Equilibrium and transport properties of CO2+N2O and CO2+NO mixtures: a molecular simulation and equation of state modelling study.

V. Lachet, B. Creton, T. De Bruin, E. Bourasseau, Nicolas Desbiens, O. Wilhelmsen, M. Hammer

To cite this version:

V. Lachet, B. Creton, T. De Bruin, E. Bourasseau, Nicolas Desbiens, et al.. Equilibrium and transport properties of CO2+N2O and CO2+NO mixtures: a molecular simulation and equation of state modelling study.. Fluid Phase Equilibria, Elsevier, 2012, 322, pp.66-78. <10.1016/j.fluid.2012.03.011>. <hal-00681797>

HAL Id: hal-00681797
https://hal-ifp.archives-ouvertes.fr/hal-00681797
Submitted on 22 Mar 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Equilibrium and transport properties of CO$_2$+N$_2$O and CO$_2$+NO mixtures. A molecular simulation and equation of state modelling study.

V. Lachet$^{a,*}$, B. Creton$^a$, T. de Bruin$^a$, E. Bourasseau$^b$, N. Desbiens$^b$, Ø. Wilhelmsen$^c$, M. Hammer$^c$

$^a$ IFP Energies nouvelles, 1 et 4 avenue de Bois Préau, 92852 Rueil-Malmaison, France
$^b$ CEA, DAM, DIF, F-91297 Arpajon, France
$^c$ SINTEF Energy Research, Kolbjørn Hejes vei 1A, 7465 Trondheim, Norway

Abstract
In the present study, the thermodynamic behaviour and transport properties of CO$_2$+N$_2$O and CO$_2$+NO mixtures have been investigated using molecular simulation and equation of state modelling. Molecular simulations were based on Monte Carlo and Molecular Dynamics calculations using force fields calibrated from pure component properties and no adjustment of mixture properties was performed. Original force fields were proposed for N$_2$O, NO and N$_2$O$_2$ molecules. Special attention must be paid when studying nitric oxide containing systems because this compound can exist as a mixture of monomers (NO) and dimers (N$_2$O$_2$) under certain pressure and temperature conditions. Liquid-vapour coexistence properties of the reacting NO-N$_2$O$_2$ system were thus first investigated using combined reaction ensemble and Gibbs ensemble Monte Carlo methods. Using the new force fields proposed, phase compositions, phase densities and phase viscosities were determined for CO$_2$+NO mixture. Due to the strong similarities between carbon dioxide and nitrous oxide ($T_c$(CO$_2$) = 304.21 K; $T_c$(N$_2$O) = 309.57 K; $P_c$(CO$_2$) = 7.38 MPa; $P_c$(N$_2$O) = 7.24 MPa), the obtained thermodynamic and transport properties for a CO$_2$+N$_2$O mixture with 10 mol% of N$_2$O are similar to pure CO$_2$ properties in the whole range of studied temperatures (273 – 293 K), in agreement with available experimental data. Calculations of CO$_2$+NO equilibrium and transport properties were also performed at three different temperatures in the range of 253 – 273 K. At these temperatures, only the monomer form of the nitric oxide (NO) has to be accounted for. The performed calculations are pure predictions since no experimental data are available in the open literature for this system. For a mixture containing 10 mol% of NO, the simulation results show a decrease of the liquid densities and viscosities of 9% and 24% with respect to corresponding pure CO$_2$ values, respectively. The new pseudo-experimental data generated in this work were finally used to calibrate binary interaction parameters required in standard cubic equations of states. Both Peng-Robinson and Soave-Redlich-Kwong equations of state have been considered and after the regression, they display a decent match with experimental and pseudo-experimental data of the vapour-liquid equilibrium for the two studied mixtures.

Keywords: CO$_2$ capture and storage; VLE data; Viscosity; Molecular simulation; Equation of state.

1. Introduction
In Carbon dioxide Capture and Storage (CCS) operations, the captured CO$_2$ stream from industrial installations is not a pure CO$_2$; it contains some associated compounds, also called
contaminants, such as N₂, O₂, Ar, SOₓ, NOₓ... [1]. This mixture of gases may have significantly different thermo-physical properties as compared to a pure carbon dioxide. This may have impacts on the different stages of the CCS chain: capture, transportation, compression, injection and storage. To globally account for this impact and for a precise specification of maximal amounts of contaminants that can be tolerated in CO₂ flues, further investigations are strongly desired. Obtaining accurate knowledge of the thermodynamic and transport behaviour of CO₂+contaminant mixtures is part of the studies that are necessary in order to develop optimized carbon dioxide capture and storage processes. Some of these CO₂+contaminant mixtures, like CO₂+O₂ and CO₂+N₂ for instance, have already been studied over a large range of pressures and temperatures. A comprehensive review of available equilibrium and transport properties of CO₂+contaminant mixtures is proposed in two recent papers by Li and co-workers [2,3]. In the case of CO₂+NOₓ mixtures, data are very scarce or nonexistent. As far as the CO₂+NO mixture is concerned, to the best of our knowledge, no experimental data are available in the literature. Concerning liquid-vapour equilibrium of the CO₂+N₂O mixture, some experimental data are reported in the works of Caubet [4,5], of Cook [6] and of Rowlinson [7]. These liquid-vapour equilibrium data cover some temperatures between 277 and 311 K and pressures between 3.5 and 7.5 MPa. Excess properties of CO₂+N₂O mixtures are also reported in the literature: excess enthalpies and excess volumes have been measured by Wormald [8] and by Cabanas [9] for both liquid and vapour CO₂+N₂O mixtures. Concerning CO₂+N₂O viscosities, some values at atmospheric pressure are reported by Kestin [10] for temperatures in the range 298 – 473 K and for N₂O contents of 31 and 65 mol%.

The objective of the present work is to compensate the lack of experimental data by generating so-called pseudo-experimental data based on numerical experiments using molecular simulation calculations. Molecular simulation is a widespread technique which consists of performing a detailed simulation of microscopic systems and of calculating appropriate averages in order to derive macroscopic fluid properties. Phase compositions, phase densities and phase viscosities of CO₂+N₂O and CO₂+NO mixtures have been determined using Monte Carlo and/or Molecular Dynamics simulations for temperatures in the range 253 – 293 K. These calculations have been performed using force fields based on pure component properties and no adjustment on mixture properties was required. In order to achieve accurate predictions, new optimized force fields were proposed for both nitrous oxide and nitric oxide molecules. Finally, standard cubic equations of states have been optimized in order to reproduce the thermodynamic behaviour of both mixtures. Available experimental data or our new simulated data were taken into account in the parameter regression procedure.

This article is organized as follows. In Section 2, the description of the simulation methods and expressions used to compute intermolecular potential energy are given. The new force fields developed to model N₂O and NO molecules are presented in Section 3.1 where they are tested with respect to their ability to reproduce thermodynamic and transport properties of pure compounds. In Sections 3.2 and 3.3, we present and discuss the simulated results obtained for the two studied binary mixtures. Section 3.4 is devoted to the calibration of standard thermodynamic models. This paper ends with a fourth section which contains our conclusions.

2. Simulation methods

2.1. Monte Carlo method
The liquid–vapour equilibrium data of pure compounds and binary mixtures were obtained with Monte Carlo (MC) simulations using the GIBBS Monte Carlo code [11]. These simulations were performed in the Gibbs NVT ensemble (constant number of particles N, constant total volume V and constant temperature T) or Gibbs NPT ensemble (constant number of particles N, constant pressure P and constant temperature T) [12]. In such simulations, the two phases are simulated in individual boxes without an explicit interface, and particle transfers between boxes are performed in order to ensure phase equilibrium. In most cases, the following Monte Carlo moves were used in order to sample the configurational space:
- internal moves (rigid body translation and rotation of a molecule),
- volume changes (opposite volume changes $+\Delta V$ and $-\Delta V$ are applied to the two boxes in the case of Gibbs NVT simulations in order to keep the total volume constant),
- transfers between phases based on the pre-insertion bias. This pre-insertion bias algorithm, used to improve the efficiency of the sampling [13], involves two steps. The first step consists in the selection of a suitable location for inserting a new molecule by testing several places with a simple Lennard-Jones particle. The second step involves the test of several molecular orientations with the centre of mass at the location selected in the first step.
In the case of NO-containing systems, one additional Monte Carlo move, the reaction move, has been used in order to account for the possible dimerization of two NO molecules into $N_2O_2$. These particular simulations are described in section 3.1.2. For all other studied systems, the selected probabilities for the different Monte Carlo moves are 0.3 for translations, 0.3 for rotations, 0.395 for transfers, and 0.005 for volume changes. A total number of 500 to 800 molecules has been considered in our MC simulations, depending on the proximity of the studied temperature to critical temperatures of involved species. A total number of at least 50 million Monte Carlo iterations have been performed for each studied condition.

