Evaluation of the Efficiency of Clathrate Hydrates in Storing Energy Gases

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Abstract. We use Grand Canonical Monte Carlo simulations to examine the efficiency of hydrates in storing hydrogen. In this way, the hydrate lattice is treated as a solid substrate where gas adsorption takes place. Special focus is given to the study of multiple occupancy, namely the presence of more than one gas molecules in the same hydrate cavity. This phenomenon occurs in the case of hydrogen hydrates and may drastically increase their storage capacity. A parametric analysis is also carried out to quantify the correlation between the change in the lattice constant and the storage capacity since small changes in the size of the crystal unit cell may induce significant changes in the storage capacity especially in cases were multiple occupancy occurs.

1. Introduction
Clathrate hydrates are crystalline materials made of water molecules that are stable at low temperatures or high pressures. Their crystal lattice consists of cavities where gas molecules can be entrapped. The guest molecules are essential for the stability of the hydrate structures [1, 2]. As such, they have attracted extensive interest as potential materials for the storage of energy and environmental-related gases (e.g., hydrogen [3–6], methane, carbon dioxide). Storage and transportation of energy gases are of primary interest to the current study. Additional important applications of hydrates include the flow assurance in the oil and gas industry [7], gas mixture separation applications [8, 9], and the use of methane stored in geologic formation in the form of hydrates as a possible future energy source [10].

The most common hydrate structures are sI, sII, and sH. In the current study we use Monte Carlo simulations to examine the efficiency of the hydrate structure sII in storing hydrogen. Special focus is given to the study of multiple occupancy, i.e., the presence of more than one gas molecules in the same hydrate cavity. The existence of multiple occupancy was reported initially based on the experiments of Kuhs et al. [11]. Subsequently, a number of experimental [12, 13] and computational studies [14–17] confirmed the initial experimental observations. Such behaviour occurs also in the case of hydrogen hydrates and may drastically increase their storage capacity.

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A parametric analysis is carried out to quantify the correlation between the change in the lattice constant and the storage capacity since small changes in the size of the crystal unit cell may induce large changes in the storage capacity, especially in cases where multiple occupancy occurs.

Monte Carlo studies have been used extensively in order to estimate the storage capacity of different hydrate structures and guest gases [14–22]. Such studies used different water models (e.g., SPC/E [23], TIP4P [24]). Of interest to the current study is the case of TIP4P/Ice water model [25]. The particular model has been identified recently [26] as the most appropriate to predict accurately the three-phase equilibrium conditions for methane hydrate using molecular dynamics. The study identified that in order to obtain accurate predictions two requirements are needed. First, the solubility of the methane gas has to be accurately described and second, the water model should predict an accurate melting point for ice. These two requirements are met by TIP4P/Ice and therefore should be used in methane hydrate studies. It is the purpose of the current study to examine the effect of the particular water model on the storage capacity of hydrogen hydrates with respect to the size of the hydrate unit cell (expressed through the lattice constant).

2. Methodology

Monte Carlo simulations are performed in the Grand Canonical ensemble (GCMC) with the MCCCS Towhee code [27]. In this way, the hydrate lattice is treated as a solid substrate where gas adsorption takes place. Hydrate structure sII is examined over a wide range of temperatures (200 – 300 K) and pressures (1 – 500 MPa).

Both the lattice constant, and the space group symmetry of the examined hydrate structure have been determined from XRD measurements [28]. Oxygen atoms are placed exactly at the positions defined by the space group symmetry. For the selection of proton configuration the “ice-rules” (Bernal–Fowler [29]) have been obeyed and the proton configuration with the minimum dipole moment was adopted. The values of the lattice constants are kept fixed for the entire pressure and temperature range that was considered. In this work 3-D periodic boundary conditions are applied. Water molecules are kept at fixed positions throughout each simulation. Figure 1 shows a schematic of the sII hydrate structure.

![Figure 1. Hydrate structure sII showing the centres of the large and small cavities.](image)

Water molecules in the current study are simulated by the TIP4P/Ice model [25]. The TIP4P/Ice is a rigid 4-site model in which a LJ sphere is fixed on the oxygen site. The electrostatic contributions are implemented by positive partial charges located on each hydrogen atom and a negative partial charge fixed on an “M-site”, located on the bisector of the H–O–H angle at 0.1577 Å from the oxygen
atom. The O–H bond length is 0.9572 Å and the H–O–H angle is 104.52°. All parameters of the TIP4P/Ice model are shown in Table 1.

H$_2$ molecules in the current study are simulated by the Silvera–Goldman [30] model. In this approach the length of the H–H bond in the H$_2$ molecule is taken as 0.7414 Å. H$_2$–H$_2$ interactions are described with an LJ potential based on the Silvera–Goldman isotropic pair potential for gas H$_2$. The simplest way to derive the LJ parameters from the Silvera–Goldman potential is to keep the same well depth $\varepsilon$ and the zero-potential distance $\sigma$ [31]. This set of parameters, shown in Table 1, is among the most common for simulations of hydrogen hydrates [14, 15].

