cluster. The 11<sup>th</sup> to 16<sup>th</sup> solvent molecules are indirectly connected to the nC<sub>7</sub> molecule,  
483 but only the 11<sup>th</sup> solvent molecule is considered to be in the cluster due to the added criterion  
484 of a limited region defined by  $R_{cluster}$ .



485  
486 Figure 11. Radial distribution functions between CO<sub>2</sub> and nC<sub>7</sub> at infinite dilution ( $x_{nC7} \rightarrow 0.0$ )  
487 and  $T = 313.25$  K and  $P = 10.11$  MPa.

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489



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Figure 12. Schematic description of the definition of CO<sub>2</sub> molecules belonging to the cluster. Green large circle corresponds to the nC<sub>7</sub> molecule. Small grey circles are the CO<sub>2</sub> molecules belonging to the cluster. Small white circles are the CO<sub>2</sub> molecules that do not belong to the cluster.

### 495 B. Properties of CO<sub>2</sub> molecules belonging to a cluster

496

In a first step, the number  $N_{CO_2\text{-cluster}}$  of CO<sub>2</sub> molecules belonging to the cluster as defined in section 4.3.A, , was computed, using:

498

$$N_{CO_2\text{-cluster}} = \sum_i \delta_i \quad (33)$$

499

where  $\delta_i = 1$  if the  $i^{th}$  CO<sub>2</sub> molecule belongs to the cluster and  $\delta_i = 0$  otherwise. It should be emphasized that there is a simple link between the number  $N_{CO_2\text{-cluster}}$ , and the excess number of CO<sub>2</sub> molecule,  $N_{CO_2}^{excess}$ , as:

502

$$N_{CO_2}^{excess} = N_{CO_2\text{-cluster}} - \rho_{CO_2}^* V_{clust} , \quad (34)$$

503

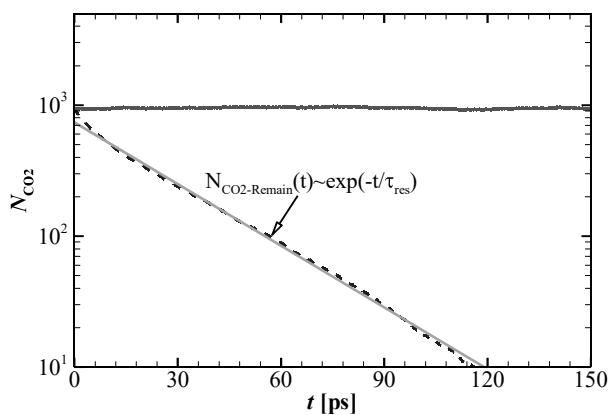
where  $V_{clust}$  is the volume of the cluster.

504

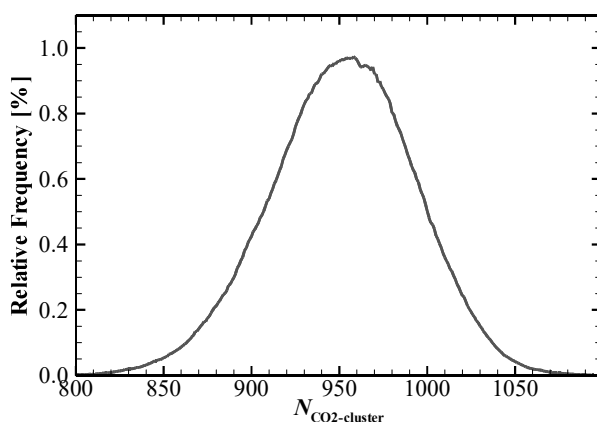
Figure 13 depicts the variations of  $N_{CO_2\text{-cluster}}$  with the time. It is shown that the number of CO<sub>2</sub> molecules belonging to the cluster region continuously fluctuates around an average value of  $952 \pm 3.5$ , as shown in Fig. 14. Interestingly, the distribution of the fluctuations of the number of CO<sub>2</sub> molecules belonging to the cluster exhibits a Gaussian form with a standard deviation of  $55 \pm 2.7$  as shown in Fig. 14. This is a signature that the fluctuations are

509 mainly due to a continuous exchange between the CO<sub>2</sub> molecules of the cluster and those  
 510 surrounding the cluster [15]. These results indicate so a weak nature of the cluster so defined.

511 In addition, assuming that the cluster is spherically symmetric and approximating its  
 512 radius by  $R_{cluster}$ , one can deduce that  $V_{clust} = (4\pi/3 R_{cluster}^3)$ . Using Eq. (34), we have  
 513 obtained from the MD simulations  $N_{CO_2-cluster}^{excess} = 4.6 \pm 3.5$  that is consistent with the value of  
 514  $N_{CO_2}^{excess} = 6.3 \pm 1.6$  given by Eq. 31. The difference is probably related to the fact that the  
 515 volume of the cluster is overestimated when using  $R_{cluster}$  as, by definition (section 4.3.A), not  
 516 all CO<sub>2</sub> molecules located at a distance below  $R_{cluster}$  from the nC<sub>7</sub> molecule belong to the  
 517 cluster.



520  
 521 Figure 13. Variation of numbers of CO<sub>2</sub> molecules of the cluster with the time. (Red color)  
 522 Solid line corresponds to  $N_{CO_2-cluster}$ . (Blue color) Dashed-dotted line corresponds to  
 523  $N_{CO_2-remain}$ .



525  
 526 Figure 14. Relative frequency distributions of the number of CO<sub>2</sub> molecules of the cluster.