For the different studied molecules, the molar enthalpy of vaporization was computed at different temperatures as the difference between the average molar enthalpies of the vapour and liquid simulation boxes. The statistical uncertainties of the calculated phase properties were estimated by the block averaging technique [14]. The statistical uncertainties on the molar enthalpy of vaporization are typically 2–3%. The saturated vapour pressure was computed using the Virial equation, and the associated statistical uncertainty was less than 5%. The average liquid density was generally determined with a statistical uncertainty of 1–2% for both pure compounds and mixtures, but higher values are found at near-critical temperatures as a result of larger fluctuations.

2.2. Molecular Dynamics

Properties such as the density and the dynamic viscosity have been calculated using Molecular Dynamics (MD) simulations with NEWTON, a MD code developed for flexible and rigid molecules [15]. In contrast to the MC procedure, MD simulations follow the time evolution of a molecular system by numerically integrating Newton's equations of motion. Simulations in the isobaric-isothermal ensemble (NPT) were performed to compute the density and the viscosity of the considered systems. Up to 1000 molecules were considered in our MD simulations. The velocity Verlet algorithm was used to integrate the equations of motion, with a time step of 1 fs. Practically, MD simulations were split in two parts: (i) one having a 0.2 ns length ($2.10^5$ steps) intended to the equilibration of the system, (ii) one with a 5 ns length ($5.10^6$ steps) that is dedicated to the calculation of the desired properties.
As described in previous works [16,17], the viscosity can be calculated either in the canonical ensemble (NVT) or in the isobaric-isothermal ensemble (NPT). The Einstein relation was employed to compute the viscosity $\eta$ of systems of interest using the following expression

$$\eta = \frac{1}{20 k_B T} \lim_{t \to \infty} \frac{d}{dt} \left[ \sum_{\alpha} \langle \Delta P_{\alpha \alpha}^T(t)^2 \rangle + 2 \sum_{\alpha \neq \beta} \langle \Delta P_{\alpha \beta}^T(t)^2 \rangle \right]$$

(1)

where, $\alpha$ and $\beta$ run over the three cartesian coordinates, $k_B$ is the Boltzmann constant, $V$ is the volume, $T$ the temperature and $\Delta P_{\alpha \beta}$ denotes the displacement of the elements of the pressure tensor $P_{\alpha \beta}$.

2.3. Interaction potential and calculation procedure

All the molecules involved in this study have been considered to be rigid, thus no intramolecular energy has been accounted for. Only intermolecular energy has been calculated with the two following contributions: dispersion - repulsion and electrostatic. Dispersion-repulsion energy between two force centres is represented as a function of their separation distance $r$ with a Lennard-Jones (LJ) potential:

$$U_{\text{LJ}} = U_{\text{rep}} + U_{\text{disp}} = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}$$

(2)

In the case of binary interactions involving different force centres $i$ and $j$, two combining rules have been used following requirements of intermolecular potentials. Lorentz-Berthelot combining rules are defined by:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (3)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (4)$$

The geometric combining rules are defined by:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (5)$$

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad (6)$$

Unless specified otherwise, Lorentz-Berthelot combining rules have been used to be consistent with previous studies [18-20].

Electrostatic energy is computed from the Coulomb law, assuming that the molecules bear electrostatic point charges:

$$U_{\text{elec}} = \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}$$

(7)

where $q_i$ and $q_j$ are two charges belonging to different molecules, $r_{ij}$ is the distance separating the charges and $\varepsilon_0$ is the vacuum permittivity.

Numerical values of the involved parameters for all studied molecules, i.e. Lennard-Jones diameters, Lennard-Jones well depths and electrostatic charges, will be discussed and given in the following sections.

Calculation of intermolecular energy is made by applying periodic boundary conditions, following classical procedures of molecular simulations [14,21]. Lennard-Jones interactions
have been computed by applying a cut-off distance set to half of the box length. A standard
long distance correction was used to account for interactions beyond the cut-off distance. The
calculation of electrostatic interactions has been done using the Ewald summation method
with 7 vectors in each space direction and a Gaussian width set to $2\pi/L$, where $L$ is the size of
the simulation box.

3. Results

3.1. New interaction potentials for $\text{N}_2\text{O}$ and NO

3.1.1. Model for nitrous oxide

Two intermolecular potentials suitable for liquid-vapour equilibrium studies are available in
the literature to model nitrous oxide ($\text{N}_2\text{O}$) molecules. Both are based on Lennard-Jones plus
point charge models. The first one has been proposed by Costa Gomes et al. in 2006 [22] and
the second one by Hansen et al. one year later [23]. The parameters of these two potentials are
summarized in Table 1. The accuracy of the models can be evaluated from Fig. 1 to 3 where
calculated equilibrium properties are compared to available experimental data. Note that for
simulations employing the Costa Gomes force field geometric mixing rules are used for both
the size and the energy parameters, whereas classical Lorentz-Berthelot combining rules are
used in the Hansen potential. Although both models have been fitted to vapour-liquid
equilibrium data, the degree of agreement between experimental and simulated values is not
fully satisfying. The first step of the present work was thus the determination of a new
interaction potential for nitrous oxide that allows a better quantitative agreement between
simulation and experiment over a wide range of temperatures. In the proposed model, the N-N
and N-O distances, as well as the N-N-O angle, were fixed to their experimental values [24]
($l_{\text{N}_1-\text{N}_2} = 1.1282$ Å; $l_{\text{N}_2-\text{O}} = 1.1842$ Å and $l_{\text{N}_1-\text{N}_2-\text{O}} = 180^\circ$). Three Lennard-Jones and three
point charges have been considered located on the three atoms of the molecule. In order to
achieve a good degree of accuracy, the two nitrogen atoms of the molecule have been
modelled by two different force centres as previously proposed by Hansen et al. The point
charges and the Lennard-Jones parameters of the two nitrogen atoms and of the oxygen atom
have been optimized using the following objective function [25]:

$$F = \sum_{i=1}^{a} \left( \frac{X_i^\text{sim} - X_i^\text{exp}}{S_i} \right),$$

where the sum runs over saturation properties (density, vaporization enthalpy and saturated
vapour pressure), $X_i^\text{exp}$ stands for experimental measurements, $X_i^\text{sim}$ denotes the associated
computed properties, and $S_i$ are the estimated statistical uncertainties on $X_i^\text{sim}$ calculated by
the block averaging technique. The minimization of the $F$ function was realized as described
in previous works [13,26] using a first-order Taylor expansion of thermodynamic properties
versus potential parameters. For this purpose the gradient of $F$ versus the potential parameters
was obtained by a fluctuation method [11,27]. It was found that any direct optimization
attempt involving more than two parameters failed to converge towards a better optimum,
which is a known result from statistical uncertainties in a context where some parameter
variations may compensate for each other (this is for instance the case between the Lennard
Jones diameters of oxygen and nitrogen atoms). Thus the optimization has been performed by
successive steps using 1D- and 2D-subspaces of the full parameter set. Moreover, due to the
similar electronic environments of the $\text{N}_1$ and the O atoms in the $\text{N}_2\text{O}$ molecule, identical
charges on these two atoms have been imposed. The optimization procedure leads to the charges and Lennard-Jones parameters presented in Table 1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Site</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O (this work)</td>
<td>N1</td>
<td>78.107</td>
<td>3.116</td>
<td>-0.3400</td>
<td>$l_{N1-N2} = 1.1282$</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>34.647</td>
<td>2.927</td>
<td>0.6800</td>
<td>$l_{N2-O} = 1.1842$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>65.891</td>
<td>3.044</td>
<td>-0.3400</td>
<td></td>
</tr>
<tr>
<td>N$_2$O (Costa Gomes et al. [22])</td>
<td>N1</td>
<td>56.527</td>
<td>3.150</td>
<td>-0.2497</td>
<td>$l_{N1-N2} = 1.1280$</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>56.527</td>
<td>3.150</td>
<td>0.5159</td>
<td>$l_{N2-O} = 1.1840$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>78.177</td>
<td>3.050</td>
<td>-0.2662</td>
<td></td>
</tr>
<tr>
<td>N$_2$O (Hansen et al. [23])</td>
<td>N1</td>
<td>79.167</td>
<td>3.120</td>
<td>-0.3630</td>
<td>$l_{N1-N2} = 1.1282$</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>27.000</td>
<td>2.800</td>
<td>0.7130</td>
<td>$l_{N2-O} = 1.1842$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>79.000</td>
<td>3.050</td>
<td>-0.3500</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 to 3 compare experimental data and results obtained by Monte Carlo simulations in the Gibbs NVT ensemble using the models of Costa Gomes, of Hansen and our new force field. The respective average absolute deviations for the densities, the vaporization enthalpies and the saturated vapour pressures are 2.6, 9.5 and 24.7% for Costa Gomes intermolecular potential, 0.9, 7.4 and 6.7% for Hansen intermolecular potential and 1.0, 3.5 and 5.8% for our intermolecular potential.

