MONTE CARLO SIMULATIONS OF METHANE HYDRATES

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ABSTRACT
In this study we perform Grand Canonical Monte Carlo simulations in order to estimate the amount of methane gas that can be stored inside hydrate structure sI over a wide range of temperatures and pressures that are of interest to practical applications (e.g. methane storage, methane transportation, methane hydrates in nature). The results from this work are presented as “adsorption isotherms” of methane in the hydrate structure. In particular the methane content is given as a function of pressure where the parameters of this function are temperature-dependent. The results of this work can be a valuable tool in the process of refining the estimates of methane gas “in-place”, in hydrate bearing sediments, provided the conditions prevailing at the hydrate reservoir are known. The cage-occupancy estimates are compared against available experimental data with good agreement.

Keywords: methane hydrates, Monte Carlo simulations, cage occupancies, gas content

INTRODUCTION
Clathrate hydrates are nonstoichiometric, crystalline materials that are formed at high-pressure and low-temperature natural or artificial environments. Hydrogen-bonded water molecules can form various types of cages/cavities [e.g. pentagonal dodecahedron (5\textsuperscript{12}), tetrakaidecahedron (5\textsuperscript{12}6\textsuperscript{2}), hexakaidecahedron (3\textsuperscript{13}6\textsuperscript{2}), irregular dodecahedron (4\textsuperscript{3}5\textsuperscript{10}6\textsuperscript{3}), and icosahedron (5\textsuperscript{12}6\textsuperscript{2})] that are stabilized by the presence of methane or other guest molecules of particular sizes that can fit within the cages. The unit cells of the three, most common, hydrate structures (i.e. sI, sII and sH) are formed by the appropriate combination of different numbers and types of cages [1, 2].

During the recent years, large amounts of methane (CH\textsubscript{4}) hydrates have been discovered in natural, geologic environments (e.g. inside oceanic sediments and at the Arctic permafrost regions), rendering them as possible future energy sources [3-5]. The possible energy resources stored in the

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The aforementioned hydrate deposits are estimated to be larger than the combined resources from all the other fossil fuels [6, 7]. The total amount of methane gas that is stored in hydrate deposits is an issue, still, under debate in the scientific literature [8]. However, the possibility of making available large amounts of methane gas (for future energy use), makes the study of methane hydrates very attractive.

The abrupt release, to the atmosphere, of the encaged methane inside the geologic hydrate deposits can have a significant effect on the environment, contributing significantly to the global warming [9-11]. Methane is a “greenhouse” gas that has a higher heat-trapping ability than carbon dioxide, and therefore, a stronger effect on the global warming problem.

As a result of their increased storage capacity, clathrate hydrates are also considered as possible candidates for storing and transporting “energy-carrier” gases (e.g. methane [12, 13], and hydrogen [14, 15]), by the industry. In either case of methane hydrates in nature and industry, knowledge of the storage capacity of the methane hydrate is an important issue that needs to be addressed adequately. This can be either measured experimentally, or calculated computationally.

In recent years sophisticated experimental methods have been used successfully in order to measure the methane content in hydrates [16-21]. A detailed discussion on experimental issues related to measuring the gas composition of hydrates can be found in the work of Circone et al. [21].

An alternative, low-cost, approach to obtain complementary information of the gas content of hydrates is through Grand Canonical Monte Carlo (GCMC) simulations [22]. An important advantage of the GCMC approach is that the method allows the separate calculation of occupancy in each type of cavity present in the hydrate structure. Furthermore, this approach can be easily extended to mixtures of methane with other gases (e.g. carbon dioxide).

As a result of their importance the methane hydrates have attracted significant attention from the scientific and industrial communities. Research topics of considerable interest include the insitu formation of methane hydrate in natural porous media [23-31], and the production of methane from hydrate deposits [32-40].

Often in the natural environments, inside oceanic sediments, where methane hydrates have been discovered, the pressure is significantly higher than the hydrate equilibrium pressure [41]. This is clearly demonstrated in Figure 1, where we plot the prevailing pressure and temperature conditions of some known oceanic hydrate sites. As we can see at the Figure, certain sites have pressures that are close to the hydrate equilibrium pressure, while others can have pressures that are approximately 450 bars above the hydrate equilibrium pressure (e.g. Nankai-2, Peru-Chile-1). Interesting questions that arise from cases where the pressure is higher than the hydrate equilibrium pressure are:

(i) “Is the amount of methane enclathrated in the hydrate increased when compared to amount at the equilibrium conditions?”