### Table 1: Interaction parameters between different types of atoms

| Molecule (model used) | atom     | $\sigma$ (Å) | $\varepsilon$ (kJ/mol) | charge ($e$) | $d_{OH}$ (Å) |
|-----------------------|----------|--------------|------------------------|--------------|---------------|
| H$_2$O (TIP4P/Ice)    | O        | 3.1668       | 0.8822                 | 0.0000       | $d_{OH} = 0.9572$ Å |
|                       | H        | 0.0000       | 0.0000                 | +0.5897      | $d_{OM} = 0.1577$ Å |
|                       | Point M  | 0.0000       | 0.0000                 | -1.1794      | $\theta_{HOH} = 104.52^\circ$ |
| H$_2$ (Silvera-Goldman)| H        | 0.000        | 0.0000                 | +0.4932      | $d_{HH} = 0.7414$ Å |
|                       | Center of mass | 3.038       | 0.2852                 | -0.9864      |                |

Interaction parameters between different types of atoms are calculated using the Lorentz–Berthelot combining rules [32] and there is a cutoff distance of 15 Å for any type of interaction. The Ewald summation [32] has been used for the long-range electrostatic interactions.

For the current study we used the GCMC approach developed by Metropolis et al. [33]. An extensive series of simulations were performed using the MCCCS Towhee open-source software package [27]. For each temperature and pressure an MC simulation is performed in the Grand-Canonical ensemble, i.e. under constant volume, temperature and gas fugacity (which is an alternative for chemical potential). The hydrogen fugacity at the specific conditions is calculated with a component-specific equation of state which gives very accurate calculations [34]. Each run consists of an equilibration stage of $2\cdot10^6$ MC steps that is followed by a production stage of $5\cdot10^6$ MC steps. Four MC moves are applied with equal probabilities: insertion 25%, destruction 25%, rotation 25%, and translation 25%. One out every 50 steps of the production stage ($10^5$ steps in total) are recorded and taken into account for the statistics. To determine the occupancy, for each type of cavity separately, each hydrogen molecule is assigned to the closest center of cavity. In this way, the average occupancy of every cavity during the simulation is calculated.

### 3. Results and Discussion

In order to examine the effect of the hydrate lattice constant on the calculation of the storage capacity of sII hydrogen hydrates we vary the lattice size by 0.6%, and 1.5% from the reference value which has been reported [3] to be equal to 17.047 Å. We consider only the case of increasing the lattice size, since if we decrease the lattice size will result in reducing the storage capacity. Please recall that we are motivated for this study by our interest to use hydrates as gas-storing materials. Therefore, cases that result a priori in reduced storage capacity are of no practical interest and are not considered in the current study.

Figure 2 shows the hydrogen storage capacity (wt. %) as a function of pressure for three different temperatures, 200 K, 250 K, and 300 K, and the three different lattice constants considered. In general, the following general observations can be made:
- Lower temperatures result in higher storage capacities.
- Increasing the pressure results in increasing the storage capacity.
- Increasing the lattice constant results in increasing the storage capacity. This result is primarily due to the increase of the storage capacity of the large cavities. The increase of the storage capacity of the small cavities is very minimal.
Figure 2. Hydrogen storage capacity (wt. %) as a function of pressure for three different temperatures: (a) 200 K, (b) 250 K, and (c) 300 K. Notation: LC denotes Lattice Constant; R denotes the reference case, LC–1 denotes the case with deviation + 0.6 % in the size of lattice and LC–2 deviation + 1.5 %.

Figure 3. Percentage Average Absolute Deviation (% AAD) of the hydrogen storage capacity as a function of pressure for three different temperatures: (a) 200 K, (b) 250 K, and (c) 300 K. Notation is the same as in figure 2.
In close agreement with the literature and regardless of which water model is used, the small cavity of hydrates cannot store more than one hydrogen molecule for most cases. From the current simulations we observe that only a very limited amount of double occupancy occurs at the higher pressures, when we use increased lattice constants. However, the large cavities of the sII structure can store up to 4 molecules. Higher occupancies have been reported [15] for the large cavities of structure sH hydrates.

In order to quantify the effect of using larger lattice constants we plot in Figure 3 the percentage Average Absolute Deviation (% AAD) of the hydrogen storage capacity from the reference case, as a function of pressure for the three different temperatures. We observe that when we increase the lattice constant by 0.6 % the storage capacity increases by 1–2 %, with respect to the reference case. Lower values correspond to lower pressures. On the other hand, when we increase the lattice constant by 1.5 % the storage capacity increases by 1–6 %, with respect to the reference case.

4. Conclusions
We have used Grand Canonical Monte Carlo simulations to examine the efficiency of hydrate structure sII in storing hydrogen. Special focus was given to the study of multiple occupancy, namely the presence of more than one gas molecules in the same hydrate cavity. In particular, a parametric analysis was carried out to quantify the correlation between the change in the lattice constant and the storage capacity. It was found that the major contribution to the increase of the gas-storage capacity results from the large cavities, while the contribution of the small cavities is very limited.

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