![Graph](image-url)

Fig. 1: Liquid-vapour coexisting densities of N$_2$O obtained by Monte Carlo simulations using the Hansen force field, the Costa Gomes force field and our new proposed force field. Experimental values shown for comparison are taken from the DIPPR data bank [28] for the liquid phase, and from the work of Quinn and Wernimont [29] for the vapour phase.
Fig. 2: Vapour pressures of N$_2$O obtained by Monte Carlo simulations using the Hansen force field, the Costa Gomes force field and our new proposed force field. Experimental values taken from the DIPPR data bank [28] are also shown for comparison.

Fig. 3: Vaporization enthalpies of N$_2$O obtained by Monte Carlo simulations using the Hansen force field, the Costa Gomes force field and our new proposed force field. Experimental values taken from the DIPPR data bank [28] are also shown for comparison.

Fig. 4 presents the results obtained for nitrous oxide transport properties using MD simulations. The liquid viscosities are obtained with average absolute deviations from experiments of 35.2%, 22.3%, and 11.8% using the Hansen force field, the Costa Gomes force field, and our new force field, respectively. These comparisons show that our new force field allows a better accuracy also for transport properties compared to existing force fields. Note that densities obtained by MD are consistent with those computed using MC simulations.
Fig. 4: Comparison of vapour and liquid viscosities of N$_2$O obtained by Molecular Dynamics simulations using the Hansen potential, the Costa Gomes potential and our new proposed potential. Experimental values are taken from the saturation properties of N$_2$O on the NIST website [30].

The accuracy of our force field in the vicinity of the critical point has also been investigated. Because of the large characteristic size of the density fluctuations, Gibbs Ensemble simulations cannot be performed in the close vicinity of the critical point. Therefore, the critical temperature $T_c$ and the critical density $\rho_c$ have been obtained by extrapolation from simulation points sufficiently far away from the critical point, assuming the following scaling law:

$$\rho^V - \rho^L = \gamma(T - T_c)^\beta$$ \hspace{1cm} (9)

where $\beta$ is a characteristic universal exponent [31,32]. It is also assumed that the densities of the coexisting liquid and vapour obey the so-called law of rectilinear diameters:

$$\frac{\rho^V + \rho^L}{2} - \rho_c = \lambda(T - T_c)$$ \hspace{1cm} (10)

Practically, $T_c$ and $\rho_c$ have been regressed by a least square method minimizing the average deviation between the above equations and the simulated coexistence densities. Once these properties were obtained, the critical pressure was then estimated by extrapolating the Clapeyron plot (see Fig. 2) to $1/T_c$. The resulting critical coordinates, as well as the normal boiling point, are gathered in Table 2 where they are compared to experimental values taken from the DIPPR data base [28] and to simulated values obtained using the Costa Gomes and the Hansen models. A very accurate restitution of the critical point is obtained using our new force field with deviations from experiments of 1.6% for the critical temperature, 3.2% for the critical pressure and 0.1% for the critical density.

Table 2: N$_2$O critical coordinates and normal boiling temperature.

<table>
<thead>
<tr>
<th>Model</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (MPa)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$T_{eb}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New force field</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vap.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Costa Gomes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vap.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hansen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vap.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New force field</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Costa Gomes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hansen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liq.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental data
### 3.1.2. Model for nitric oxide

Systems containing nitric oxide are particularly challenging because this compound may exist as a mixture of monomers (NO: nitrogen monoxide or nitric oxide) and dimers (N₂O₂: dinitrogen dioxide). The composition of the NO-N₂O₂ equilibrium mixture depends on pressure and temperature conditions: the dimer is favoured at higher pressures and lower temperatures. The chemical equilibrium between N₂O₂ and 2 NO has been the subject of some experimental works [33-38] and of some theoretical investigations [34,39-41]. In the liquid state, this reaction has been studied by Smith et al. [33] and Guedes [34] who reported equilibrium constants from 110 K to 170 K. The mole fraction of dimers in saturated liquid nitric oxide was found to vary from more than 90% at 110 K down to ~40% at 170 K. From these studies, it can be inferred that nitric oxide is strongly associated in the saturated liquid phase at low temperatures and that this degree of association decreases with increasing temperatures. In the gas phase, dimerization can also occur but the fraction of associated molecules (N₂O₂) is very small. Equilibrium constants of the reaction in the gas phase along the saturation curve have been reported by Kohler et al. [42] showing a molar fraction of dimer in the vapour phase around 0.64 to 2.89% for temperatures in the range of 115 – 177 K. In addition to these studies of the N₂O₂ ⇌ 2NO chemical equilibrium, phase behaviours and phase properties of the NO-N₂O₂ reacting system have also been investigated in the literature from experimental studies [42-49] or from empirical modelling approaches [28,50]. Among others, we can cite Johnston and Giauque [44] who have reported heat capacity measurements from 14 K up to the boiling point, as well as vaporization enthalpies and vapour pressures.

In the present work, the vapour-liquid equilibrium of the NO-N₂O₂ reacting system has been simulated at a molecular level using simultaneously the reaction ensemble and the Gibbs NVT ensemble Monte Carlo methods [19,51]. The reaction ensemble Monte Carlo method (ReMC) [52,53] allows the study of chemically reacting mixtures. No detailed description of this ensemble is proposed here and we invite interested readers to investigate the papers cited above for more details. In comparison with classical Gibbs ensemble simulations, two additional constraints are applied:

- The number of atoms is fixed for each atom type, so the number of different molecules in the system is controlled by the chemical equation which defines the chemical equilibrium:

\[ \sum _{i=1} v_i a_i = 0 \]  

where \( v_i \) is the stoichiometric coefficient of chemical species \( i \).

For example, 2NO ⇌ N₂O₂.

- The sum of chemical potentials \( \mu_i \) over the different molecular species implied in the chemical reaction, weighted by stoichiometric coefficients, is equal to zero:
\[
\sum_{i=1}^{s} v_i \mu_i = 0 \quad (12)
\]

For example, \(2\mu_{\text{NO}} = \mu_{\text{N}_2\text{O}_2}\).

In order to satisfy these constraints during the simulation, an additional Monte Carlo move is used: the reaction move. This move consists in firstly choosing a direction to perform the reaction, second in deleting a set of reactant molecules randomly chosen in the system, and finally inserting product molecules. In our case, the reaction move is

\[2\text{NO} \rightarrow \text{N}_2\text{O}_2\]

where two randomly chosen NO molecules are deleted and one \(\text{N}_2\text{O}_2\) is inserted, or

\[\text{N}_2\text{O}_2 \rightarrow 2\text{NO}\]

where one \(\text{N}_2\text{O}_2\) molecule randomly selected is deleted and two NO molecules are inserted. The acceptance probability of such Monte Carlo move can be found in reference [19], together with some details on its implementation in the GIBBS Monte Carlo software used in this study.

Table 3: Intermolecular potential parameters for NO.

