Prediction of experimental properties of CO$_2$, improving actual force fields.

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Abstract

Most of the existing classical CO$_2$ models fail to reproduce some or many experimental properties such as surface tension, vapor pressure, density and dielectric constant at different thermodynamic conditions. Therefore, it is proposed a new computational model to capture better structural, dynamical and thermodynamic properties for CO$_2$. By scaling the Lennard Jones parameters and point charges; three target properties, static dielectric constant, surface tension and density, were used to fit actual experimental data. Moreover, by constructing a flexible model, effects of polarization might be included by variations of the dipole moment. Several tests were carried out in terms of the vapour-liquid equilibria, surface tensions and saturated pressures showing good agreement with experiments. Dynamical properties were also studied, such as diffusion coefficients and viscosities at different pressures, and good trends were obtained with experimental data.

I. Introduction

CO$_2$ is the major waste contribution of the energy production and the most important greenhouse gas leading to global climate change. Since the Industrial Revolution anthropogenic emissions, primarily from fossil fuels and deforestation, have rapidly increased their concentration in the atmosphere, driving to global warming. Therefore, capture and retention of CO$_2$ became matter of several studies, not only for scientist but also for engineers. From the experimental point of view several techniques have been developed, however theoretical approaches have been used, such as computer simulations, as alternatives to study the phenomena. Therefore, from the computer simulations perspective is important to have realible models to produce good result compared with experimental data.

Nowadays, there are several CO$_2$ models, i.e. force fields, described in the literature. Murthy et al. developed two- and three-site force fields with Lennard Jones (LJ) interactions that included a point-quadrupole moment located at the center of mass of the molecule. Möller and Fischer presented a force field with two interacting LJ sites with a point-quadrupole, with parameters that fit experimental data of vapour-liquid equilibrium coexistence (VLEC). Vrabec et al. reparametrized the model to improve VLEC. The EPM and EPM2 (elementary physical models), developed by Harris and Yung, are CO$_2$ force fields widely used with LJ sites and point charges in every atom. The Lennard Jones parameters of EPM model were obtained through the production of the internal energy and pressure at temperature of $T = 239$ K whereas the parameters of the EPM2 were obtained to reproduce the critical properties. The TraPPE$_{Flex}$ model developed by Potoff and Siepmann was obtained to fit the VLEC of the CO$_2$ - propane mixture. Another common CO$_2$ force field, proposed by Potoff et al., was obtained by modifying the parameters in the attractive term of the interaction potential and it included point charges to adjust the VLEC data.

On the other hand, Zhang and Duan developed a force field with three LJ sites and point charges and Merker et al. reported a force field with three LJ sites with a point-quadrupole represented by three point charges. That model was optimized for VLEC data to obtain 0.4% deviation from the experiments in the saturated liquid density and 1.8% in
the vapour pressure. Persson developed a “One-Center” force field with a quadrupole for the CO$_2$ with parameters adjusted to the VLEC data. Ab initio methods have been also used to construct CO$_2$ force fields, for instance Bock et al. proposed an intermolecular potential with 5 interacting sites and Bukowski et al. proposed an intermolecular potential from a perturbation theory, however, Bratschi et al. concluded that the VLEC behavior is not accurately represented with those models.

Despite the fact that CO$_2$ is quite polarizable, polarizability effects are not expected in the thermophysical properties of pure CO$_2$. However, in CO$_2$ mixtures with polar components, like water, the properties may not be exact when using non-polarizable force fields. Vlcek et al. obtained new optimized parameters for a CO$_2$ - H$_2$O mixture using SPC/E water and EPM2 force field, however, the compositions of the CO$_2$-rich phase at 348 K were not adequately represented. Recently, Orozco et al. performed MC simulations in the Gibbs ensemble to study the VLEC of the CO$_2$ - H$_2$O mixture. It was found that non-polarizable force fields, such as the TraPPE model, have limitations in the prediction of compositions and densities for steam and liquid phases.