(ii) “By what percent does the storage capacity increases?”

This study is part of an effort to address the aforementioned questions. In particular, the main objective of this paper is to calculate the methane storage capacity of structure sI hydrate, as a function of pressure, using a Monte Carlo simulation approach. We obtain mathematical expressions for the cavity occupancies, $\theta_i$ (with $i=S, L$, where $S$ denotes the small cage and $L$ the large cage), as a function of pressure, $P$, and temperature, $T$.

![Figure 1. Prevailing $P$, $T$ conditions at various oceanic sites (denoted with circles) where hydrates have been identified (Makogan et al. [41]). The solid line corresponds to the methane hydrate equilibrium curve $P_{eq}=f(T_{eq})$ [34].](image)
Once we have available the mathematical expressions for the cavity occupancies, as a function of pressure and temperature, then we can estimate the methane content for any given pressure and temperature of interest.

This paper is organized as follows: Initially, we present a brief theoretical background on hydrates. Next, the simulation details are described. Then, we present the results from the MC simulations and we discuss their comparison with available experimental data. Finally, we end this paper with the conclusions.

BACKGROUND
Hydrate structure
Methane hydrate has been identified as a structure sI hydrate [2]. The unit cell of the sI hydrate (cubic Pm3n space group) consists of 46 water molecules that form two types of cavities: the small (S), a pentagonal dodecahedron (5\(^{12}\)), and the large (L) that is formed by twelve pentagons and two hexagons (5\(^{12}\)6\(^{2}\)). There are two small and six large cavities per unit cell of sI hydrate [1, 2].

Methane hydrate formation/dissociation can be described through the following chemical reaction:

\[
CH_4 \cdot n_wH_2O \rightleftharpoons CH_4(g) + n_wH_2O(j)
\]

where \(n_w\) is the hydration number (or hydrate number), which gives the number of water molecules per guest methane molecule. The chemical reaction, Eq. (2), is valid for all temperatures higher than 273.15 K. For lower temperatures the water phase is in the form of ice. For the case of structure sI hydrates, the hydration number is related to the cage occupancies through:

\[
n_w = \frac{46}{6\theta_L + 2\theta_S} = \frac{23}{3\theta_L + \theta_S}
\]

Since \(\theta_i = f(P,T)\), the hydration number is a function of pressure and temperature as well, \(n_w = f(P,T)\). We can estimate the methane content, wt %, for any given pressure and temperature with the following expression:

\[
(wt \%) = 100 \times \frac{MW_g}{MW_g + n_w \cdot MW_w}
\]

where \(MW\) denotes the molecular weight and subscripts \(g\) and \(w\) denote “gas” and “water” respectively.

Monte Carlo Method
The MC approach has been proven to be a very effective methodology for the study of gas hydrates [42-45]. Since the hydrate cage structures are known from crystallographic experiments, for a given hydrate structure, we can simulate the process of hydrate formation, as a process of gas adsorption inside a solid material.

Contrary to the classical theory of van der Waals and Platteeuw (vdWP) [46], there is no need for any assumptions concerning the number of gas molecules enclathrated in each cavity. The vdWP theory is valid only when each cavity is occupied by a single guest-gas molecule, at most. During the MC simulations, the occupancy of each type of cavity occurs as a straightforward result. Note, however, that the MC method, as applied in this work, cannot provide any information about the stability of the hydrate crystal, which must be explicitly assumed a priori.

In this work, the well-established GCMC approach developed by Metropolis et al. [47] has been used to study the methane storage capacity of pure sI hydrates. A detailed presentation of the method is beyond the scope of this paper and can be found in the book of Allen and Tildesley [22], as well as, in published studies that utilized this method for simulations on hydrates [42-45, 48-52].