In addition, the stability of the cluster has been investigated by computing the residence time of CO<sub>2</sub> molecules belonging to a cluster [16]. More precisely, the residence time measures how long the CO<sub>2</sub> molecules reside in the cluster, and so how long it takes to the cluster to lose its identity. To compute this quantity, we have estimated the number of CO<sub>2</sub> molecules remaining in the cluster  $N_{\text{CO}_2\text{-remain}}(t)$ , during the time window 0 to  $t$ , which is defined as [16]:

$$N_{\text{CO}_2\text{-remain}}(t) = \sum_i \delta_i^0(t) \quad (34)$$

where,  $\delta_i^0(t) = 1$  if the  $i^{\text{th}}$  CO<sub>2</sub> molecule resides in the cluster during the time interval  $[0, t]$ , and  $\delta_i^0(t) = 0$  otherwise. Fig. 13 displays the variation of  $N_{\text{CO}_2\text{-remain}}$  with the time. Results show that  $N_{\text{CO}_2\text{-remain}}$  exponentially decays with time, exhibiting a diffusive type behavior, which allows to deduce the residence time  $\tau_{res}$  from the following equation [16]:

$$N_{\text{CO}_2\text{-remain}}(t) = N_{\text{CO}_2\text{-remain}}(t = 0) \times \exp\left[-\frac{t}{\tau_{res}}\right] \quad (35)$$

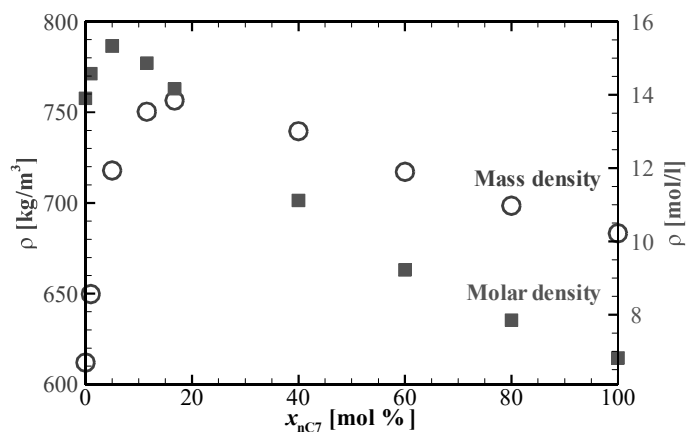
By doing so, it is possible to deduce an average residence time of CO<sub>2</sub> molecules in a cluster  $\tau_{res} = 27.5 \pm 1.5\text{ps}$  which is of the same order of magnitude than the diffusion characteristic time [66] deduced from CO<sub>2</sub> diffusion coefficient [67]. This result further confirms the weak nature of the cluster and its diffusive behavior.

#### 4.4. Effect of clustering on the macroscopic non-ideal behavior of the mixture

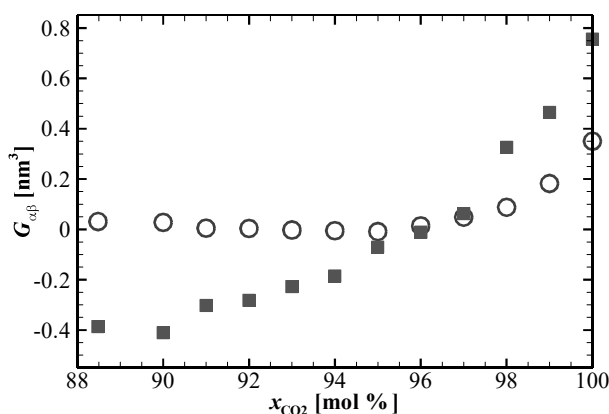
Indeed, clustering effect can be used to microscopically interpret the non-monotonic variation in the density with composition at  $T=313.25\text{K}$  and  $P=10.11\text{MPa}$ , see Fig. 15. To do so, it is easier to perform the interpretation by using molar density than mass density, to remove the effects of the molecular masses. Such a representation shows as well a non-monotonic variation of the molar density, see Fig. 15, but the maximum is reached at  $x_{\text{CO}_2}$  around 95.0 mol% rather than at  $x_{\text{CO}_2}$  around 85.0 mol% when using the mass density.

Qualitatively the interpretation of the data shown in Fig. 15 is the following. At infinite dilution of nC<sub>7</sub>, i.e. when the CO<sub>2</sub> clustering effect is present, adding some nC<sub>7</sub> leads to the formation of more clusters which in turns leads to an overall increase of the density, as average density of CO<sub>2</sub> is higher in the cluster than in the bulk. This trend is confirmed by the negative value of the partial molar value of nC<sub>7</sub> for low nC<sub>7</sub> content, see Fig. 10. The molar density still increases by further adding nC<sub>7</sub>, but the rate of increase is reduced because of the progressive overlapping of the clusters. At a certain value of nC<sub>7</sub> mole fraction,  $x_{\text{nC}_7} \approx 5.0\text{ mol\%}$  as shown in Fig. 15, the clusters tend to overlap more and more and so adding some extra nC<sub>7</sub> leads

558 progressively to a decrease of the molar density of mixture as the molar density of nC<sub>7</sub> is lower  
 559 than that of the CO<sub>2</sub>. The composition for which there is a change of behavior of molar density  
 560 with composition is consistent with the change of sign of the partial molar value of nC<sub>7</sub> between  
 561  $x_{nC7}=1.0$  mol% and  $x_{nC7}=5.0$  mol%, see Fig. 10.