It is worthy mentioning that the existing models, using molecular dynamics, reproduce some of the CO$_2$ properties but they fail to reproduce others, i.e. there is not a CO$_2$ model which captures most of the actual experimental properties. However, the EPM2 model using Monte Carlo methods captures several properties such as densities, VLEC and vapour pressures but it does not reproduce surface tension or dielectric constants. Recently a polarizable model proposed by Jiang et al. with gaussian charges using monte carlo methods reproduced correctly VLEC and vapour pressures and they obtained good dynamical properties, however, they did not calculate surface tensions neither dielectric constants.

In the present paper we propose a new simple flexible CO$_2$ force field to reproduce better thermodynamic, structural and dynamical experimental data. The interest of having a flexible model is to study changes in the molecular geometry to search thermodynamic states due to dipole moment variations. A flexible molecule can be obtained with changes in the O-C-O angle which could modify the dipole moment and consequently producing fluctuations in the dielectric constant.

The remaining of the paper goes as follows. In section 2 the new model for the CO$_2$/ε is introduced. In section 3, the methodology to obtain of the new parameters is described, section 4 shows the simulation details and the results are analysed in section 5. Conclusions are presented in section 6.

II. The CO$_2$/ε Model

Carbon dioxide, CO$_2$, is a linear and symmetric molecule with zero dipole moment. The model consists of intra and intermolecular potentials. In fact, in order to have a flexible model an harmonic potential was included in the intramolecular interaction, see figure ??.

\[
U(\theta) = \frac{k_\theta}{2} (\theta - \theta_0)^2,
\]  

(S.1)

where \(\theta\) is the angle O-C-O and \(\theta_0\) refers to the equilibrium value, \(k_\theta\) is the spring constant.
TABLE S 1: Parameters of the CO\(_2\) models considered in this work.

| model     | \(d_{OC}\) (Å) | \(k_θ\) (kJ/mol rad\(^2\)) | \(θ_{OCO}\) (deg) | \(ε_{O−O}\) kcal/mol | \(σ_{O−O}\) Å | \(ε_{C−C}\) kcal/mol | \(σ_{C−C}\) Å | \(q_Ο\) (e) | \(q_C\) (e) |
|-----------|-----------------|----------------------------|------------------|---------------------|------------|---------------------|------------|-----------|-----------|
| CO\(_2/ε\) | 1.170           | 500                         | 180              | 0.03547             | 2.363      | 0.220578            | 2.62585   | -0.6204   | 1.2408   |
| EPM2      | 1.149           | 1236                        | 180              | 0.669335            | 3.033      | 0.669335            | 3.033      | -0.3256   | 0.6512   |
| TraPPE    | 1.160           | 1236                        | 180              | 0.656806            | 3.050      | 0.224478            | 2.800      | -0.3500   | 0.7000   |

For the intermolecular potential, between two CO\(_2\) molecules, the Lennard Jones (LJ) and Coulomb interactions are used,

\[
u(r) = 4\epsilon_{αβ} \left[ \left( \frac{\sigma_{αβ}}{r} \right)^{12} - \left( \frac{\sigma_{αβ}}{r} \right)^{6} \right] + \frac{1}{4\pi\epsilon_0} \frac{q_α q_β}{r} \tag{S.2}
\]

where \(r\) is the distance between sites \(α\) and \(β\), \(q_α\) is the electric charge of site \(α\), \(ε_0\) is the permittivity of vacuum, \(ε_{αβ}\) is the LJ energy scale and \(σ_{αβ}\) the repulsive diameter for an \(α−β\) pair. The cross interactions between unlike atoms are obtained using the Lorentz-Berthelot mixing rules,

\[
σ_{αβ} = \left( \frac{σ_{αα} + σ_{ββ}}{2} \right) ; \quad ε_{αβ} = (ε_{αα} ε_{ββ})^{1/2} \tag{S.3}
\]