SIMULATION DETAILS
Hydrate Structure
For the current study, the simulation box consists of 8 unit cells, \((2 \times 2 \times 2)\), of sI hydrate. It contains 368 water molecules that form a total of 16 small and 48 large cavities. Both the lattice constant (11.8875 Å), and the space group symmetry (Pm3n) of the hydrate crystal have been determined from XRD measurements [53]. Oxygen atoms are placed exactly at the positions defined by the space group symmetry. In this work 3-D periodic boundary conditions are applied.
Methane and water models

The methane molecule is represented as a single-interaction site (united-atom approach) that interacts via a 12-6 Lennard-Jones (LJ) potential. The OPLS-UA [54] model has been used for methane and the SPC/E [55] model for water. The LJ parameters for both molecules are presented in Table 1. The net charge of the methane molecule is zero and consequently there are no electrostatic interactions, neither between methane molecules nor between methane and water. Since the hydrogen atoms of water (according to the SPC/E model) participate only in electrostatic interactions there is no need for knowing their exact positions. Alternatively, one could select among all proton configurations complying with the Bernal-Fowler [56] “ice rules”, the one with the minimum total dipole moment. This is an important advantage of the united-atom approach, along with the reduction in the required computational time.

Table 1. LJ parameters for methane and water.

<table>
<thead>
<tr>
<th>molecule</th>
<th>model</th>
<th>atom</th>
<th>σ (Å)</th>
<th>ε  (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>OPLS-UA</td>
<td>united atom</td>
<td>3.7300</td>
<td>1.2301</td>
</tr>
<tr>
<td>H₂O</td>
<td>SPC/E</td>
<td>O</td>
<td>3.1656</td>
<td>0.6502</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 2. Hydrate equilibrium pressures, \( P_{eq}^{H} = f(T) \), calculated with the correlation of Moridis [34].

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>253</td>
<td>1.325</td>
</tr>
<tr>
<td>263</td>
<td>1.840</td>
</tr>
<tr>
<td>273</td>
<td>2.515</td>
</tr>
<tr>
<td>283</td>
<td>7.082</td>
</tr>
<tr>
<td>293</td>
<td>23.42</td>
</tr>
<tr>
<td>303</td>
<td>78.36</td>
</tr>
</tbody>
</table>

Figure 2. Probability density of finding a methane molecule inside a small (left) and a large (right) cage. Red areas represent high probability and blue areas low probability.

RESULTS AND DISCUSSION

General

In this study we performed a series of GCMC simulations for structure sI methane hydrate.

The cavity occupancy ratio (%), obtained from the GCMC simulations of the sI methane hydrate, in the pressure range 0.1–100 MPa, and a series of isotherms is shown in Figure 3a for the small, and in Figure 3b for the large cavities. In particular, in
Figure 3. Cavity occupancy ratio (%) obtained from GCMC simulations of sI methane hydrate in the pressure range (0.1–100) MPa, and various isotherms for (a) the small cavities, and (b) the large cavities. Circles denote the GCMC results and solid lines are the Langmuir-type isotherm-fitted curves. Isotherm info depicted with the same color.

Table 3. The obtained parameters for the Langmuir-type curves, describing the cavity occupancies resulting from the GCMC simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Small Cavity</th>
<th>Large Cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$ (K)</td>
<td>$i=S$</td>
<td>$i=L$</td>
</tr>
<tr>
<td>0.043539</td>
<td>0.167371</td>
<td></td>
</tr>
<tr>
<td>$B_i$ (K)</td>
<td></td>
<td>2465.594</td>
</tr>
</tbody>
</table>

This study, we performed simulations for the following temperatures (isotherms): 253 K, 263 K, 273 K, 283 K, 293 K, and 303 K. The corresponding values for the methane hydrate equilibrium pressure, calculated using the correlation given in Moridis [34] are presented in Table 2.

The pressure range considered in this study includes two distinct pressure zones. One pressure zone (corresponding at higher $P$'s) where the hydrate is thermodynamically stable, $[P_{eq}(T)-100$ MPa], and a second pressure zone (corresponding at lower $P$'s) where the hydrate is thermodynamically unstable, $[0.1$ MPa–$P_{eq}(T)]$. In the second pressure zone we have assumed the existence of a hypothetical methane hydrate of structure sI and performed the GCMC simulations in order to estimate the amount of methane that the hypothetical structure can adsorb.

In this study we considered the entire pressure range (0.1–100 MPa) for all the six isotherm curves in order to be able to correlate the GCMC calculations for the cage occupancies $\theta_i$, using Langmuir-type curves.

In particular the GCMC results for the cage-occupancies, $\theta_i$ (with $i=S$, $L$), are fitted to the following type of curves:

$$\theta_i(P) = \frac{C_i(T) \cdot P}{1 + C_i(T) \cdot P}$$  \hspace{1cm} (5)

where the parameter $C_i(T)$, is given by:

$$C_i(T) = \frac{A_i}{T} \cdot \exp\left(\frac{B_i}{T}\right)$$  \hspace{1cm} (6)

The obtained optimum values for the set of parameters $A_i$, and $B_i$, which describe the cavity occupancies resulting from the GCMC simulations, are given in Table 3.

