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# MOLECULAR DYNAMICS AND THERMODYNAMICAL MODELLING USING SAFT-VR TO PREDICT HYDRATE PHASE EQUILIBRIA: APPLICATION TO CO<sub>2</sub> HYDRATES

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## ABSTRACT

This work was dedicated to the prediction of the three phase coexistence line (CO<sub>2</sub> hydrate–liquid H<sub>2</sub>O–liquid/vapour CO<sub>2</sub>) for the H<sub>2</sub>O+CO<sub>2</sub> binary mixture by using (i) molecular dynamics simulations, and (ii) the well known van der Waals-Platteeuw (vdWP) model combined with the SAFT-VR equation of state. Molecular dynamics simulations have been performed using the simulation package GROMACS. The temperature at which the three phases are in equilibrium was determined for different pressures, by using direct coexistence simulations. Carbon dioxide was modelled as a linear-rigid chain molecule with three chemical units, the well-known version TraPPE molecular model. The TIP4P/Ice model was used for water. To perform the thermodynamical modelling, the SAFT-VR EOS was incorporated in the vdWP framework. The values of the cell model parameters were regressed and discussed together with the influence of some assumptions of the vdWP model. Since SAFT-VR can describe most of fluids involved in hydrate modelling (inhibitors, salts...), this study is a first step in the description of hydrate forming conditions of more complex systems. Finally, the three-phase coexistence temperatures obtained with both simulations and theory at different pressures were compared with experimental results.

*Keywords:* gas hydrates, water, carbon dioxide, molecular dynamics, van der Waals-Platteeuw, SAFT.

## NOMENCLATURE

$\theta_L$ : Occupancy of large cages  
 $\theta_S$ : Occupancy of small cages  
MD: Molecular dynamic simulation

NPT: Isothermal-Isobaric ensemble  
 $\epsilon$ ,  $\sigma$ : Lennard-Jones potential well depth and size  
 $q$ : Partial electric charges  
 $S_{L-L}$ : Liquid H<sub>2</sub>O-liquid CO<sub>2</sub> equilibrium state  
 $S_{H-L}$ : Hydrate-liquid CO<sub>2</sub> equilibrium state

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$T_3$ : Three phase coexistence temperature (hydrate-liquid H<sub>2</sub>O-liquid CO<sub>2</sub>)

$\mu_w^H$ : chemical potential of water in the hydrate phase

$\mu_w^{LW}$ : chemical potential of water in the liquid water phase

$\mu_w^\beta$ : chemical potential of water in the empty hydrate phase

$v_i$ : number of i-type cavities per water molecule

$\theta_{ji}$ : fractional occupancy of i-type cavities with j-type guest molecules

$k_B$ : Boltzmann constant

$\Delta\mu_w$ : water chemical potential difference between the liquid water phase and the empty hydrate phase

$\Delta H_w$ : water enthalpy difference between the liquid water phase and the empty hydrate phase

$\Delta V_w$ : water volume difference between the liquid water phase and the empty hydrate phase

$\Delta C_p$ : water molar heat capacity difference between the liquid water phase and the empty hydrate phase

$x_w$ : mole fraction of water in the water phase

## INTRODUCTION

Molecular simulation of hydrates and thermodynamic modelling are of great importance for both fundamental research and hydrate-based applications. Developing novel approaches to study hydrate phase equilibria is thus very interesting and challenging. In some practical applications, such as the use of hydrates in gas separation processes and/or for refrigeration [1], some technological options are based on the formation/dissociation of carbon dioxide hydrates.

## MOLECULAR MODELS AND SIMULATION DETAILS

CO<sub>2</sub> hydrate adopts the sI structure. It is simple cubic and has the space group  $Pm\bar{3}n$ . The unit cell consists of 46 water molecules and it contains eight water cages (six tetradecahedra  $5^{12}6^2$  and two dodecahedra  $5^{12}$ ). On one hand, oxygen coordinates were generated from the crystallographic parameters provided in Yousuf et al. [1]. On the other hand, hydrates present proton disorder. Hydrogens were placed using the algorithm proposed by Buch *et al.* [2] to generate

solid configurations satisfying the Bernal–Fowler rules [3] and with zero dipole moment.

For our study, the hydrate configuration was obtained replicating this unit cell two times in each dimension (a total of 368 water molecules forming 64 cavities). In the case of CO<sub>2</sub> hydrates, most experimental estimation of the occupancy range vary from 80% to 100% [4-7]. In this work, we have chosen to start the simulations with a cage occupancy of 87.5 %, corresponding to all the large cages and half of the small ones occupied by CO<sub>2</sub> (see Table 1).