<table>
<thead>
<tr>
<th>Model</th>
<th>Site</th>
<th>(\varepsilon/\kappa B \text{ (K)})</th>
<th>(\sigma \text{ (Å)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO - Hirschfelder 1 [54]</td>
<td>NO</td>
<td>91.0</td>
<td>3.60</td>
</tr>
<tr>
<td>NO - Hirschfelder 2 [54]</td>
<td>NO</td>
<td>119.0</td>
<td>3.47</td>
</tr>
<tr>
<td>NO - Kohler [55]</td>
<td>NO</td>
<td>125.0</td>
<td>3.17</td>
</tr>
<tr>
<td>NO - New force field (this work)</td>
<td>NO</td>
<td>130.0</td>
<td>3.40</td>
</tr>
</tbody>
</table>

To model NO and \(\text{N}_2\text{O}_2\) molecules, we have parameterized a force field that treats NO as a single Lennard-Jones sphere and \(\text{N}_2\text{O}_2\) as a two-site Lennard-Jones molecule. The parameterization procedure we have used is similar to the one previously described for \(\text{N}_2\text{O}\) force field development. The accuracy of the new proposed force field is compared to those obtained using existing models available in the literature [54,55]. Since the dipole moment of NO is rather small, electrostatic forces are neglected by all these models. The parameters of these different intermolecular potentials are summarized in Table 3. In order to test these models, we have performed NVT ReMC GEMC simulations at different temperatures in the 120 - 160 K range and computed the phase diagram of the reactive NO-N\(_2\)O\(_2\) system. To model \(\text{N}_2\text{O}_2\) molecules, we have used two NO LJ sites separated by 2.237 Å; the individual LJ parameters for each NO site in the dimer being the same as those for the monomer. The standard Gibbs free energies of the reaction \(2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2\) needed to perform the reaction moves during these simulations were calculated from the Gibbs free energies of formation of NO and \(\text{N}_2\text{O}_2\) taken from the TRC (Thermodynamics Research Center) thermochemical tables [56]. The numerical values of these Gibbs free energies are gathered in Table 4. Tests of these potentials have been performed by calculating thermodynamic properties of the NO-N\(_2\)O\(_2\) system along the saturation curve. The obtained results (coexistence densities, vaporization enthalpies and vapour pressures) are presented in Fig. 5, 6 and 7, where they are compared to experimental or modelling data given in the DIPPR database [28]. For vapour pressures, results of Lísal et al. [57] using the Kohler force field are also plotted in Fig. 7, showing a very good agreement with our data using the same model. For all studied properties,
significant deviations between DIPPR and simulated data are observed when using either potentials of Hirschfelder or the potential of Kohler. The degree of agreement is much more satisfying with our new force field. The temperature dependence of liquid densities and vaporization enthalpies is correctly described by this model, although it slightly overestimates the liquid density and the vaporization enthalpy at low temperature and underestimates them at higher temperatures in the vicinity of the critical point. The respective average absolute deviations for the densities, the vaporization enthalpies and the saturated vapour pressures are 3.3, 8.0 and 27.0%. Such results show that this model allows a reasonable agreement between simulation and experiment over a wide range of temperatures.

Table 4: Standard Gibbs free energy changes ($\Delta_r G^\circ$) of the reaction $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ at the temperatures studied using reaction ensemble Monte Carlo. These values were evaluated by means of the TRC thermochemical tables [56].

<table>
<thead>
<tr>
<th>T (K)</th>
<th>120.00</th>
<th>130.00</th>
<th>140.00</th>
<th>150.00</th>
<th>160.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_r G^\circ$ (kJ mol$^{-1}$)</td>
<td>5.344</td>
<td>6.726</td>
<td>8.126</td>
<td>9.530</td>
<td>10.936</td>
</tr>
</tbody>
</table>

Fig. 5: Temperature dependence of density in the liquid-vapour coexistence region of the NO-N$_2$O$_2$ system. The line represents the recommended values of the DIPPR data bank [28] whereas symbols represent our Monte Carlo simulation results obtained using different interaction potentials to model the NO and N$_2$O$_2$ molecules.
Fig. 6: Temperature dependence of vaporization enthalpies in the liquid-vapour coexistence region of the NO-N$_2$O$_2$ system. The line represents the recommended values of the DIPPR data bank [28] whereas symbols represent our Monte Carlo simulation results obtained using different interaction potentials to model the NO and N$_2$O$_2$ molecules.

Fig. 7: Inverse temperature dependence of pressure in the liquid-vapour coexistence region of the NO-N$_2$O$_2$ system, in logarithmic scale. The line represents the recommended values of the DIPPR data bank [28] whereas symbols represent our Monte Carlo simulation results obtained using different interaction potentials to model the NO and N$_2$O$_2$ molecules. Results of Lísal et al. [57] using the Kohler force field are also shown for comparison.

The NO-N$_2$O$_2$ critical point coordinates ($T_c$, $\rho_c$ and $x_c$) have been approximated by the use of extended scaling laws [11]:

$$\rho_p = \rho_c + \lambda (T_c - T) + \epsilon \frac{\gamma}{2} (T_c - T)^\beta$$

$$x_p = x_c + \left( \lambda_1 - \frac{\lambda_2}{2} \right) (T_c - T) - \frac{\mu}{2} (T_c - T)^\beta$$

(13)
where \( \varepsilon = 1 \) for the liquid phase (\( \varphi = \text{liq} \)) and \( \varepsilon = -1 \) for the vapour phase (\( \varphi = \text{vap} \)). \( T_c, \rho_c, x_c \) (critical coordinates) and \( \lambda, \lambda_1, \lambda_2, \gamma, \mu \) (adjustable coefficients) are regressed by a least square method from a set of coexistence points \((T, x_{\text{liq}}, x_{\text{vap}}, \rho_{\text{liq}}, \rho_{\text{vap}})\) below the critical point. The critical pressure was then estimated by extrapolating the Clapeyron plot (see Fig. 7) to \( 1/T_c \). The resulting critical coordinates, obtained using the different studied force fields, are gathered in Table 5 where they are compared to experimental values taken from the DIPPR data base [28].

Table 5: Nitric oxide critical coordinates.

<table>
<thead>
<tr>
<th>Model</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (MPa)</th>
<th>( \rho_c ) (kg/m(^3))</th>
<th>( x_c ) (N(_2)O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation (New force field)</td>
<td>174.03</td>
<td>6.37</td>
<td>466.60</td>
<td>0.03</td>
</tr>
<tr>
<td>Simulation (Hirschfelder 2 force field [54])</td>
<td>165.80</td>
<td>5.86</td>
<td>442.88</td>
<td>0.06</td>
</tr>
<tr>
<td>Simulation (Kohler force field [55])</td>
<td>171.19</td>
<td>7.64</td>
<td>540.86</td>
<td>0.04</td>
</tr>
<tr>
<td>DIPPR data</td>
<td>180.15</td>
<td>6.48</td>
<td>517.35</td>
<td>-</td>
</tr>
</tbody>
</table>

We have also compared the fractions of dimers in the saturated liquid phase given by the different studied models. Results are shown in Fig. 8 together with the experimental point of Smith [33] obtained by measurements of magnetic susceptibility. Fig. 8 shows nearly complete dimerization at low temperatures. Further, the degree of dimerization decreases with increasing temperature and at \( T > T_c \), the system becomes monomeric. For the vapour phase at a pressure of 0.1 MPa and a temperature of 121.40 K we obtain, using our new model, a mole percent of monomers of 99.6%, which is in agreement with both Guggenheim's estimate based on analysis of second Virial coefficient data [58] and Turner's estimate based on Monte Carlo simulations [59]. To assess the possible effect of pressure on the degree of dimerization, one simulation of the NO-N\(_2\)O\(_2\) system has been conducted in the monophasic liquid region at 253.15 K and 12.0 MPa, showing a mole fraction of monomers of 99.8%.

This study shows that our simulations are consistent with data available in the literature for both the liquid and the gas phases. The obtained results also show that for temperatures above the critical temperature of the NO-N\(_2\)O\(_2\) system (\( T_c \) exp = 180.15 K), associations have disappeared and only the monomer form (NO) has to be accounted for.

Fig. 9 illustrates the results obtained for the transport properties of the NO-N\(_2\)O\(_2\) system using MD simulations. The degree of dimerization for each studied temperature was taken from MC simulation results presented in Fig. 8, with a total number of 1000 NO particles. The viscosity calculations were thus performed at fixed chemical composition.

The liquid viscosities are obtained with average absolute deviations from experiments of 43.7%, 39.2%, and 22.0% using the Kohler force field, our new force field, and the Hirschfelder 2 force field, respectively. Such comparisons show that the Hirschfelder force field allows a better degree of accuracy for the liquid viscosity compared to Kohler and our new force fields, especially at low temperatures. However, considering both transport and thermodynamic properties, our new force field appears as the best compromise.
Fig. 8: Mole fraction of N$_2$O$_2$ as a function of temperature along the saturation line for the bulk liquid phase of the 2NO N$_2$O$_2$ system from Monte Carlo simulations.

Fig. 9: Comparison of vapour and liquid viscosities of the NO-N$_2$O$_2$ system obtained by Molecular Dynamics simulations. Experimental values are taken from the saturation properties of NO on the NIST website [30].