562  
 563 Figure 15: Dependence of density on the mole fraction of CO<sub>2</sub> at  $T=313.25$ K and  $P=10.11$ MPa.  
 564 (Blue) Open circles correspond to the mass density. (Red) Solid squares correspond to the molar  
 565 density.



567  
 568 Figure 16: Comparison between the KBIs of the mixture at  $T=313.25$  K and  $P=10.11$ MPa  
 569 obtained from the molecular simulations at high CO<sub>2</sub> content. Circles correspond to the KBI of  
 570 CO<sub>2</sub>-CO<sub>2</sub>. Squares correspond to the KBI of CO<sub>2</sub>-nC<sub>7</sub>.

571 Quantitatively, an analysis could be achieved using the values of the KBIs, which  
 572 quantify the excess (or deficiency) of one species around another one relatively to a  
 573 homogeneous molecules distribution, as follows. An addition of an infinitesimal amount of nC<sub>7</sub>

574 to the pure CO<sub>2</sub> results in an increase of the molar density of the mixture as  $G_{CO_2-nC_7}^\infty >$   
575  $G_{CO_2-CO_2}^\infty$ , see the KBIs in Tables A. 5 – A. 7 of the Appendix. This increase should hold up to  
576 a mole fraction for which  $G_{CO_2-nC_7} \approx G_{CO_2-CO_2}$ . To confirm this expectation, we have  
577 additionally performed MD computations of the KBIs for CO<sub>2</sub> mole fraction varying from  
578 90.0% to 99.0%. Results shown in Fig. 16 indicate that  $G_{CO_2-nC_7} \approx G_{CO_2-CO_2}$  occurs at a CO<sub>2</sub>  
579 mole fraction around 96.0%, a value that is consistent with the one that can be deduced from  
580 the location of the maximum of the molar density, see Fig. 15, and with the change of sign of  
581 the partial molar value of nC<sub>7</sub>, see Fig. 10.

## 582 V. Conclusion

583 This work forms the second part of a combined experimental [1] and numerical study  
584 of binary mixtures composed of carbon dioxide and n-heptane at two temperatures (303.35K  
585 and 313.25 K) and at pressures from 10 to 70 MPa. In this part, molecular simulations have  
586 been performed to investigate the thermodynamics and structural properties in order to  
587 complement the experimental results [1]. For that purpose, the Mie Chain Coarse Grained force  
588 field has been used to model carbon dioxide and n-heptane molecules and has been combined  
589 with Monte Carlo and Molecular Dynamics simulations.

590 In a first step, the thermodynamic properties including density, isothermal  
591 compressibility, speed of sound, isentropic compressibility and the corresponding excess  
592 properties obtained from Monte-Carlo simulations were systematically compared to those  
593 obtained from experiments. It has been found that the simulation results are fully consistent  
594 with the experimental ones, showing nevertheless larger deviations when approaching the  
595 critical point of CO<sub>2</sub> at high content of CO<sub>2</sub>. Interestingly, one of the most peculiar behavior  
596 noticed experimentally, the non-monotonic variation of the density with the mole fraction of  
597 CO<sub>2</sub> at  $T=313.25K$  and  $P=10.11MPa$ , is very well captured by the molecular simulations.

598 In a second step, the Kirkwood-Buff theory has been used to directly compute the partial  
599 molar volumes of components from the simulations of the radial distribution functions.  
600 Interestingly, this direct method has provided results in good agreement with the experimental  
601 results. In particular, the noticeably negative value of partial molar volume of n-heptane at  
602 infinite dilution at  $T=313.25K$  and  $P=10.11MPa$ , computed indirectly from the experiment by  
603 a fitting procedure, was confirmed from molecular simulation results. Such a result confirms  
604 the occurrence of a clustering phenomenon in such conditions, i.e. CO<sub>2</sub> molecules tend to form  
605 a cluster around a nC<sub>7</sub> molecule, as deduced indirectly from volumetric experimental data. In

606 addition, the computed excess number of CO<sub>2</sub> was found to be in good agreement with the  
607 experimental indirect estimation.

608 To provide a microscopic picture of the clustering phenomenon, static and dynamic  
609 properties of the CO<sub>2</sub> cluster have been computed by molecular dynamics simulations at infinite  
610 dilution of nC<sub>7</sub> at  $T=313.25\text{K}$  and  $P=10.11\text{MPa}$ . It has been found that the CO<sub>2</sub> molecules are  
611 affected by the presence of the nC<sub>7</sub> solute over a distance of about 3 nm (the clustering region).  
612 This corresponds to about 950 CO<sub>2</sub> molecules located in the cluster, a value two order of  
613 magnitude higher than the excess number of CO<sub>2</sub>. Concerning the dynamic properties, the  
614 residence time of CO<sub>2</sub> molecules in the clustering region has been found to be diffusive like  
615 with an average value equal to about 25ps confirming the weak nature of the cluster.

616 Finally, thanks to the molecular simulations results and the Kirkwood-Buff Integrals, it  
617 has been possible to provide a microscopic explanation of the link between the clustering effect  
618 and the non-monotonic variation in the density with composition. Indeed, the increase of  
619 density with the mole fraction of n-heptane at high CO<sub>2</sub> content results from the clustering  
620 effect, as the number of CO<sub>2</sub> molecules surrounding a nC<sub>7</sub> molecule is larger than that  
621 surrounding a CO<sub>2</sub> molecule. Thus, adding n-heptane at low content of n-heptane increases  
622 globally the molar density of the mixture. This increase in density, which is reduced when the  
623 clusters overlap, holds up to a mole fraction for which  $G_{CO_2-nC_7} \approx G_{CO_2-CO_2}$  that is  
624 corresponding to a mole fraction of CO<sub>2</sub> of about 96 %, consistently with the noticed change of  
625 sign of the partial molar volume of nC<sub>7</sub> for a similar composition.