Notation	Occupancy(%)	$\theta_L$	$\theta_S$
87% <sub>S</sub>	87.5	1	0.5

Table 1: Cage occupancy for the initial hydrate structure ( $\theta_L$  Occupancy of Large Cages;  $\theta_S$ : Occupancy of Small Cages)

Note that the filling of the small cages was done randomly.

To generate the initial configuration we followed the methodology proposed by *Fernandez et al.*[8]: obtaining an initial configuration formed by a slab of liquid H<sub>2</sub>O surrounded at one side by a slab of the CO<sub>2</sub> hydrate and at the other site by a slab of CO<sub>2</sub> molecules in the liquid phase. This technique was used by M.M. Conde and C. Vega [9,10] to predict the three-phase coexistence line in CH<sub>4</sub> hydrates. The details about the composition of the phases are given in Table 2.

Hydrate phase	H <sub>2</sub> O Liquid phase	CO <sub>2</sub> Liquid phase
368H <sub>2</sub> O/56 CO <sub>2</sub>	368H <sub>2</sub> O	192 CO <sub>2</sub>

Table 2: Number of molecules situated in the different phases for the system studied in this work.

The typical size of the simulation box for the initial configuration was 80x24x24 Å<sup>3</sup>. The interfaces between the three phases are perpendicular to the  $x$  axis. Periodic boundary conditions were employed in the three directions of space. The initial arrangements allow us having each phase in contact with the other two.

We have performed *NPT* molecular dynamic simulations at different temperatures and pressures at 60, 100, 200, 400, 1000 and 3000 bar using the molecular dynamics package GROMACS (version 4.6.1) [11]. The temperature was fixed using a Nosé–Hoover thermostat [12,13] with a relaxation time of 2 ps. To keep the pressure constant, a Parrinello–Rahman barostat [14,15] was used. The relaxation time of the barostat was 2 ps. The time-step used in the simulations was 2 fs. The typical length of the simulations was 400ns. The Lennard-Jones part of the potential was truncated at 9 Å. Ewald sums were used to deal with electrostatic interactions. The real part of the Coulombic potential was truncated at 9 Å. The Fourier part of the Ewald sums was evaluated by using the PME method [16]. The width of the mesh was 1 Å and we used a fourth order polynomial to evaluate Coulombic interactions.

The water was modelled, following the well-known TIP4P[17] molecular model geometry: four interacting centres, with the oxygen atom O as the only LJ interaction site, a partial charge (M-site) located along the H-O-H angle bisector, and two hydrogen atoms H, which are represented by partial point electric charges. M.M. Conde and C. Vega [9,10] showed that the combination of TIP4P/Ice [18] model for water and a single LJ centre for methane reproduces nicely the three phase coexisting line (hydrate-H<sub>2</sub>O-CH<sub>4</sub>) in methane hydrates. Therefore, we have chosen the TIP4P/Ice molecular model for water in this work.

In the case of carbon dioxide, the most usual model is a linear-rigid chain molecule with three chemical units, representing each of the C and O atoms, and each unit or interacting site consists of a combination of a LJ site plus an electric point charge. Among the available parameterizations for this molecular structure, the TraPPE (transferable potentials for phase equilibria) [19] model was tested. This model has been shown to provide accurate estimation of interfacial properties of CO<sub>2</sub>, as shown by *Miguez et al.* [20]. Table 3 summarizes the characteristic parameters for all the molecular models studied in this work.

Atom	$\epsilon/\kappa(\text{K})$	$\sigma/\text{Å}$	$q(\text{e})$	Geometry
TIP4P/Ice H <sub>2</sub> O				
O	106.1	3.1668	0.0	O-H: 0.9572 Å
H	0.0	0.0	0.5897	O-M: 0.1577
M	0.0	0.0	-1.1794	H-O-H:104.5°

TraPPE CO <sub>2</sub>				
C	27.0	2.80	0.70	C-O:1.16 Å
O	79.0	3.05	-0.35	O-C-O:180°

Table 3: Lennard-Jones potential well depth  $\epsilon$  and size  $\sigma$ , partial charges  $q$ , and geometry, of the H<sub>2</sub>O and CO<sub>2</sub> models used.

All of these models used in this work are rigid and non polarizable.