3.2. Study of CO$_2$+N$_2$O mixtures

3.2.1. Vapour-liquid phase diagrams
To model CO$_2$ molecules, we have chosen the EPM2 rigid version of the force field proposed by Harris and Yung [60]. This force field, which involves three Lennard-Jones sites and three electrostatic charges, is known to represent the liquid-vapour coexistence data of pure CO$_2$ as well as phase diagrams of mixtures with other gases fairly well [18-20]. The parameters of this potential are given in Table 6. Note that Harris and Yung have developed their model using geometric combining rules for LJ sigma and epsilon. Nevertheless, in this work, Lennard-Jones parameters for the unlike interactions have been obtained using Lorentz-Berthelot rules. The use of an arithmetic combining rule for the calculation of sigma instead
of a geometric rule is not expected to have a significant impact on the simulation results since O and C atoms do not exhibit a substantial size difference ($\sigma_O = 3.033 \text{ Å}$ and $\sigma_C = 2.757 \text{ Å}$). The use of an arithmetic combining rule leads to a cross diameter $\sigma_{CO}$ equal to 2.895 Å, whereas a value of 2.892 Å is obtained with a geometric rule. Moreover, the paper of Nieto-Draghi and co-workers in 2007 shows that the combination of the Harris and Yung potential with the Lorentz-Berthelot rules allows a good restitution of both thermodynamic and transport properties.

Table 6: Intermolecular potential parameters for CO$_2$.

<table>
<thead>
<tr>
<th>Model</th>
<th>Site</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ - EPM2 [60]</td>
<td>O</td>
<td>80.507</td>
<td>3.033</td>
<td>-0.3256</td>
<td>$l_{C-O} = 1.1490$</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>28.129</td>
<td>2.757</td>
<td>0.6512</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>80.507</td>
<td>3.033</td>
<td>-0.3256</td>
<td></td>
</tr>
</tbody>
</table>

In order to increase the accuracy of the calculations performed for the CO$_2$+N$_2$O binary system, we have used the reaction Gibbs Ensemble Monte Carlo method proposed by Lísal et al. [61]. This approach uses a modified GEMC technique that treats the phase equilibrium as a special type of chemical reaction and incorporates knowledge of pure component vapour pressure data into the simulations. The present paragraph provides just a brief summary of the involved algorithm, the reader is referred to the paper of Lísal et al. for more details. From a practical point of view, this method is similar to the Gibbs Ensemble method except that the acceptance probabilities of particle transfers from one box to the other are modified according to the following equations:

$$P_{\text{acc}}^{\text{liq}\rightarrow \text{gas}}(a \rightarrow b) = \min \left( 1, \frac{N_{\text{liq}}V_{\text{gas}}}{(N_{\text{gas}} + 1)V_{\text{liq}}} \exp(-\beta \Delta U) \right)$$  \hspace{1cm} (14)

$$P_{\text{acc}}^{\text{gas}\rightarrow \text{liq}}(a \rightarrow b) = \min \left( 1, \frac{1}{\Gamma_i} \frac{N_{\text{gas}}V_{\text{liq}}}{(N_{\text{liq}} + 1)V_{\text{gas}}} \exp(-\beta \Delta U) \right)$$  \hspace{1cm} (15)

where $\beta = 1/(k_B T)$ and $k_B$ is Boltzmann’s constant, $\Delta U$ is the change in configurational energy, $V_{\alpha}$ is the volume of the simulation box $\alpha$, and $N_{\alpha}$ is the total number of molecules in box $\alpha$. In equations (14) and (15), the term $\Gamma_i$ ($i = \text{CO}_2$ or N$_2$O) is given by:

$$\Gamma_i = \frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}}$$  \hspace{1cm} (16)

with $P_{i,\text{GEMC}}^{\text{sat}}$ being the vapour pressure of component $i$ calculated using standard GEMC and $P_{i,\text{exp}}^{\text{sat}}$ the corresponding experimental value. If $\Gamma_i = 1$, equations (14) and (15) correspond to standard GEMC simulations. In our simulations, we have used a constant $\Gamma_i$ factor equal to 0.95 for the two involved compounds at the different studied temperatures. This choice is justified by the fact that the force fields used for N$_2$O and for CO$_2$ both lead to almost the same overestimate of vapour pressures whatever the temperature. All these simulations have
been performed at constant total volume and constant temperature. Note that no experimental information concerning the mixtures is required, making this approach totally predictive for mixture studies.

The phase envelopes of the CO₂+N₂O binary mixture have been calculated at three different temperatures: 273 K, 283 K and 293 K. These phase envelopes are presented in Fig. 10 together with experimental data of Cook measured at 293 K, 298 K and 303 K [6] and of Rowlinson measured at 283 K and 293 K [7]. All these temperatures are below the critical temperatures of both CO₂ and N₂O, thus none of the phase diagrams exhibits a critical point. Due to the strong similarities between carbon dioxide and nitrous oxide (T_c(CO₂) = 304.21 K; T_c(N₂O) = 309.57 K; P_c(CO₂) = 7.38 MPa; P_c(N₂O) = 7.24 MPa), the two-phase region is very narrow and very flat at all studied temperatures. Differences between the compositions of the liquid and the vapour phases at equilibrium are very small which means that the system may be considered to be azeotropic over the whole range of compositions. A good agreement between experimental and simulated data is obtained at 283 K and 293 K which validates our methodological approach. The numerical values obtained from the Monte Carlo simulations are gathered in Table 7. Fig. 11 presents the pressure-density diagrams obtained from our simulations.

Fig. 10: Pressure-composition diagram of the CO₂+N₂O mixture at different temperatures. Experimental data at 283.15 K, 293.15 K, 298.15 K and 303.15 K are taken from Cook [6] and Rowlinson [7] whereas pure component vapour pressures at 273.15 K and 283.15 K are taken from the DIPPR data base [28].
Table 7: Calculated vapour-liquid equilibrium pressures, compositions and densities for the CO$_2$+N$_2$O mixture at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
<th>$x^{\text{vap}}$ (CO$_2$)</th>
<th>$\rho^{\text{vap}}$ (kg/m$^3$)</th>
<th>$x^{\text{liq}}$ (CO$_2$)</th>
<th>$\rho^{\text{liq}}$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15 K</td>
<td>5.14</td>
<td>0.000</td>
<td>140.73</td>
<td>0.000</td>
<td>741.55</td>
</tr>
<tr>
<td></td>
<td>5.23</td>
<td>0.264</td>
<td>143.90</td>
<td>0.255</td>
<td>727.55</td>
</tr>
<tr>
<td></td>
<td>5.50</td>
<td>0.507</td>
<td>155.52</td>
<td>0.496</td>
<td>760.40</td>
</tr>
<tr>
<td></td>
<td>5.51</td>
<td>0.747</td>
<td>155.96</td>
<td>0.739</td>
<td>736.62</td>
</tr>
<tr>
<td></td>
<td>5.53</td>
<td>0.883</td>
<td>154.75</td>
<td>0.878</td>
<td>736.49</td>
</tr>
<tr>
<td></td>
<td>5.66</td>
<td>1.000</td>
<td>162.48</td>
<td>1.000</td>
<td>752.45</td>
</tr>
<tr>
<td>283.15 K</td>
<td>4.14</td>
<td>0.000</td>
<td>110.19</td>
<td>0.000</td>
<td>831.33</td>
</tr>
<tr>
<td></td>
<td>4.26</td>
<td>0.267</td>
<td>113.94</td>
<td>0.255</td>
<td>835.39</td>
</tr>
<tr>
<td></td>
<td>4.31</td>
<td>0.511</td>
<td>116.15</td>
<td>0.496</td>
<td>837.43</td>
</tr>
<tr>
<td></td>
<td>4.42</td>
<td>0.750</td>
<td>120.34</td>
<td>0.739</td>
<td>839.75</td>
</tr>
<tr>
<td></td>
<td>4.44</td>
<td>0.884</td>
<td>119.24</td>
<td>0.878</td>
<td>835.64</td>
</tr>
<tr>
<td></td>
<td>4.59</td>
<td>1.000</td>
<td>125.41</td>
<td>1.000</td>
<td>849.76</td>
</tr>
<tr>
<td>273.15 K</td>
<td>3.19</td>
<td>0.000</td>
<td>82.29</td>
<td>0.000</td>
<td>888.59</td>
</tr>
<tr>
<td></td>
<td>3.38</td>
<td>0.269</td>
<td>88.35</td>
<td>0.255</td>
<td>900.56</td>
</tr>
<tr>
<td></td>
<td>3.39</td>
<td>0.513</td>
<td>87.86</td>
<td>0.497</td>
<td>900.40</td>
</tr>
<tr>
<td></td>
<td>3.51</td>
<td>0.752</td>
<td>92.48</td>
<td>0.739</td>
<td>912.48</td>
</tr>
<tr>
<td></td>
<td>3.55</td>
<td>0.885</td>
<td>93.12</td>
<td>0.879</td>
<td>910.45</td>
</tr>
<tr>
<td></td>
<td>3.59</td>
<td>1.000</td>
<td>94.55</td>
<td>1.000</td>
<td>914.55</td>
</tr>
</tbody>
</table>