III. Parametrization Approach

Using molecular dynamics (MD) simulations two CO\(_2\) models, TraPPE\(_F\)lex (flexible)\(^{18}\) and EPM2\(^{17}\) were initially tested to evaluate some thermodynamic properties such as the surface tension. Then, with the method suggested by Alejandre et al.\(^{20}\) the surface tension was determined, however, the computational results did not agree well with the experiments. Therefore, in order to improve the actual CO\(_2\) models series of molecular dynamics were conducted to find a set of parameters of a CO\(_2\) flexible model to reproduce better the experiments. The procedure started using a CO\(_2\) TraPPE\(_F\)lex force field following the method of Salas et al.\(^{21}\) i.e. by modification of the \(ε\) and \(σ\) Lennard Jones parameters to fit the experimental surface tension and the density. In the same procedure, as Fuentes et al. reported,\(^{22,23}\) the site charges were also scaled until the static dielectric constant was improved.

The purpose of the present work is also to built a flexible model, then the harmonic potential constant is also parametrized to increase flexibility that is linked to the polarity of the molecule and the dielectric constant by the dipole moment.

IV. Simulation Details

Molecular dynamic simulations were performed using GROMACS\(^{26}\) software and the new CO\(_2\) parameters were estimated with three target properties, the static dielectric constant, the surface tension and density. For the surface tension calculations a CO\(_2\) slab was located
in a parallelepiped cell with dimensions $L_x = L_y = 9.269$ nm and $L_z = 3L_x$, i.e. the surface area was large enough to avoid any finite size effects and 5324 molecules were used in the simulations. Then, simulations in the NVT ensemble with periodic boundary conditions applied in all three directions were conducted. The equations of motions were solved using the leapfrog algorithm with a time step of 2 fs using the Nose-Hoover thermostat with a parameter of 1.4 and LINCS algorithm to keep bond distances. Electrostatic interactions were handled with the particle mesh Ewald (PME) method with a grid space of 0.35 nm and a spline of order 4. The truncation potential distance was 2.6 nm. Liquid phase simulations were performed in the isotropic NPT ensemble with a fixed number of molecules, $N=500$. The LJ and the real part of electrostatic interactions were truncated at 1 nm, and the PME method was used for the long-range electrostatic part with the following settings: a tolerance of $10^{-5}$ for the real space contribution, a grid spacing of 0.12 nm and a 4-order interpolation. The energy and pressure corrections implemented in GROMACS were also applied due to the use of a finite cut-off for LJ interactions.

V. Results

It is already known that the important parameter to modify the surface tension is the $\epsilon_{LJ}$ parameter. Therefore, simulations at different $\epsilon_{LJ}$ values, by scaling all $\epsilon_{LJ}$ parameters, were conducted until the error with the target property was less than 5.6 % with respect to the experimental value. The average components of the pressure tensor were obtained for 30 ns after an equilibration period of 5 ns. The corresponding surface tension, $\gamma$, for planar interfaces was calculated from the mechanical definition:

$$\gamma = \frac{1}{2} L_z [P_{zz} - \frac{1}{2}(P_{xx} + P_{yy})]\quad (S.4)$$

where $P_{\alpha\alpha}$ are the diagonal elements of the microscopic pressure tensor. The factor 1/2 takes into account the two symmetrical interfaces in the system.

In figure 1 the surface tension results of the new CO$_2$/\(\varepsilon\) force field with other most common models are shown. In the figure, it is observed that the new CO$_2$/\(\varepsilon\) force field describes better the experimental surface tension values at different temperatures. In general, the other CO$_2$ models fail to reproduce the experiments, only the EPM2 has good agreement with experimental data between temperatures $T = 260$ K and $T = 280$ K whereas TraPPE$_{Flex}$ results are even further away from the experiments.