Following the ensuing discussion, the intermolecular potential between molecules  $i$  and  $j$  was computed by the following equation where the Lennard-Jones and Columbic interactions are considered as the main contributors:

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

The H<sub>2</sub>O-CO<sub>2</sub> interaction is described using a LJ potential with the cross interaction parameters given by the Lorentz–Berthelot rules [21]:

$$\epsilon_{CH_4-H_2O} = \sqrt{\epsilon_{CH_4-CH_4} \cdot \epsilon_{H_2O-H_2O}} \quad (2)$$

$$\sigma_{CH_4-H_2O} = \frac{(\sigma_{CH_4-CH_4} + \sigma_{H_2O-H_2O})}{2} \quad (3)$$

## THERMODYNAMIC MODELLING

The well-known van der Waals-Platteeuw (vdWP) theory [22] was used to compute the hydrate formation conditions. The basic assumption of the vdWP model is the balance of the chemical potential of water in all phases at equilibrium:

$$\mu_w^H - \mu_w^\beta = \mu_w^{LW} - \mu_w^\beta \quad (4)$$

where the superscript  $\beta$  denotes an hypothetical empty hydrate lattice. Similarly to the Langmuir adsorption theory and following several assumptions (see [22] for more details), van der Waals and Platteeuw derived the following expression for the chemical potential difference of water between the empty and actual hydrate phase:

$$\frac{\mu_w^H - \mu_w^\beta}{k_B T} = \sum_i v_i \ln \left( 1 - \sum_j \theta_j \right) \quad (5)$$

where  $v_i$  is the number of  $i$ -type cavities per water molecule and  $\theta_j$  is the fractional occupancy of  $i$ -

type cavities with J-type guest molecules.  $\theta_{ji}$  is described by

$$\Theta_J = \frac{C_{Ji} f_J}{1 + \sum_K C_{Ki} f_K} \quad (6)$$

where  $f_J$  is the fugacity of gas component J and is calculated in this work with the SAFT-VR equation of state [23]. Van der Waals and Platteeuw used the Lennard-Jones-Devonshire cell theory to estimate the Langmuir constants  $C_{Ji}$  and proposed

$$C_{Ji} = \frac{4\pi}{kT} \int_0^{\bar{r}} \exp\left(-\frac{\omega(r)}{kT}\right) r^2 dr \quad (7)$$

where  $\omega(r)$  is a spherically symmetric potential,  $r$  being the radial distance from the center of the cavity. In this work, we have used the Kihara cell potential derived by Parrish and Prausnitz [24] for the interaction between guest and host molecules. The chemical potential difference between liquid water and water in the empty lattice are calculated from the equations given by Holder et al. [25]

$$\frac{\mu_w^{Lw} - \mu_w^\beta}{RT} = \left(\frac{\Delta\mu_w}{RT}\right)_{T_0, P_0} - \int_{T_0}^T \left(\frac{\Delta H_w}{RT^2}\right) dT + \int_0^P \left(\frac{\Delta v_w}{RT}\right) dP - \ln(\gamma_w x_w) \quad (8)$$

Here, the activity coefficient of water  $\gamma_w$  was taken equal to 1 due to the negligible deviation from ideality obtained by dissolution of CO<sub>2</sub> in water [26,27]. The other thermodynamic properties were computed with the SAFT-VR equation of state. Moreover, the enthalpy difference was taken temperature dependent via

$$\Delta H_w = \Delta H_w^0 + \int_{T_0}^T [\Delta C_p^0 + b(T - T_0)] dT \quad (9)$$

The parameters for CO<sub>2</sub> and water in the SAFT-VR framework were taken from dos Ramos et al. [28] together with the interaction parameter that dos Ramos et al. had fitted to predict the phase behavior of the water + CO<sub>2</sub> binary mixture.

The thermodynamic reference properties used in this work are given in Table 4.

		Reference
$\Delta v_w$ (m <sup>3</sup> /mol)	4.5959	[29]
$\Delta C_p^0$ (J/mol.K)	-38.12	[29]
$b$ (J/mol.K <sup>2</sup> )	0.141	[29]
$\Delta\mu_w^0$ (J/mol)	1287	[30]
$\Delta h_w^0$ (J/mol)	-5080	[30]

Table 4: thermodynamic reference properties for structure I.

Hence, by solving Eq. (4) and specifying either pressure or temperature, one can determine the equilibrium conditions of hydrates.

## RESULTS

The main goal of this work is to estimate the three-phase (hydrate-H<sub>2</sub>O-CO<sub>2</sub>) coexistence line in CO<sub>2</sub> hydrates by molecular simulations and the vdWP/SAFT-VR modelling.