3.2.2. Densities and viscosities

In this section, we report results obtained using MD simulations for a CO$_2$+N$_2$O binary mixture containing 10 mol% of N$_2$O. The density and the viscosity of this mixture have been calculated at two temperatures: 283 K and 293 K. The obtained results are presented in Table 8 and illustrated in Fig. 12 and 13, together with experimental and simulated data for pure CO$_2$. Experimental data for pure CO$_2$ were extracted from the NIST website [30].
Densities simulated for pure CO$_2$ are in excellent agreement with respect to experimental data. When considering a CO$_2$+N$_2$O binary mixture containing 10 mol% of N$_2$O at 283 K and 293 K, Molecular Dynamics simulations lead to density values almost equal to the corresponding pure CO$_2$ values at the same temperatures. As far as the viscosity is concerned, data simulated for pure CO$_2$ show a reasonable agreement with respect to experimental data. Within the computed statistical uncertainties, the obtained viscosities for the mixture are similar to those calculated for pure CO$_2$ at the same temperature and pressure conditions.

![Fig. 12: Pressure-density diagram of the CO$_2$+N$_2$O mixture with 10 mol% of N$_2$O, at 283.15 K and 293.15 K. Experimental densities for pure CO$_2$ have been taken from the NIST website [30].](image1)

![Fig. 13: Pressure-viscosity diagram of the CO$_2$+N$_2$O mixture with 10 mol% of N$_2$O, at 283.15 K and 293.15 K. Experimental viscosities for pure CO$_2$ have been taken from the NIST website [30].](image2)

Table 8: Molecular Dynamics simulation results computed for the CO$_2$+N$_2$O mixture with 10 mol% of N$_2$O. Simulated data obtained for the mixture are compared to experimental and simulated data for pure CO$_2$. 

---

**Table 8:** Molecular Dynamics simulation results computed for the CO$_2$+N$_2$O mixture with 10 mol% of N$_2$O. Simulated data obtained for the mixture are compared to experimental and simulated data for pure CO$_2$. 

- CO$_2$-N$_2$O / Sim. / 283.15 K
- CO$_2$ / Sim. / 283.15 K
- CO$_2$/ Experimental data
- CO$_2$-N$_2$O / Sim. / 293.15 K
- CO$_2$ / Sim. / 293.15 K
- CO$_2$/ Experimental data
These calculations show that both thermodynamic and transport properties of CO$_2$+N$_2$O mixtures are similar to the properties of pure CO$_2$ in the whole range of studied temperatures, pressures and compositions. Such behaviour is reasonable due to the strong similarities between carbon dioxide and nitrous oxide in terms of molecular weights, vapour pressures and critical coordinates.

3.3. Study of CO$_2$+NO mixtures

3.3.1. Vapour-liquid phase diagrams
The phase envelopes of the CO$_2$+NO binary mixture have been calculated at three different temperatures: 253 K, 263 K and 273 K, using standard Gibbs NPT simulations. As discussed previously, nitric oxide is fully monomeric in this temperature range. The calculated phase envelopes are presented in Fig. 14 (pressure-composition diagrams) and Fig. 15 (pressure-density diagrams). The corresponding numerical values are gathered in Table 9. As expected, the extend of the two-phase region decreases as the temperature increases. The three studied temperatures are below the critical temperature of carbon dioxide ($T_c = 304.21$ K) and above the critical temperature of nitric oxide ($T_c = 180.15$ K), thus all phase diagrams exhibit a critical point. The coordinates of these critical points and the near-critical phase behaviour have been determined using extended scaling laws [11]. Obtained critical coordinates are: $P_c = 11.48$ MPa, $\rho_c = 526.75$ kg/m$^3$, $x_c$(NO) = 0.512 at 253 K; $P_c = 11.21$ MPa, $\rho_c = 529.88$ kg/m$^3$, $x_c$(NO) = 0.427 at 263 K and $P_c = 10.95$ MPa, $\rho_c = 515.18$ kg/m$^3$, $x_c$(NO) = 0.351 at 273 K.
Fig. 14: Pressure-composition diagram of the CO$_2$+NO mixture at 253.15 K (blue), 263.15 K (red) and 273.15 K (black). The symbols represent the simulated results. The lines are guides for the eyes.

Fig. 15: Pressure-density diagram of the CO$_2$+NO mixture at 253.15 K (blue), 263.15 K (red) and 273.15 K (black). The symbols represent the simulated results. The lines are guides for the eyes.

Table 9: Calculated vapour-liquid equilibrium pressures, compositions and densities for the CO$_2$+NO mixture at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
<th>$x_{vap}$ (NO)</th>
<th>$\rho_{vap}$ (kg/m$^3$)</th>
<th>$x_{liq}$ (NO)</th>
<th>$\rho_{liq}$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>253.15 K</td>
<td>2.25</td>
<td>0.000</td>
<td>58.85</td>
<td>0.000</td>
<td>1020.5</td>
</tr>
<tr>
<td>3.00</td>
<td>0.218</td>
<td>73.61</td>
<td>0.025</td>
<td>1007.8</td>
<td></td>
</tr>
<tr>
<td>4.00</td>
<td>0.371</td>
<td>94.71</td>
<td>0.059</td>
<td>985.82</td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>0.467</td>
<td>118.09</td>
<td>0.095</td>
<td>961.58</td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>0.527</td>
<td>142.58</td>
<td>0.135</td>
<td>934.64</td>
<td></td>
</tr>
<tr>
<td>7.00</td>
<td>0.561</td>
<td>171.90</td>
<td>0.172</td>
<td>909.53</td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td>0.586</td>
<td>204.36</td>
<td>0.215</td>
<td>877.65</td>
<td></td>
</tr>
</tbody>
</table>
In this section, we report results obtained using Molecular Dynamics (MD) simulations for a CO₂+NO binary mixture containing 10 mol% of NO. The density and the viscosity of this mixture have been calculated at two temperatures: 263 K and 273 K. As previously shown from Monte Carlo (MC) simulation results, the nitric oxide is fully monomeric at these temperatures, and no N₂O₂ has been considered in the MD simulations. The obtained results are presented in Table 10 and illustrated in Fig. 16 and 17, together with experimental and simulated data for pure CO₂.

Experimental data for pure CO₂ were extracted from the NIST website [30].

Densities and viscosities simulated for pure CO₂ are in excellent agreement with respect to experimental data. When considering a CO₂+NO binary mixture containing 10 mol% of NO at 263 K and 273 K, Molecular Dynamics simulations lead to liquid density values much lower than corresponding pure CO₂ values (about 9%). Similarly, the addition of 10 mol% of NO to CO₂ at 263 K and 273 K leads to a decrease of liquid viscosities of about 24% with respect to corresponding pure CO₂ viscosities.