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632

633 **Appendix**

634 In this appendix, density, isothermal compressibility, isentropic compressibility and speed of  
 635 sound obtained from MC simulations are first presented. Then, the KBI computed by using the  
 636 approach described in Sect. 3. 2., are provided.

637

638 Table A. 1: Density data of CO<sub>2</sub> + nC<sub>7</sub> obtained from MC simulations.

T (K)	P (MPa)	$\rho$ (kg.m <sup>-3</sup> )									
		$\pm$ Error bars									
X <sub>CO<sub>2</sub></sub> /mol%		0.00%		20.14%		40.00%		60.00%		83.26%	
303.35	10.12	691.8	0.5	708.4	0.8	729.2	0.6	756.0	0.5	790.4	2.0
303.35	20.14	701.1	0.4	719.2	0.4	742.5	0.8	774.4	1.0	826.0	1.4
303.35	30.18	709.7	0.8	728.8	0.6	753.7	0.4	788.8	0.2	851.2	1.0
303.35	40.25	717.8	1.0	737.3	0.3	763.8	0.2	802.2	0.6	872.4	0.7
303.35	50.35	724	0.7	745.8	0.5	773.4	0.7	814.1	0.7	891.0	0.6
303.35	60.47	731.3	0.6	752.9	0.4	781.7	0.5	824.7	0.5	906.8	0.5
303.35	70.62	737.6	0.5	759.6	0.8	789.9	0.2	834.1	0.5	920.4	0.5
313.25	10.11	683	0.5	698.7	0.4	717.5	0.7	739.7	1.1	757.7	2.6
313.25	20.13	693.1	1.0	710.2	0.6	732	0.4	759.9	1.1	799.3	1.7
313.25	30.16	701.9	0.4	720.1	0.4	743.8	0.4	776.1	0.9	831.0	1.8
313.25	40.23	709.8	0.7	729.4	1.0	754.5	1.0	790.6	0.6	854.3	1.4
313.25	50.31	717.5	0.3	737.6	0.8	764.4	0.6	802.3	0.8	873.4	0.7
313.25	60.41	724.1	0.8	745.7	0.3	773.4	1.0	813.5	0.7	890.9	0.6
313.25	70.54	730.5	0.6	752.6	0.3	781.4	0.7	823.9	0.1	905.3	0.8
X <sub>CO<sub>2</sub></sub> /mol%		88.49%		95.00%		99.00%		100%			
303.35	10.12	792.9	4.6	784	3.9	772.2	4.1	760.9	8.1		
303.35	20.14	839.7	3.4	858.3	2.4	868.8	1.6	873	6.4		
303.35	30.18	870.2	3.1	898.5	3.1	923.2	1.5	927.3	2.0		
303.35	40.25	896.2	1.9	930.6	0.8	957.0	2.1	965.9	1.5		
303.35	50.35	916.4	0.1	955.8	0.8	985.9	2.0	996.2	1.5		
303.35	60.47	933.9	0.7	978	0.5	1011.0	0.9	1020	0.6		
303.35	70.62	949.5	1.0	996.4	0.6	1033.0	0.4	1043	0.2		
313.25	10.11	750.9	2.3	716.1	6.8	647.5	6.6	606.9	21.0		
313.25	20.13	809.4	3.4	822.2	4.1	820.2	3.6	819.7	3.6		
313.25	30.16	844.9	2.2	868.9	2.9	884.2	3.5	888.6	4.0		
313.25	40.23	874.3	0.6	901.7	2.5	925.8	1.0	932.5	1.5		
313.25	50.31	895.8	1.3	931.7	1.3	958.4	1.2	965.4	1.3		
313.25	60.41	915.9	0.5	955.1	1.4	985.4	0.4	993.4	1.1		
313.25	70.54	932	0.8	975.4	0.4	1008.0	1.2	1017	1.5		