In Figure 3 the GCMC simulation results are denoted with circles and the solid lines show the Langmuir-type, isotherm-fitted curves. The GCMC results and the solid lines that are depicted with the same color correspond to the same temperature.

Figure 4 shows a pressure subdomain of Figure 3. In particular, emphasis is given in the pressure zone where the methane hydrate is stable,
Figure 4. Cavity occupancy ratio (%) obtained from GCMC simulations of sI methane hydrate in the pressure range \([P_{\text{eq}}(T)-100]\) MPa, and various isotherms for (a) the small cavities, and (b) the large cavities. Circles denote the GCMC results and solid lines are the Langmuir-type isotherm-fitted curves. Isotherm info depicted with the same color.

Table 4. Maximum (%) absolute deviation between the GCMC simulation points and the Langmuir-type curves.

<table>
<thead>
<tr>
<th>T  (K)</th>
<th>Max (%) AD Small Cage</th>
<th>Max (%) AD Large Cage</th>
</tr>
</thead>
<tbody>
<tr>
<td>253</td>
<td>2.35</td>
<td>2.62</td>
</tr>
<tr>
<td>263</td>
<td>4.23</td>
<td>2.84</td>
</tr>
<tr>
<td>273</td>
<td>2.85</td>
<td>2.98</td>
</tr>
<tr>
<td>283</td>
<td>1.37</td>
<td>1.63</td>
</tr>
<tr>
<td>293</td>
<td>0.38</td>
<td>0.36</td>
</tr>
<tr>
<td>303</td>
<td>0.15</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 5. Methane content (wt %) as a function of pressure for the sI hydrate, in the pressure range \([P_{\text{eq}}(T)-100]\) MPa, and for various isotherms. Circles denote the GCMC simulation results and solid lines are those calculated from the Langmuir-type isotherm-fitted curves.

Figure 5 shows the methane content (wt %) of the sI hydrate as a function of pressure in the pressure range \([P_{\text{eq}}(T)-100]\) MPa and for various isotherms. Very good agreement between the GCMC results and the Langmuir-type curves, fitted to the GCMC simulation results, is obtained. This is also shown in Table 4, where we present the maximum values for the (%) absolute deviation between the cage occupancies from the GCMC simulation data and the calculated cage occupancies using the mathematical expressions for the fitted curves (Equation 5), in the pressure range \([P_{\text{eq}}(T)-100]\) MPa. The maximum values occur for the equilibrium pressures, \(P_{\text{eq}}(T)\). The (%) absolute deviation is defined as:

\[
% \ AD = 100 \times \left| \frac{\theta_i^{\text{MC}} - \theta_i^{\text{fit}}}{\theta_i^{\text{MC}}} \right|
\]

(7)

where the superscripts (MC, fit) denote cage-occupancy values from GCMC simulations, and calculated using Equation (5) respectively.
isotherms. For a given isotherm curve, $T = T_H^{eq}$, the minimum value for the methane content corresponds to a pressure equal to the hydrate equilibrium case ($P = P_H^{eq} = f(T_H^{eq})$) for that particular $T$. All the other values for the methane content correspond to pressures such that $P > P_H^{eq}$. We observe that, for any given temperature, by increasing the pressure above the equilibrium value we can increase the methane content of the sI hydrate only by a limited amount. This is due to the fact that the cages have already high occupancies at the hydrate equilibrium conditions. Therefore, no significant increase can occur by increasing the pressure above the equilibrium value. In particular, let’s consider the case of 273 K and 2.515 MPa as an example. From the GCMC simulations we obtain that the cage occupancies are equal to: $\theta_S = 0.7929$ and $\theta_L = 0.9160$, and therefore, the methane content is equal to 12.06 wt %. By increasing the pressure to 100 MPa the calculated values become $\theta_S = 0.9948$ and $\theta_L = 0.9982$, and therefore, the methane content becomes equal to 13.38 wt %. This is a 10.9 % increase in the methane content while the pressure has increased by 3,876.0 %. Similar behavior is observed for the other isotherms.