The selection of the charges in the new model was determined by calculation of the dielectric constant obtained by calculation of the dipole moment $\mathbf{M}$, $\epsilon = 1 + \frac{4\pi}{3k_B T V} (<\mathbf{M}^2> - <\mathbf{M}>^2)\quad (S.5)$

where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The dielectric constant was obtained for long simulations, 40ns, using isotropic NPT ensemble. The new set of charges were obtained by variation of the original ones, of all atomic sites, until the target
Figure 1: Surface tension as a function of temperature for the different CO$_2$ models. The simulation results for the EPM2, TraPPE$_{Flex}$ and CO$_2$/\(\varepsilon\) were obtained from this work. The continuous line represents the experimental data. 

property, the dielectric constant was about 22.2\% with respect to the TraPPE$_{flex}$ and it does not cause other properties to be lost.

The proper evaluation of the dielectric constant needs long simulations to have the average dipole moment of the system around zero. Results of the dielectric constant at 273.15K of temperature at different pressures are show in the figure where it is observed that the new force field CO$_2$/\(\varepsilon\) shows better agreement with the experiments.

The reproduction of the dielectric constant show that the new force field can modify the CO$_2$ structure in order to capture the change in the dipole moment.

With the new \(\epsilon_{LJ}\) and charges values the \(\sigma_{LJ}\) of all atoms were also scaled to match the density at 50 bar and 280K of pressure and temperature repectively with errors less than 17\%. The new parameters of the CO$_2$/\(\varepsilon\) model are indicated in table 1. Finally, to have a flexible model the angular potential was reduced from the original one, using an angular constant of \(k_\theta = 500\). This value was chosen since it reproduced better the experimental data. For all those last calculations simulations in the NPT ensemble were carried out with different pressures using Nose-Hoover barostat.

Flexibility of the model was tested at temperature of T = 300 K and pressure of P = 1 bar by measuring the average O-C-O angle over the simulation time, see table 2. From table 2 is observed that the new model is a little more flexible than the others as a consequence of the reduction of the spring constant, \(k_\theta\), in the angular potential. In fact, it is observed that the dipole moment increased with respect to the other models by improving the dielectric constant. Since fluctuations in the dipole moment are related with the instantaneous polarization then the factor \(G_K\) (equation S.6) was introduced to calculate the differences in the polarization.
Figure 2: Dielectric constant as a function of pressure at 273.15K of temperature for the CO2/\varepsilon, EPM2 and TraPPE force fields. The continuous line represents the experimental data.\[53\]

Figure 3: Graphical representation of CO2 in gas phase at 300K and 1 bar of temperature and pressure, respectively; According to the data reported in table 2 among the different models studied in the present work,

\[ G_K = \langle M^2 \rangle / N \mu^2 \]  \hspace{2cm} (S.6)

where \( M \) is the total dipole moment of the system, \( N \) is the number of molecules and \( \mu \) is the dipole moment of a single molecule. From the results it is depicted that \( G_K \) increase for CO2/\varepsilon table 2 then the polarizations change in order to improve the dielectric constant figure 2.

Based on the optimal point charge approximation of Anandakrishnan et al.\[50\] described in figure 3. We calculated the dipole and quadrupole moments, using S.7 and S.8 that describe well these dipole and quadrupole moments of the CO2 molecule in this context. The values are given in table 2.

\[ \mu = 2qz \]  \hspace{2cm} (S.7)
It is observed that the calculated dipole and quadrupole moments of the CO$_2$/ε model are higher than those obtained with the other models. Due to the flexibility of CO$_2$/ε model and the new parameters the electrostatic moments produce high electrostatic moments. Even though the CO$_2$/ε dipolar moment is higher respect to the other models all values are small. On the other hand, the quadrupole moment reported in the literature is 4.3 DÅ (1D = 0.2082 eÅ$^2$) and from table 2 is noted that none of the models have good values, the TraPPE and the EPM2 force fields underestimate the data with an error of 21 % and 28 %, respectively whereas the CO$_2$/ε overestimate the value with 42 % error. However, in order to have similar quadrupole effects of all the models, we keep the CO$_2$/ε quadrupole moment per charge the same as given in the other models (see last column in table2). With this approximation not only the dielectric constant is improved but also other thermodynamics properties remained.