639

640

641 Table A. 2: Isothermal compressibility data of CO<sub>2</sub> + nC<sub>7</sub> obtained from MC simulations.

T (K)	P (MPa)	$\kappa_T (GPa^{-1})$									
		$\pm$ Error bars									
X <sub>CO<sub>2</sub></sub> /mol%		0.00%		20.14%		40.00%		60.00%		83.26%	
303.35	10.12	1.485	0.101	1.583	0.069	1.945	0.167	2.550	0.184	5.048	1.137
303.35	20.14	1.249	0.029	1.380	0.066	1.635	0.131	2.176	0.111	3.699	0.471
303.35	30.18	1.199	0.074	1.211	0.053	1.386	0.094	1.722	0.104	2.381	0.192
303.35	40.25	1.108	0.079	1.061	0.088	1.230	0.073	1.471	0.078	2.109	0.568
303.35	50.35	0.980	0.058	1.025	0.052	1.115	0.052	1.340	0.087	1.834	0.098
303.35	60.47	0.851	0.059	0.876	0.039	1.005	0.031	1.202	0.069	1.711	0.114
303.35	70.62	0.780	0.048	0.891	0.038	0.929	0.040	1.071	0.024	1.399	0.083
313.25	10.11	1.439	0.090	1.762	0.044	2.053	0.142	2.994	0.167	7.204	0.472
313.25	20.13	1.365	0.070	1.447	0.045	1.742	0.077	2.328	0.088	4.335	0.515
313.25	30.16	1.187	0.053	1.282	0.093	1.514	0.041	1.972	0.124	3.136	0.338
313.25	40.23	1.108	0.066	1.149	0.039	1.442	0.047	1.631	0.106	2.159	0.255
313.25	50.31	1.049	0.061	1.083	0.031	1.237	0.045	1.365	0.061	1.978	0.066
313.25	60.41	0.949	0.020	0.960	0.046	1.100	0.040	1.272	0.057	1.752	0.082
313.25	70.54	0.882	0.041	0.890	0.072	0.992	0.025	1.130	0.078	1.549	0.087
X <sub>CO<sub>2</sub></sub> /mol%		88.49%		95.00%		99.00%		100%			
303.35	10.12	7.120	1.356	13.370	2.842	16.937	5.611	27.651	5.372		
303.35	20.14	4.192	0.322	5.824	0.592	7.168	0.631	7.578	1.132		
303.35	30.18	3.150	0.196	4.040	0.552	4.265	0.524	4.748	0.414		
303.35	40.25	2.536	0.397	2.868	0.190	3.122	0.100	3.309	0.126		
303.35	50.35	2.126	0.134	2.359	0.098	2.581	0.071	2.695	0.159		
303.35	60.47	1.781	0.103	1.966	0.061	2.089	0.150	2.266	0.056		
303.35	70.62	1.548	0.079	1.732	0.065	1.805	0.044	1.933	0.139		
313.25	10.11	11.473	3.313	25.939	7.663	74.370	19.951	116.3	13.5		
313.25	20.13	5.213	0.687	7.263	0.372	9.481	1.230	11.063	2.079		
313.25	30.16	3.915	0.421	4.461	0.280	5.575	0.788	5.567	0.442		
313.25	40.23	2.786	0.110	3.497	0.415	4.063	0.112	3.956	0.377		
313.25	50.31	2.352	0.158	2.733	0.093	2.959	0.106	3.191	0.169		
313.25	60.41	1.939	0.085	2.178	0.127	2.519	0.162	2.558	0.145		
313.25	70.54	1.676	0.100	1.816	0.063	2.088	0.034	2.153	0.097		

642

643 Table A. 3: Isentropic compressibility data of CO<sub>2</sub> + nC<sub>7</sub> obtained from Eq. 9 using the  
 644 simulation data.

T (K)	P (MPa)	$\kappa_s (GPa^{-1})$ $\pm$ Error bars										
X <sub>CO<sub>2</sub></sub> /mol%		0.00%		20.14%		40.00%		60.00%		83.26%		
303.35	10.12	1.144	0.113	1.199	0.078	1.394	0.202	1.676	0.225	2.647	1.490	
303.35	20.14	0.981	0.033	1.056	0.078	1.193	0.157	1.432	0.142	1.963	0.659	
303.35	30.18	0.929	0.089	0.939	0.063	1.023	0.113	1.181	0.123	1.426	0.270	
303.35	40.25	0.864	0.092	0.838	0.114	0.923	0.085	1.032	0.100	1.256	0.746	
303.35	50.35	0.776	0.066	0.798	0.059	0.843	0.063	0.939	0.107	1.097	0.130	
303.35	60.47	0.688	0.067	0.700	0.046	0.764	0.039	0.854	0.086	1.017	0.155	
303.35	70.62	0.638	0.055	0.696	0.044	0.712	0.050	0.772	0.030	0.871	0.113	
313.25	10.11	1.142	0.100	1.322	0.053	1.504	0.164	1.950	0.208	3.580	0.623	
313.25	20.13	1.062	0.079	1.117	0.053	1.279	0.091	1.566	0.104	2.314	0.762	
313.25	30.16	0.945	0.059	0.997	0.108	1.126	0.044	1.348	0.152	1.750	0.488	
313.25	40.23	0.878	0.074	0.904	0.046	1.056	0.062	1.136	0.133	1.328	0.311	
313.25	50.31	0.829	0.069	0.844	0.037	0.923	0.055	0.982	0.073	1.198	0.084	
313.25	60.41	0.761	0.022	0.764	0.052	0.834	0.049	0.904	0.071	1.063	0.111	
313.25	70.54	0.707	0.046	0.707	0.081	0.763	0.032	0.821	0.093	0.950	0.116	
X <sub>CO<sub>2</sub></sub> /mol%		88.49%		95.00%		99.00%		100%				
303.35	10.12	3.337	1.897	4.660	4.827	5.188	4.069	6.871	10.070			
303.35	20.14	2.110	0.497	2.514	0.930	2.759	0.972	2.802	1.820			
303.35	30.18	1.643	0.268	1.812	0.818	1.802	0.814	1.871	0.594			
303.35	40.25	1.371	0.541	1.400	0.279	1.409	0.150	1.418	0.233			
303.35	50.35	1.164	0.188	1.191	0.145	1.193	0.109	1.207	0.242			
303.35	60.47	1.012	0.141	1.025	0.085	1.004	0.227	1.035	0.076			
303.35	70.62	0.896	0.106	0.907	0.092	0.887	0.062	0.902	0.203			
313.25	10.11	4.529	5.287	8.227	13.149	13.546	37.932	17.990	23.832			
313.25	20.13	2.591	1.034	3.065	0.503	3.538	1.950	3.810	3.407			
313.25	30.16	2.008	0.556	2.056	0.488	2.270	1.155	2.246	0.709			
313.25	40.23	1.507	0.140	1.674	0.606	1.760	0.229	1.699	0.560			
313.25	50.31	1.300	0.219	1.351	0.119	1.353	0.159	1.400	0.266			
313.25	60.41	1.108	0.121	1.132	0.180	1.161	0.252	1.178	0.220			
313.25	70.54	0.977	0.132	0.970	0.096	1.000	0.043	1.003	0.147			