### Table 10

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Density</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>263.15 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.01</td>
<td>0.000</td>
<td>80.22</td>
</tr>
<tr>
<td>4.00</td>
<td>0.203</td>
<td>101.37</td>
</tr>
<tr>
<td>5.00</td>
<td>0.322</td>
<td>123.86</td>
</tr>
<tr>
<td>6.00</td>
<td>0.406</td>
<td>148.25</td>
</tr>
<tr>
<td>7.00</td>
<td>0.441</td>
<td>181.94</td>
</tr>
<tr>
<td>8.00</td>
<td>0.478</td>
<td>215.90</td>
</tr>
<tr>
<td>9.00</td>
<td>0.503</td>
<td>252.28</td>
</tr>
<tr>
<td>10.00</td>
<td>0.507</td>
<td>302.78</td>
</tr>
<tr>
<td>11.21*</td>
<td>0.427*</td>
<td>529.88*</td>
</tr>
<tr>
<td><strong>273.15 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.88</td>
<td>0.000</td>
<td>107.84</td>
</tr>
<tr>
<td>5.00</td>
<td>0.160</td>
<td>134.21</td>
</tr>
<tr>
<td>6.00</td>
<td>0.263</td>
<td>160.59</td>
</tr>
<tr>
<td>7.00</td>
<td>0.333</td>
<td>188.68</td>
</tr>
<tr>
<td>8.00</td>
<td>0.380</td>
<td>222.09</td>
</tr>
<tr>
<td>9.00</td>
<td>0.406</td>
<td>264.35</td>
</tr>
<tr>
<td>10.00</td>
<td>0.413</td>
<td>319.10</td>
</tr>
<tr>
<td>10.95*</td>
<td>0.351*</td>
<td>515.18*</td>
</tr>
</tbody>
</table>

* Critical coordinates obtained using extended scaling laws.
Fig. 16: Pressure-density diagram of the CO$_2$+NO mixture with 10 mol% of NO, at 263.15 K and 273.15 K. Experimental densities for pure CO$_2$ have been taken from the NIST website [30].

Fig. 17: Pressure-viscosity diagram of the CO$_2$+NO mixture with 10 mol% of NO, at 263.15 K and 273.15 K. Experimental viscosities for pure CO$_2$ have been taken from the NIST website [30].

Table 10: Molecular Dynamics simulation results computed for the CO$_2$+NO mixture with 10 mol% of NO. Simulated data obtained for the mixture are compared to experimental and simulated data for pure CO$_2$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
<th>$\rho$ (kg.m$^{-3}$)</th>
<th>$\eta$ (mPa.s)</th>
<th>$\rho$ (kg.m$^{-3}$)</th>
<th>err. (%)</th>
<th>$\eta$ (mPa.s)</th>
<th>err. (%)</th>
<th>$\rho$ (kg.m$^{-3}$)</th>
<th>$\eta$ (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>2.0</td>
<td>45.6</td>
<td>0.014</td>
<td>44.5</td>
<td>-2.3</td>
<td>0.014</td>
<td>-3.7</td>
<td>42.3</td>
<td>0.016</td>
</tr>
<tr>
<td>273.15</td>
<td>4.0</td>
<td>932.1</td>
<td>0.101</td>
<td>923.4</td>
<td>-0.9</td>
<td>0.099</td>
<td>-2.2</td>
<td>801.9</td>
<td>0.064</td>
</tr>
<tr>
<td>273.15</td>
<td>6.0</td>
<td>948.2</td>
<td>0.106</td>
<td>939.5</td>
<td>-0.9</td>
<td>0.108</td>
<td>2.0</td>
<td>838.6</td>
<td>0.079</td>
</tr>
</tbody>
</table>
3.4. Optimization of thermodynamic models for CO$_2$+N$_2$O and CO$_2$+NO mixtures

The last part of the work is devoted to the calibration of standard cubic equations of state (EoS). Because of their simplicity and robustness, cubic EoS are often used to calculate the thermodynamic properties in the oil and gas process industry. Such EoS perform well for vapour-liquid equilibrium calculations and may perform well for densities, at least away from the critical region. Because they have few empirical parameters, they are easily fitted to new experimental data. In the present work, the available liquid-vapour experimental data or the pseudo-experimental data generated by molecular simulation have been used to regress binary interaction parameters for both Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) EoS for the CO$_2$+N$_2$O and CO$_2$+NO mixtures. Binary interaction parameters $k_{ij}$ are required to calculate the attractive parameter $a_{mix}$ and the co-volume $b_{mix}$ of the mixture from a given mixing rule. In the present work, classical mixing rules have been used:

$$a_{mix} = \sum_{ij} z_i z_j \sqrt{a_i a_j (1-k_{ij})},$$
$$b_{mix} = \sum_i z_i b_i,$$

where the summations are over the mixture components $i$ and where $a_i$, $b_i$, and $z_i$ are the pure component attractive parameter, co-volume and molar fraction, respectively. For a given binary mixture and EoS, an unique binary interaction parameter has been regressed. The fitting of this interaction parameter has been performed by minimizing the objective function $Y(k_{ij})$, which is a sum over deviations for calculated data from experimental or pseudo-experimental data, with respect to $k_{ij}$:

$$Y(k_{ij}) = \left( \sum_{r=1}^{N} \sum_{i=1}^{y} \left( x_{r,i~,exp,} - x_{r,i~,calc} \right)^2 + \left( y_{r,i~,exp,} - y_{r,i~,calc} \right)^2 \right)^{1/2}$$

Here, the experimental data consists of $N$ measurements (CO$_2$+N$_2$O) or data from molecular simulations (CO$_2$+NO) of the liquid compositions $x_{exp,r}$ and gas compositions $y_{exp,r}$, taken at a given point $r$ in the pressure-temperature space. This is the same objective function as used by Wilhelmsen et al. [62]. $Y(k_{ij})$ is preferred compared to objective functions involving relative values, because molar fractions $x$ and $y$ may be small in terms of absolute values. A small absolute deviation may then result in a large relative deviation, and a biased regression. The performance of the EoS is measured by the absolute average deviation (AAD) of the liquid and gas compositions:

$$ADD = \frac{1}{2N} \sum_{r=1}^{N} \sum_{i=1}^{y} \frac{|x_{r,i~,calc} - x_{r,i~,exp}|}{x_{r,i~,exp}}$$

### Table

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (bar)</th>
<th>$x_{1}$</th>
<th>$y_{1}$</th>
<th>$x_{2}$</th>
<th>$y_{2}$</th>
<th>$x_{3}$</th>
<th>$y_{3}$</th>
<th>$x_{4}$</th>
<th>$y_{4}$</th>
<th>$x_{5}$</th>
<th>$y_{5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>8.0</td>
<td>0.110</td>
<td>0.111</td>
<td>0.6</td>
<td>0.111</td>
<td>0.087</td>
<td>0.087</td>
<td>0.087</td>
<td>0.087</td>
<td>0.087</td>
<td>0.087</td>
</tr>
<tr>
<td>263.15</td>
<td>2.0</td>
<td>0.014</td>
<td>0.015</td>
<td>10.2</td>
<td>44.8</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>263.15</td>
<td>4.0</td>
<td>0.121</td>
<td>0.123</td>
<td>1.4</td>
<td>892.2</td>
<td>0.086</td>
<td>0.086</td>
<td>0.086</td>
<td>0.086</td>
<td>0.086</td>
<td>0.086</td>
</tr>
<tr>
<td>263.15</td>
<td>6.0</td>
<td>0.125</td>
<td>0.125</td>
<td>0.5</td>
<td>911.8</td>
<td>0.094</td>
<td>0.094</td>
<td>0.094</td>
<td>0.094</td>
<td>0.094</td>
<td>0.094</td>
</tr>
<tr>
<td>263.15</td>
<td>8.0</td>
<td>0.129</td>
<td>0.129</td>
<td>-0.1</td>
<td>926.5</td>
<td>0.103</td>
<td>0.103</td>
<td>0.103</td>
<td>0.103</td>
<td>0.103</td>
<td>0.103</td>
</tr>
</tbody>
</table>
and

$$\text{ADD}_y = \frac{1}{2N} \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} \frac{|y_{i,r}(k_{ij}) - y_{\text{exp},i,r}|}{y_{\text{exp},i,r}}$$

(20)

The optimized parameters obtained for the two binary mixtures and the two studied EoS are gathered in Table 11, together with the corresponding performance.

Table 11: Optimized binary interaction parameters for the two studied mixtures and the two studied equations of state.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$+N$_2$O</th>
<th>CO$_2$+NO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRK</td>
<td>PR</td>
</tr>
<tr>
<td>$k_{ij}$</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>AAD$_x$</td>
<td>5%</td>
<td>1%</td>
</tr>
<tr>
<td>AAD$_y$</td>
<td>5%</td>
<td>3%</td>
</tr>
</tbody>
</table>

The phase envelopes of the CO$_2$+N$_2$O binary mixture as calculated by optimized cubic equations of state at 273 K, 283 K, 293 K, 298 K and 303 K are presented in Fig. 18 (pressure-composition diagrams) and Fig. 19 (pressure-density diagrams), together with the experimental data available in the literature and the Monte Carlo pseudo-experimental data obtained in the present work.