One important property within the chemical engineering community is the calculation of vapour pressures. In figure 4 the results of the vapour pressure calculated with the perpendicular component of the pressure tensor respect to the surface are shown for different CO$_2$ force fields. It is observed that the new CO$_2$/ε describes well the vapour pressure, the EPM2 increases its value from 220K and overestimates the experimental value at high temperatures however the trappe flexible force field overestimate the experimental values.
Figure 5: Vapour - Liquid phase equilibrium. CO$_2$/$\varepsilon$ obtained from this work and the values of EPM2$_{MC}$ are taken from Harris et al.\cite{7} The continuous line represents the experimental data.\cite{31}

The vapour and liquid densities were calculated with the slab method described above and the results are plotted in figure 5. It is noted that the liquid and vapour branches are well described with the Monte Carlo EPM model\cite{2} The CO$_2$/$\varepsilon$ model produces good vapour branch although the liquid line is not as good as the EPM model.
In order to test the new force field at different thermodynamic conditions calculations of the density as function of the temperature at different pressures are shown in figure 6. As a general trend the CO$_2$/$\varepsilon$ capture the liquid branch reasonably well at high pressures. However, at high temperatures different issues are depicted.

The structure of CO$_2$ is represented by the proposed CO$_2$/$\varepsilon$ force field and plotted in terms of the pair distribution function (g(r)) in figure 7. It is observed that the CO$_2$/$\varepsilon$ captures better the first peak indicated by the experiments, i.e. at 0.319 nm very close to the experimental data, 0.332 nm. In fact, there is a second peak around 0.434 nm close to the experimental value of 0.405 nm, figure 8B, is noted the second peak, in the g(r), higher than the first one whereas the experiments show two peaks nearly at the same height. Due to the flexibility of the model it is possible that the CO$_2$ molecule bends more and more attraction between O-O atoms compare with the C-O interactions could be produced by increasing the second peak of the g(r), i.e the larger number of second nearest neighbors. At large distances the g(r) of the CO$_2$/$\varepsilon$ looks more similar than the experimental one.

Experiments of the liquid CO$_2$ structure were obtained from van Tricht et al. using neutron diffraction experiments. 35

Dynamical properties were also calculated with the new CO$_2$/$\varepsilon$ model. In figure 8,9 results of the diffusion coefficients as function of the pressure at two different temperatures are shown. At T = 223 K the CO$_2$/$\varepsilon$ in general reproduces better the values better than the others models respect to the experiments. At T = 298 K the CO$_2$/$\varepsilon$ captures well the shape of the experimental data, in particular at low pressures, however data for all models are not good compared with the experiments.

It is important to mention that the size of the simulated system for the diffusion coefficients calculations were big enough to avoid any size effects as indicated in previous works. 36 The diffusion coefficient was obtained from the long-time limit of the mean square displacement according to the Einstein relation, 37

$$D = \lim_{t \to \infty} \frac{< (r(t) - r(0))^2 >}{6t} \tag{S.9}$$

where r(t) corresponds to the position vector of the center of mass at time t and the averaging $< ... >$ is performed over both time origins.

Finally, another dynamical property was also calculated, the viscosity ($\eta$), and plotted in figure 9. The viscosity was calculated with the GreenKubo formula 5 relates the shear

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TABLE S 2: Results at T = 300 K and P = 1 bar for the CO$_2$ models considered in this work.

|          | $\theta_{prom}$ | $G_K$ | Dipole moment | $|Q_T|$ | $|Q_T/q_0|$ |
|----------|-----------------|-------|---------------|--------|------------|
|          | degree          |       | debye (D)     | DA     | DA/e       |
| TraPPE$_{flex}$ | 179.168         | 1.26086 | 0.0283        | 3.385  | 9.6        |
| EPM2     | 179.174         | 1.24966 | 0.0269        | 3.096  | 9.5        |
| CO$_2$/$\varepsilon$ | 178.2           | 1.40647 | 0.1095        | 6.117  | 9.8        |
Figure 6: Logarithmic of the density as a function of temperature at different pressures
A) P = 50 bar. B) P = 100 bar. C) P = 1000 bar. D) P = 2000 bar. The simulation results for TraPPE*Flex, EPM2 and CO₂/ε were obtained from this work. The solid black line represents the experimental data of the liquid phase and the solid black line with stars represents experimental data of the vapour phase.