In molecular dynamics simulations, the energy of the system fluctuates in *NPT* simulations. Systematic changes in the energy are associated with phase transitions. At high temperatures the region formed by hydrate will melt, resulting in a system with two phases (liquid H<sub>2</sub>O and CO<sub>2</sub>) when reaching the equilibrium state denoted as  $S_{L-L}$  (see Figure 1). However, at low temperatures the liquid water will crystallize forming a system with other two phases (hydrate-liquid CO<sub>2</sub>) when reaching the equilibrium state denoted as  $S_{H-L}$  (see Figure 1). At a certain temperature, the three phases will be in equilibrium. This temperature will be denoted as  $T_3$ .

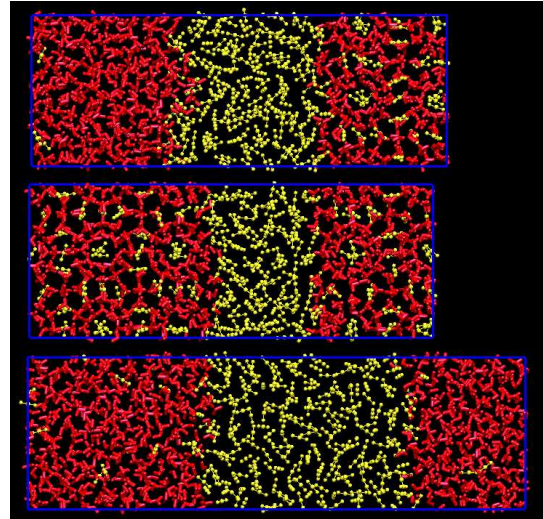


Figure 1. Snapshots for three-phase system (hydrate-liquid H<sub>2</sub>O-liquid CO<sub>2</sub>) at 400 bar. The initial configuration is shown on the top, whereas the final configuration at 265K is shown in the middle ( $S_{H-L}$ ), and the final configuration at 275K is shown at the bottom ( $S_{L-L}$ ). H<sub>2</sub>O molecules are plotted in red and CO<sub>2</sub> molecules in yellow.

We shall start by presenting the results obtained at 400 bar. The time evolution of the potential energy for the system at this pressure is shown in Figure 2. In the initial configuration we have a three-phase system composed by hydrate, liquid water and CO<sub>2</sub> liquid (see Figure 1). For all temperatures, we have used the same initial configuration.

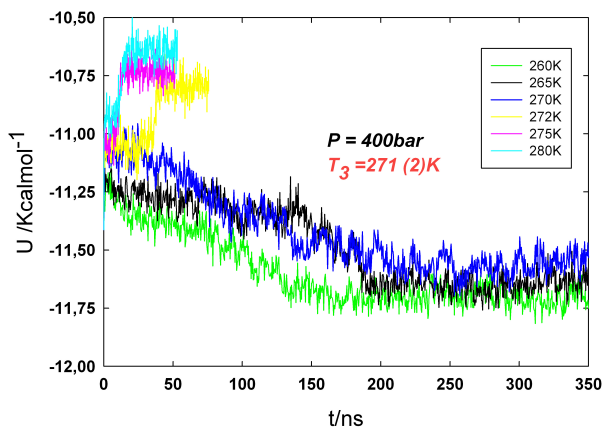


Figure 2. Evolution of the potential energy as a function of time for the *NPT* runs for three-phase system (hydrate-liquid H<sub>2</sub>O-liquid CO<sub>2</sub>) at 400 bar. Results only for a few representative temperatures are shown.

For temperatures above  $T_3$  the potential energy increases with time, indicating the melting of the CO<sub>2</sub> hydrate. This is the case for the temperatures from 272 to 285 K, which are plotted in Figure 2. The plateau that is visible for these temperatures corresponds to a liquid equilibrium state (i.e. liquid H<sub>2</sub>O-liquid CO<sub>2</sub>)

For temperatures below  $T_3$  the potential energy decreases very slowly with time until liquid H<sub>2</sub>O freezes completely in the subsequent 200 ns. CO<sub>2</sub> hydrate phase grows very slowly layer by layer. The fast growth of the CO<sub>2</sub> hydrate manifested by the presence of CO<sub>2</sub> bubbles is not observed in our simulations [31]. This is the case for the temperatures from 260 to 270 K. The final plateau of these runs indicates the complete formation of the CO<sub>2</sub> hydrate in coexistence with liquid CO<sub>2</sub> at the new equilibrium state.

In summary, the CO<sub>2</sub> hydrate melts at 400 bar for temperatures above 272 K, and the system crystallise for temperatures below 270 K. We will estimate  $T_3$  as the arithmetic average of the highest

temperature at which the CO<sub>2</sub> hydrate forms and the lowest temperature at which the hydrate dissociates. According to this criterion, the three phase coexistence temperature for the TIP4P/Ice model of water and the TraPPE model of carbon dioxide is  $T_3 = 271$  K at 400 bar. Finally, this methodology was applied to predict  $T_3$  at 60, 100, 200, 1000 and 3000 bar.