Fig. 18: Pressure-composition diagram of the CO$_2$+N$_2$O mixture at different temperatures; symbols: experimental or simulated results; solid lines: PR EoS results; dashed lines: SRK EoS results.
The regression of binary interaction parameters for SRK and PR EoS based on experimental data allows a good description of the pressure-composition phase envelopes of the CO$_2$+N$_2$O mixture for all studied temperatures. For the two studied EoS, very small values of $k_{ij}$ are obtained, which is reasonable since no significant cross interactions are expected in this system. Concerning coexisting densities, both EoS predict the densities well in the gas phase, but only the PR EoS allows a reasonable restitution of the liquid densities. SRK EoS underpredicts the liquid densities by more than 10%. Such behaviour was pointed out in recent work by Wilhelmsen et al. [62] involving different CO$_2$-containing systems. Note that no volume shift has been used to correct the obtained densities.

The phase envelopes of the CO$_2$+NO mixture calculated by the two cubic equations of state at 253 K, 263 K and 273 K are presented in Fig. 20 (pressure-composition diagrams) and Fig. 21 (pressure-density diagrams), together with the pseudo-experimental data from Monte Carlo simulations. In addition, the critical points of the CO$_2$+NO mixture at the three studied temperatures obtained from cubic equations of state are given in Table 12.

Table 12: Critical point predictions given by SRK EoS, PR EoS and Monte Carlo simulations for the CO$_2$+NO mixture at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$P_c$ (MPa)</th>
<th>$x_{NO,c}$ (-)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$P_c$ (MPa)</th>
<th>$x_{NO,c}$ (-)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
<th>$P_c$ (MPa)</th>
<th>$x_{NO,c}$ (-)</th>
<th>$\rho_c$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>253.15</td>
<td>13.7</td>
<td>0.562</td>
<td>510.2</td>
<td>13.6</td>
<td>0.554</td>
<td>559.1</td>
<td>11.48</td>
<td>0.512</td>
<td>526.8</td>
</tr>
<tr>
<td>263.15</td>
<td>13.2</td>
<td>0.483</td>
<td>491.4</td>
<td>13.1</td>
<td>0.476</td>
<td>537.5</td>
<td>11.21</td>
<td>0.427</td>
<td>529.9</td>
</tr>
<tr>
<td>273.15</td>
<td>12.4</td>
<td>0.395</td>
<td>471.1</td>
<td>12.3</td>
<td>0.388</td>
<td>513.2</td>
<td>10.95</td>
<td>0.351</td>
<td>515.2</td>
</tr>
</tbody>
</table>
Fig. 20: Pressure-composition diagram of the CO$_2$+NO mixture at 253.15 K (blue), 263.15 K (red) and 273.15 K (black); symbols: simulated results; solid lines: PR EoS results; dashed lines: SRK EoS results.

Fig. 21: Pressure-density diagram of the CO$_2$+NO mixture at 253.15 K (blue), 263.15 K (red) and 273.15 K (black); symbols: simulated results; solid lines: PR EoS results; dashed lines: SRK EoS results.

Fig. 20 shows that the largest deviations between the pseudo-experimental Monte Carlo data and the cubic equations of state may be found at large pressures in the vicinity of the critical region. This overprediction by standard cubic EoS of dew pressures close to the critical point was also found in a previous work [62] for two other CO$_2$+contaminant mixtures (CO$_2$+N$_2$ and CO$_2$+O$_2$) in a comparison with experimental data. In the present work with the CO$_2$+NO mixture, none of the cubic EoS displays any clear advantage over the other for the restitution of the pressure-composition curves. For density calculations however, Fig. 21 shows that the liquid densities calculated with the PR EoS are in better agreement with the Monte Carlo data compared to the values obtained with the SRK EoS. The same behaviour was already observed in the case of the CO$_2$+N$_2$O mixture. By comparing the data in Table 12, it is
evident that the critical coordinates given by the two cubic equations of state are similar, but very different from the critical coordinates given by Monte Carlo simulations. The deviations are largest for the critical pressures, which are on average 16% larger with the cubic equations of state than with Monte Carlo simulations. The critical composition exhibits only on average 10% deviation, while the predicted critical density from the cubic equations of state deviates 2% from the Monte Carlo simulations.

4. Conclusion

Original force fields for atomistic simulations have been proposed for N₂O, NO and N₂O₂ molecules, based on Lennard-Jones parameters fitted to experimental vapour-liquid equilibrium data. We have shown that thermodynamic and transport properties along the saturation curve of both nitrous oxide and nitric oxide can be well reproduced using these new models in Monte Carlo and Molecular Dynamics simulations. Studies have also been carried out on CO₂-containing mixtures at different temperatures in the range 253 – 293 K. Phase compositions, phase densities and phase viscosities were determined for CO₂+N₂O and CO₂+NO binary mixtures. In the case of CO₂+N₂O mixtures, the liquid-vapour phase envelopes calculated at 283 K and 293 K were compared with experimental data available in the literature. Experimental and simulation results appear in good agreement, allowing reliable and accurate predictions at other temperatures. In the case of CO₂+NO mixtures, the performed calculations are pure predictions since no experimental data are available in the literature for this system. The regression of binary interaction parameters for SRK and PR EoS based on the molecular simulation pseudo-experimental data or true experimental data allows good restitution of vapour-liquid equilibrium data for the two studied mixtures and for the two studied EoS. For the prediction of liquid densities in the two-phase area, PR EoS was much closer to the pseudo-experimental data than SRK EoS.

The present study shows that molecular simulations combined with equation of state modelling can play a significant role in the context of CO₂ storage operations where the degree of purity of the captured CO₂ is a key factor for transportation, injection and sequestration. This work illustrates how molecular simulations may be used as a tool to mitigate the lack of experimental data and improve engineering equations of state to enable process simulations where accurate, robust and computationally fast models are required.

List of symbols

- $a$: cubic EoS attractive parameter (J m$^3$ mol$^{-2}$)
- $b$: cubic EoS co-volume (m$^3$ mol$^{-1}$)
- $\Delta H_{\text{vap}}$: molar vaporization enthalpy (kJ mol$^{-1}$)
- $F$: objective function used in Eq. (8)
- $i, j$: component $i$ and $j$
- $k_B$: Boltzmann's constant (J K$^{-1}$)
- $k_{ij}$: binary interaction parameter between components $i$ and $j$
- $L$: simulation box length (Å)
- $N$: number of particles
- $P$: pressure (MPa)
- $P_c$: critical pressure (MPa)
- $P_{\text{sat}}$: saturated vapour pressure (MPa)
- $q_i$: electrostatic charge (e)
- $r$: separation distance (Å)
- $P_{\alpha,\beta}$: element of pressure tensor (MPa)
- $S_i$: statistical uncertainty on simulated property $i$
\( T \) temperature (K)
\( T_c \) critical temperature (K)
\( T_{eb} \) normal boiling temperature (K)
\( U \) configurational energy (J)
\( U_{LJ} \) Lennard-Jones energy (J)
\( U_{elec} \) electrostatic energy (J)
\( V \) volume (m\(^3\))
\( x \) liquid phase mole fraction
\( X^{sim}, X^{exp} \) simulated or experimental property
\( y \) vapour phase mole fraction
\( Y \) objective function used in Eq. (18)

Greek symbols
\( \gamma, \lambda, \lambda_1, \lambda_2, \mu \) adjustable coefficients used in Eqs. (9), (10) and (13)
\( \beta \) characteristic universal exponent used in Eqs. (9) and (13)
\( \rho \) density (kg m\(^3\))
\( \rho_c \) critical density (kg m\(^3\))
\( \sigma \) Lennard-Jones diameter (Å)
\( \varepsilon \) Lennard-Jones well depth (K)
\( \varepsilon_0 \) vacuum permittivity (J\(^{-1}\) C\(^2\) m\(^{-1}\))
\( \eta \) viscosity (mPa s)
\( \nu_i \) stoichiometric coefficient of component \( i \)
\( \mu_i \) chemical potential of component \( i \) (J)
\( \Gamma_i \) ratio of experimental over simulated vapour pressures of specie \( i \)

Acknowledgment
The authors would like to acknowledge the support of the seventh framework program of the European Commission via the collaborative project COCATE “Large-scale CCS Transportation infrastructure in Europe” – GA No. 241381. VL, EB and ND also acknowledge financial help from the French Agence Nationale de la Recherche (ANR), under grant SUSHI (Grant No. ANR-07-BLAN-0268) “SimUlation de Systèmes Hétérogènes et d’Interfaces”. BC would like to thank Dr. Bernard Rousseau for the use of the NEWTON MD code.

References