Comparison with experiments

In Figure 6 we show the cavity occupancies, as a function of temperature, for the small cavities, $\theta_S$ (Figure 6a), and the large cavities, $\theta_L$ (Figure 6b), along the hydrate equilibrium curve $P^{eq}=f(T)$, for the sI methane hydrates.

We compare values for cavity occupancies calculated by using: (i) the thermodynamic model of Sun and Duan [57], (ii) the commercial simulators CSMHyd [58], and (iii) CSMGem [2], (iv) the GCMC results obtained in this work, and (v) the Langmuir-type fitted curves to the GCMC occupancy results, with the experimental data reported by Sum et al. [16], and Seo and Lee [20]. In general, better agreement is observed between the model of Sun and Duan and CSMHyd. A similar trend is shown for the GCMC results and CSMGem. We observe also that for the small cages the data of Seo and Lee [20] are closer to the GCMC results, while the data of Sum et al. [16] are close to all the considered calculation approaches (Figure 6a). On the other hand, for the large cages, both sets of experimental data [16, 20] fall closer to the calculations by CSMHyd (Figure 6b).

Figure 7 shows a similar comparison between experimental and calculated values for the hydration number, $n_w$. For this particular case, the data of Anderson [59], and Circone et al. [21] are used in addition.

Figure 8 shows the comparison of the calculated cavity occupancy ratio, $\theta_L/\theta_S$, with experimental data for sI methane hydrates. Please note that the experimental data of Sum et al. [16]
and Seo and Lee [20] are along the hydrate equilibrium line. On the other hand, the experimental data of Jager [18] are inside the hydrate stability zone (i.e. for a given temperature the corresponding experimental pressure is a few bars higher that the hydrate equilibrium pressure, as calculated with the correlation in Moridis [34]). All the calculations shown in Figure 8 are performed along the hydrate equilibrium curve \( P^{eq} = f(T) \).

Figure 9 shows the comparison of the GCMC results at temperature 273 K with the experimental data of Klapproth et al. [19] at temperature 271.15 K for the occupancies of the small cages as a function of the fugacity. Shown also is the Langmuir-type curve at 271.15 K (red dashed-line) obtained in this study from fitting the GCMC simulations. A second fitted curve that was reported by Klapproth et al. [19] is also shown in Figure 9. This Langmuir-type isotherm for the small cage has a constant \( C_S = 0.0489(62) \text{bar}^{-1} \).

Figure 10 shows the comparison of the GCMC fits with the experimental results of Uchida et al. [17] for the small and large cages. Uchida et al. [17] used Raman spectroscopy in order to measure the crystallographic hydration number. They reported experiments in the temperature range 273.6 - 278.4 K, and in the pressure range 2.99 – 8.08 MPa.

Figure 10a shows the cage occupancies for the small cages, \( \theta_S \). The experimental data are plotted versus pressure, as a series of isotherms, where we grouped data with similar temperatures and plotted...
them using an average temperature. Figure 10a shows also two Langmuir-type curves (273.6 K, and 278.4 K) using the parameters obtained in this study by fitting the GCMC simulations (Table 2). The two curves fall close to each other and overpredict, in general, the experimental data. Note, however, that both curves fall within the experimental error, from the data reported by Uchida et al. [17]. The isotherm curve at 271.15 K proposed by Klapproth et al. [19] is closer to the experimental data.

Figure 10b shows the cage occupancies for the large cages, $\theta_L$. For this case the experimental data give an almost constant $\theta_L \approx 0.98$, for all temperatures and pressures examined, implying an almost complete cage occupancy. The Langmuir-type curves underpredict the large cage occupancy experimental data.

CONCLUSIONS

In this work we have performed Grand Canonical Monte Carlo simulations in order to calculate the methane storage capacity of structure sI hydrate as a function of pressure. We obtained Langmuir-type mathematical expressions for the cavity occupancies, $\theta_i = f(P,T)$, as functions of pressure and temperature. The simulation results were compared against experimental data with good agreement.

ACKNOWLEDGEMENTS

Partial funding by the European Commission DG Research (contract SES6-2006-518271/NESSHY) is gratefully acknowledged by all the authors.

Figure 10. Cavity occupancies as a function of pressure for (a) the small cavities, and (b) the large cavities. Comparison between: (i) the Langmuir-type fitted curve to the GCMC data, (ii) the Langmuir-type fit to the experimental data of Klapproth et al. [19], and (iii) the experimental data of Uchida et al. [17].
REFERENCES