645

646 Table A. 4: Speed of sound data of CO<sub>2</sub> + nC<sub>7</sub> calculated from Eq. 10 using the simulation data.

T (K)	P (MPa)	$w$ (m.s <sup>-1</sup> )									
		± Error bars									
X <sub>CO<sub>2</sub></sub> /mol%		0.00%		20.14%		40.00%		60.00%		83.26%	
		303.35	10.12	1124.2	55.3	1084.9	34.5	992.0	71.6	888.4	59.4
303.35	20.14	1205.8	20.2	1147.6	42.2	1062.7	69.5	949.5	46.6	785.3	131.2
303.35	30.18	1231.9	58.0	1208.6	40.3	1139.0	62.6	1036.0	54.0	907.5	85.4
303.35	40.25	1270.1	66.9	1272.6	86.3	1191.2	54.4	1099.1	52.6	955.3	283.3
303.35	50.35	1334.5	55.8	1296.5	47.2	1238.1	45.5	1143.7	64.6	1011.3	59.8
303.35	60.47	1409.9	68.1	1377.5	44.7	1294.0	32.3	1191.4	59.8	1041.6	79.3
303.35	70.62	1457.3	62.2	1375.8	42.9	1333.7	46.6	1246.3	24.1	1116.9	71.9
313.25	10.11	1132.2	49.4	1040.5	20.6	962.6	51.9	832.5	43.7	607.2	51.8
313.25	20.13	1165.4	42.4	1122.9	26.0	1033.3	36.3	916.7	29.8	735.2	120.3
313.25	30.16	1228.0	37.8	1180.1	63.3	1092.6	21.2	977.6	54.4	829.2	114.8
313.25	40.23	1266.4	52.7	1231.2	30.6	1120.5	32.1	1055.3	61.5	938.8	109.1
313.25	50.31	1296.9	53.9	1267.1	26.9	1190.3	35.2	1126.5	41.1	977.4	33.9
313.25	60.41	1347.1	18.8	1325.2	44.7	1244.9	35.9	1166.3	45.0	1027.5	53.5
313.25	70.54	1391.8	44.8	1370.6	78.5	1295.1	26.4	1215.7	68.6	1078.1	65.4
X <sub>CO<sub>2</sub></sub> /mol%		88.49%		95.00%		99.00%		100%			
303.35	10.12	614.8	173.0	523.2	269.7	499.6	194.6	437.4	318.2		
303.35	20.14	751.2	86.9	680.7	124.9	645.9	113.2	639.4	205.3		
303.35	30.18	836.4	66.6	783.8	175.5	775.4	174.4	759.2	119.6		
303.35	40.25	902.2	177.0	876.3	86.9	861.1	44.9	854.3	69.5		
303.35	50.35	968.3	78.2	937.2	56.6	922.2	41.2	911.9	90.8		
303.35	60.47	1028.7	71.3	999.0	41.2	992.6	111.8	973.2	35.5		
303.35	70.62	1084.2	63.3	1051.8	53.2	1044.4	36.3	1030.9	115.9		
313.25	10.11	542.3	315.7	412.0	327.3	337.7	471.1	302.6	195.2		
313.25	20.13	690.5	136.3	629.9	50.1	587.0	160.5	565.9	251.8		
313.25	30.16	767.7	105.3	748.2	87.6	705.9	178.2	707.9	110.1		
313.25	40.23	871.1	40.2	813.9	146.3	783.5	50.5	794.6	130.4		
313.25	50.31	926.8	77.4	891.2	38.7	878.0	51.0	860.2	81.2		
313.25	60.41	992.5	53.9	961.5	75.6	934.9	101.1	924.3	85.8		
313.25	70.54	1047.9	70.4	1027.9	50.4	996.2	21.0	990.2	71.9		

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648 Table A. 5: Kirkwood-Buff Integrals of CO<sub>2</sub>-CO<sub>2</sub>.