Concerning the thermodynamic modelling, the Kihara parameters used for CO<sub>2</sub> are given in Table 5. These parameters are generally obtained by fitting experimental data, mainly the hydrate dissociation conditions. Hence, their values depend on both the equation of state that have been used in the vdWP model and on the set of thermodynamic reference properties that have been selected. Here, the optimization was restricted to the energy interaction parameter  $\epsilon$  and the collision diameter  $\sigma$ . Indeed, the radius of the spherical molecular core  $a$  can be considered as a geometric parameter and thus its value should be considered as model independent. Solely the vapor CO<sub>2</sub>/liquid water/hydrate equilibrium conditions were used for the fitting.

		Reference
$a$ (Å)	0.6805	[29]
$\sigma$ (Å)	3.1	this work
$\epsilon/k_B$ (K)	165.1	this work

Table 5: Kihara potential parameters for CO<sub>2</sub>.

In Table 6 the values of  $T_3$  obtained from simulations at the considered pressures are presented and compared with the vdWP/SAFT-VR estimations and experimental data [32-36].

P/bar	$T_3^{MD}/K$	$T_3^{(vdWP/SAFT-VR)}/K$	$T_3^{Exp}/K$
3000	278(3)	300.04	293.8
1000	273(3)	289.24	289.6
400	271(3)	285.75	286.3
200	267(3)	284.48	284.8
100	267(3)	283.77	283.6
60	267(3)	283.47	283.2

Table 6: Three-phase coexistence temperatures ( $T_3$ ) at different pressures obtained from simulations and the vdWP/SAFT-VR modelling. The estimated error in  $T_3$  is shown within the parentheses. The experimental values are taken from Ref. [32-36].



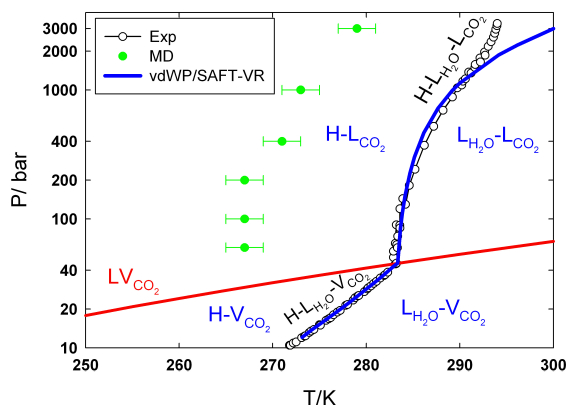


Figure 3. Representation of the three-phase coexistence temperature  $T_3$  as a function of pressure.

Results showed a deviation of 15K between the three-phase coexistence line obtained by molecular simulations and the experimental one. This deviation is likely to be an incorrect modeling of the H<sub>2</sub>O-CO<sub>2</sub> cross interaction. Indeed, in the case of CH<sub>4</sub> hydrate, by introducing positive deviations from the energetic Lorentz–Berthelot combination rule, the disagreement with experiment was reduced about 15 K [9]. In a future work, an interesting issue would be to show how  $T_3$  varies by increasing the strength of the H<sub>2</sub>O-CO<sub>2</sub> interaction while keeping constant water-water and CO<sub>2</sub>-CO<sub>2</sub> interactions.

The vdWP/SAFT-VR predictions are in good agreement with the experimental data except at  $P > 1000$  bar. Indeed, in this work, we have not considered the pressure dependence of both the volume of liquid water and the volume of the empty hydrate phase, which can not be the case at such high pressures.

Results are plotted in Figure 3.

## CONCLUSIONS

In this work, we have estimated the three-phase (hydrate-water-CO<sub>2</sub>) coexistence temperature  $T_3$  at different pressures by dynamic molecular simulation and vdWP/SAFT-VR modelling. On the one hand, molecular simulation results showed that the three-phase coexistence line obtained with the combination of TIP4P/Ice model for H<sub>2</sub>O and TraPPE for CO<sub>2</sub> is shifted of 15K from the experimental equilibrium curve. However, the general shape of the equilibrium curve is well

predicted. The introduction of positive deviations from Lorentz–Berthelot combination rule in this case should appear as an adequate choice for the study of CO<sub>2</sub> hydrates by dynamic molecular simulations. On the other hand, the vdWP/SAFT-VR modelling has allowed a good estimation of the dissociation conditions of the CO<sub>2</sub> hydrate, except at very high pressure because compressibility effects have not been taken into consideration in the present study.

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