Figure 7: Figure A. The Radial distribution functions g_{OO}, g_{OC} and g_{CC} for CO₂/ε are plotted from the calculation of molecular Dynamics at T = 239 K and P = 14.5 bar. Figure B. Radial distribution functions, g(r), for CO₂/ε and neutron weighted pair correlation function at T = 239 K and P = 14.5 bar; experimental pair correlation function is shown in black circles.
Figure 8: Diffusion coefficients as a function of pressure at A) 298 K of temperature and B) 223 K of temperature. The simulation results for the TraPPE, EPM2 and CO₂/ε are obtained from this work. The black square and solid black lines represent the experimental data.

Viscosity to the autocorrelation function ACF of the off-diagonal components of the stress tensor \( P_{\alpha\beta} \), namely,

\[
\eta = \frac{V}{k_B T} \int_0^\infty < P_{\alpha\beta}(t_0) P_{\alpha\beta}(t_0 + t) >_{t_0} dt,
\]

(S.10)

In figure 9 is observed that the CO₂/ε model gives the correct tendency with the experiments.
VI. Conclusions

Comprehensive molecular dynamics simulations were conducted to build a new flexible CO$_2$ molecule. Then, series of simulations were carried out to find a new set of parameters for the CO$_2$/\(\varepsilon\) model. The proposed flexible force field captured polarization of the molecule and reproduced correctly the experimental surface tensions, vapor pressures, densities and the static dielectric constants. Dynamical properties were also calculated, and even though the CO$_2$/\(\varepsilon\) model was not parameterized to reproduce these transport properties, the calculations with the new model are close to the experimental values.

Variation on the \(\varepsilon\)-LJ parameter influence interaction between molecules and somehow internal energy of the system, therefore thermodynamic properties might be modified and it could be the reason why the parameter is the one that correct the surface tension. On the other hand, \(\sigma\)-LJ affects the size structure and consequently the system density. Electrostatic properties can be altered by point charges and therefore properties such as the static dielectric constant can be modified by adjustment of those charges. It has been shown that changes of LJ-parameters and charges can directly affect some properties, however they also might influence any other by spoiling correct data and it could be the reason that in some case some properties fits correctly whereas others fails in other force fields. In fact, by adjusting parameters is hard to reproduce all thermodynamic and dynamical properties of the CO2, if some properties are correctly fitted there are other properties that might be wrong and vice versa, therefore the best selection of parameters are those which capture most of the properties with reasonable experimental error.
Previous works, with using polarizable models\[19\] have also shown good results with actual experiments, although they do not calculate surface tensions. Comparisons of the present results with a polarizable model are shown in the supplementary material. There, it is observed that our results agree with those data.

On the other hand, force fields using classical potentials fail to reproduce some or many experimental properties such as surface tension, vapor pressure, density and dielectric constant at different thermodynamic conditions. Therefore, in the present work, a new CO\(_2\) force field has been proposed; which reproduces several thermodynamics, structural and dynamical properties improving the present classical CO\(_2\) force fields.

It is worthy to mention that appropriate CO\(_2\) force fields can help us to perform more realistic and reliable simulations of actual system and to understand better the behaviour of real phenomena such as CO\(_2\) capture where good models are needed to explore real experiments.

VII. Conflicts of interest

There are no conflicts of interest to declare

VIII. Acknowledgments

The authors acknowledge support from DGAPA-UNAM-Mexico grant IN102017 and DGTIC-UNAM grant LANCAD-UNAM-DGTIC-238 for the supercomputer facilities. RFA thanks DGAPA-UNAM for a posdoctoral fellowship. We also acknowledge Alberto Lopez-Vivas and Alejandro Pompa for technical support. We also want to thank the reviewers for their comments of the manuscript, they help to improve significantly the paper.

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