T (K)	P (MPa)	$G_{\text{CO}_2\text{-CO}_2} (nm^3)$									
		$\pm$ Error bars		20.14%		40.00%		60.00%		83.26%	
$X_{\text{CO}_2}/\text{mol}\%$		0.00%									
303.35	10.12	-	-	0.1440	0.0051	0.1344	0.0037	0.2820	0.0286	0.1340	0.0151
303.35	20.14	-	-	0.2986	0.0356	0.1066	0.0072	0.1447	0.0027	0.0740	0.0017
303.35	30.18	-	-	0.2226	0.0217	0.0771	0.0106	0.2229	0.0153	0.0646	0.0004
303.35	40.25	-	-	0.2087	0.0184	0.0797	0.0161	0.1194	0.0088	0.1120	0.0109
303.35	50.35	-	-	0.2290	0.0245	0.0731	0.0204	0.1868	0.0098	0.1235	0.0111
303.35	60.47	-	-	0.1426	0.0112	0.1143	0.0058	0.1130	0.0073	0.1516	0.0194
303.35	70.62	-	-	0.2891	0.0432	0.1346	0.0034	0.2680	0.0315	0.1159	0.0114
313.25	10.11	-	-	-0.0618	0.0397	0.0906	0.0105	0.1580	0.0082	0.1151	0.0144
313.25	20.13	-	-	0.1890	0.0185	0.2089	0.0165	0.1785	0.0096	0.0968	0.0072
313.25	30.16	-	-	0.1329	0.0057	0.1575	0.0046	0.1359	0.0008	0.0927	0.0082
313.25	40.23	-	-	0.1550	0.0026	0.1246	0.0039	0.1392	0.0014	0.0686	0.0040
313.25	50.31	-	-	0.0172	0.0176	0.1101	0.0056	0.1541	0.0085	0.1038	0.0119
313.25	60.41	-	-	0.2785	0.0513	0.1398	0.0099	0.1778	0.0125	0.0992	0.0081
313.25	70.54	-	-	0.3168	0.0535	0.2037	0.0174	0.1581	0.0047	0.0871	0.0073
$X_{\text{CO}_2}/\text{mol}\%$		88.49%		95.00%		99.00%		100%			
303.35	10.12	0.0509	0.0039	-0.0240	0.0002	-0.0098	0.0016	0.0129	0.0047		
303.35	20.14	0.0489	0.0025	-0.0249	0.0008	-0.0477	0.0008	-0.0525	0.0004		
303.35	30.18	0.0475	0.0044	-0.0203	0.0015	-0.0554	0.0000	-0.0597	0.0001		
303.35	40.25	0.0292	0.0003	-0.0280	0.0007	-0.0581	0.0001	-0.0623	0.0002		
303.35	50.35	0.0487	0.0037	-0.0231	0.0015	-0.0582	0.0002	-0.0630	0.0001		
303.35	60.47	0.0188	0.0036	-0.0239	0.0004	-0.0583	0.0003	-0.0627	0.0001		
303.35	70.62	0.0656	0.0077	-0.0157	0.0023	-0.0571	0.0000	-0.0625	0.0001		
313.25	10.11	0.0311	0.0016	-0.0087	0.0004	0.1823	0.0237	0.3503	0.0447		
313.25	20.13	0.0590	0.0086	-0.0355	0.0012	-0.0437	0.0007	-0.0427	0.0010		
313.25	30.16	0.0326	0.0020	-0.0326	0.0005	-0.0554	0.0001	-0.0558	0.0008		
313.25	40.23	0.0228	0.0019	-0.0301	0.0000	-0.0568	0.0004	-0.0625	0.0002		
313.25	50.31	0.0504	0.0065	-0.0305	0.0004	-0.0585	0.0000	-0.0632	0.0001		
313.25	60.41	0.0330	0.0027	-0.0243	0.0016	-0.0598	0.0005	-0.0635	0.0000		
313.25	70.54	0.0518	0.0063	-0.0332	0.0009	-0.0578	0.0002	-0.0631	0.0001		

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650 Table A. 6: Kirkwood-Buff Integrals of CO<sub>2</sub>-nC<sub>7</sub>.

T (K)	P (MPa)	$G_{\text{CO}_2\text{-C}_7}$ (nm <sup>3</sup> ) ± Error bars		20.14%		40.00%		60.00%		83.26%	
				X <sub>CO<sub>2</sub></sub> /mol%		Infinite dilution					
303.35	10.12	-	-	-0.0937	0.0007	-0.1221	0.0009	-0.2644	0.0159	-0.4575	0.0310
303.35	20.14	-	-	-0.1041	0.0032	-0.1120	0.0016	-0.1844	0.0008	-0.3239	0.0045
303.35	30.18	-	-	-0.0940	0.0015	-0.1032	0.0022	-0.2184	0.0082	-0.2921	0.0012
303.35	40.25	-	-	-0.0895	0.0010	-0.1005	0.0037	-0.1615	0.0042	-0.3575	0.0171
303.35	50.35	-	-	-0.0917	0.0020	-0.0986	0.0043	-0.1899	0.0046	-0.3665	0.0167
303.35	60.47	-	-	-0.0837	0.0009	-0.1052	0.0012	-0.1523	0.0036	-0.4044	0.0295
303.35	70.62	-	-	-0.0916	0.0027	-0.1080	0.0008	-0.2228	0.0149	-0.3434	0.0168
313.25	10.11	0.0773	0.0150	-0.0778	0.0032	-0.1156	0.0024	-0.2091	0.0059	-0.4605	0.0345
313.25	20.13	-	-	-0.0970	0.0018	-0.1364	0.0035	-0.2083	0.0056	-0.3781	0.0144
313.25	30.16	-	-	-0.0906	0.0001	-0.1242	0.0012	-0.1763	0.0003	-0.3518	0.0149
313.25	40.23	-	-	-0.0910	0.0008	-0.1128	0.0009	-0.1771	0.0013	-0.2949	0.0061
313.25	50.31	-	-	-0.0783	0.0008	-0.1082	0.0012	-0.1773	0.0039	-0.3438	0.0183
313.25	60.41	-	-	-0.0946	0.0038	-0.1116	0.0019	-0.1862	0.0060	-0.3297	0.0121
313.25	70.54	-	-	-0.0975	0.0041	-0.1231	0.0034	-0.1726	0.0017	-0.3041	0.0105
X <sub>CO<sub>2</sub></sub> /mol%		88.49%		95.00%		99.00%		Infinite dilution			
303.35	10.12	-0.3983	0.0086	-0.1919	0.0115	-0.0515	0.0127	-	-	-	-
303.35	20.14	-0.3902	0.0094	-0.3063	0.0064	-0.2442	0.0046	-	-	-	-
303.35	30.18	-0.3657	0.0118	-0.3342	0.0087	-0.1923	0.0121	-	-	-	-
303.35	40.25	-0.3072	0.0006	-0.2862	0.0031	-0.2145	0.0049	-	-	-	-
303.35	50.35	-0.3453	0.0082	-0.3052	0.0066	-0.2157	0.0065	-	-	-	-
303.35	60.47	-0.2656	0.0098	-0.2975	0.0011	-0.2035	0.0094	-	-	-	-
303.35	70.62	-0.3749	0.0180	-0.3463	0.0137	-0.2271	0.0032	-	-	-	-
313.25	10.11	-0.3866	0.0110	-0.0701	0.0209	0.4651	0.0700	0.7559	0.2062	-	-
313.25	20.13	-0.4372	0.0286	-0.2449	0.0052	-0.1823	0.0039	-	-	-	-
313.25	30.16	-0.3454	0.0079	-0.2650	0.0033	-0.2032	0.0054	-	-	-	-
313.25	40.23	-0.3009	0.0050	-0.2896	0.0000	-0.2782	0.0097	-	-	-	-
313.25	50.31	-0.3591	0.0156	-0.2789	0.0017	-0.2331	0.0018	-	-	-	-
313.25	60.41	-0.3093	0.0062	-0.3071	0.0091	-0.1883	0.0155	-	-	-	-
313.25	70.54	-0.3473	0.0143	-0.2466	0.0062	-0.2307	0.0024	-	-	-	-

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652 Table A.7: Kirkwood-Buff Integrals of nC<sub>7</sub>-nC<sub>7</sub>.

T (K)	P (MPa)	$G_{C_7-C_7} (nm^3)$									
		$\pm$ Error bars									
$X_{CO_2}/mol\%$		0.00%		20.14%		40.00%		60.00%		83.26%	
303.35	10.12	-0.2345	0.0003	-0.2457	0.0004	-0.2572	0.0002	-0.2074	0.0094	0.2928	0.0674
303.35	20.14	-0.2321	0.0002	-0.2420	0.0006	-0.2568	0.0000	-0.2492	0.0004	-0.0227	0.0127
303.35	30.18	-0.2298	0.0002	-0.2407	0.0003	-0.2559	0.0002	-0.2292	0.0049	-0.0976	0.0044
303.35	40.25	-0.2278	0.0002	-0.2387	0.0003	-0.2539	0.0005	-0.2556	0.0015	-0.0007	0.0287
303.35	50.35	-0.2258	0.0002	-0.2361	0.0004	-0.2515	0.0006	-0.2402	0.0025	0.0071	0.0261
303.35	60.47	-0.2240	0.0002	-0.2346	0.0002	-0.2477	0.0001	-0.2556	0.0014	0.0666	0.0464
303.35	70.62	-0.2223	0.0002	-0.2324	0.0004	-0.2451	0.0002	-0.2199	0.0074	-0.0292	0.0259
313.25	10.11	-0.2371	0.0002	-0.2499	0.0000	-0.2617	0.0001	-0.2359	0.0049	0.4148	0.0892
313.25	20.13	-0.2345	0.0002	-0.2451	0.0005	-0.2544	0.0011	-0.2383	0.0038	0.1014	0.0313
313.25	30.16	-0.2321	0.0002	-0.2431	0.0002	-0.2534	0.0007	-0.2547	0.0006	0.0119	0.0289
313.25	40.23	-0.2297	0.0002	-0.2406	0.0004	-0.2536	0.0005	-0.2497	0.0015	-0.1032	0.0106
313.25	50.31	-0.2277	0.0002	-0.2391	0.0003	-0.2521	0.0000	-0.2487	0.0023	-0.0263	0.0297
313.25	60.41	-0.2259	0.0002	-0.2362	0.0005	-0.2491	0.0007	-0.2420	0.0032	-0.0507	0.0193
313.25	70.54	-0.2241	0.0002	-0.2339	0.0005	-0.2444	0.0010	-0.2466	0.0010	-0.0922	0.0164
$X_{CO_2}/mol\%$		88.49%		95.00%		99.00%		100%			
303.35	10.12	0.4597	0.0311	0.5377	0.0026	0.5103	0.0329	-	-		
303.35	20.14	0.3124	0.0364	0.5348	0.0631	1.9069	0.3033	-	-		
303.35	30.18	0.1721	0.0349	0.5765	0.0710	-0.6026	0.3108	-	-		
303.35	40.25	0.0022	0.0038	0.1837	0.0203	-0.2416	0.1062	-	-		
303.35	50.35	0.0834	0.0200	0.2542	0.0314	-0.3562	0.1848	-	-		
303.35	60.47	-0.1165	0.0254	0.2232	0.0036	-0.9160	0.3190	-	-		
303.35	70.62	0.1546	0.0438	0.5478	0.0875	-0.1048	0.1101	-	-		
313.25	10.11	0.7609	0.0801	1.3049	0.0894	2.7129	0.1729	-	-		
313.25	20.13	0.5062	0.0985	0.4773	0.0397	1.6688	0.2691	-	-		
313.25	30.16	0.1630	0.0302	0.2036	0.0006	0.4561	0.0630	-	-		
313.25	40.23	-0.0025	0.0171	0.2567	0.0079	1.7278	0.2969	-	-		
313.25	50.31	0.1226	0.0391	0.1596	0.0142	0.2187	0.0386	-	-		
313.25	60.41	-0.0046	0.0156	0.3026	0.0577	-1.1778	0.4613	-	-		
313.25	70.54	0.0858	0.0340	-0.0769	0.0395	0.1800	0.1103	-	-		

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