# Cage occupancy of methane hydrates from Gibbs ensemble Monte Carlo simulations

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## ABSTRACT

Isobaric-isothermal Gibbs ensemble Monte Carlo simulations of sI methane hydrates in equilibrium with bulk methane are performed to calculate large and small cage occupancies. The OPLS united-atom Lennard-Jones potential, and a variation, are used to model methane, while the TIP4P/Ice model represents water. This model system produces systematically higher total cage occupancies than those of simulations by Henley and Lucia [1] using TIP4P-Ew water and TraPPE-UA methane. We also see higher total occupancies than those observed in prior Raman spectrometry studies by Uchida et al. [2], but find good agreement for large cage occupancies. The simulations provide comprehensive predictions of large and small cage occupancies for temperatures and pressures within the ranges 270−290 K and 20−400 bar, respectively. These predictions demonstrate the advantages of the Gibbs ensemble for the simulation of clathrate hydrates; the ability to control the temperature and pressure, while not constraining the chemical composition of the hydrate phase is the key advantage of this ensemble.

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## 1. Introduction

Gas hydrates, compounds of the clathrate family, are composed of guest gas molecules trapped inside cages of hydrogen bonded water molecules [3]. In nature, gas hydrates occur under continental shelf margins, and in the permafrost [4]. Their existence presents both opportunities and risks. Safe extraction of natural gas (mostly methane) from these naturally occurring hydrate reservoirs provides an attractive, and potentially vast, energy source [5−7]. Yet, uncontrolled release of gas from these reservoirs into the atmosphere could have adverse climate effects, as methane is a potent greenhouse gas. Other examples of industrial applications pertinent to clathrate hydrates are hydrogen storage [8] and the sequestration of carbon dioxide [9]. Improved knowledge of the conditions of pressure and temperature at which clathrate hydrates are thermodynamically stable, and the precise amount of gas contained within, are therefore of importance. This forms the motivation for the current work.

At a molecular scale, the arrangements of water molecules in clathrate hydrates are classified by structure type. The most common being structures I, II and H. Structure I (denoted sI) hydrates have two types of cages: large and small, and these occur with a ratio of three to one, respectively. Certain guest molecules (e.g. $H_2$ and $N_2$) are small enough to allow more than one inside the large cages, yet others, like methane, are large enough that usually only a single molecule is within any of the cages of an sI hydrate. While the guests do not bond with the host (water) molecules, the occupancy of the cavities by the guest molecules is essential to stabilise the hydrate structure. The fraction of unoccupied cages is relatively low, but varies depending on the conditions.

One route to the prediction of cage occupancies in gas hydrates is by use of the van der Waals and Platteeuw theory [10]. It is, however, not a self-contained theory and requires experimental or simulation data. That not withstanding, this approach has seen many improvements. The inclusion of guest−guest interactions [11] and flexibility to the cage structure [12] has produced predictions that are in close agreement with simulation and experimental data. Prior predictions, without the inclusion of these two corrections, may have been fortuitously better because errors from these two sources partly cancel out [13].

Experimental studies of clathrate hydrate cage occupancies often employ spectroscopic methods: Raman [2,14−17]; NMR [18,19]; or PXRD [20]. These methods have provided a wealth of

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data on the structural and compositional properties of clathrate hydrates. However, one of the major difficulties with spectroscopic methods is determination of cage occupancies. While it is possible to measure quantities of guest molecules in one cage type relative to another cage type, determination of their absolute values remains challenging.

In recent years, studies of clathrate hydrates by molecular simulation have produced significant advances [21–23]. This is, in part, because simulations allow one to measure certain properties, including cage occupancies, directly. An additional motive is that they give exact solutions for any molecular model. Various authors [24–32] have simulated methane hydrates using molecular dynamics with the direct phase coexistence method. It is worth noting, however, that the intrinsic inhomogeneity of coexisting phases prevents straightforward application of long-range dispersion corrections [33].

Grand canonical ensemble Monte Carlo simulations, on the other hand, allow one to model a homogenous system, in equilibrium with a bulk phase reservoir. In this case, long-range dispersion corrections are simple to implement. Another attractive feature is that the ensemble does not constrain chemical composition; due to insertion and deletion moves that are part of the Monte Carlo algorithm, the number of guest molecules fluctuates. As such, the grand canonical ensemble has seen use for the calculation of sI methane hydrate cage occupancies [34–37]. Those studies which calculate cage occupancies for other guest molecules, such as Ar [38], $CO_2$ [39], He [40] and $H_2$ [41], serve to further highlight the advantages of simulating clathrate hydrates with unconstrained chemical compositions.

A drawback with the grand canonical ensemble is the lack of control over system pressure. This makes it problematic to compare with experimental data given for specific pressures and temperatures. In this respect, the isobaric-isothermal Gibbs ensemble is a natural choice for the simulation of clathrate hydrate cage occupancies where specified conditions of pressure and temperature are required. The ensemble also retains the advantage of unconstrained chemical composition.

Until recently, there had been little progress in this direction. To date, the only work we are aware of is a study by Henley and Lucia [1]. By performing Gibbs ensemble Monte Carlo simulations, they examined the influence cage flexibility has upon total cage occupancy using TIP4P-Ew water and TraPPE-UA methane. A marked difference was observed; when the water molecules were immobilised and constrained to an sI hydrate structure, overall cage occupancies were significantly higher than for the case of unconstrained water molecules.

In this work, we explore the utility of the Gibbs ensemble Monte Carlo (GEMC) method for the simulation of sI methane hydrate, specifically, taking advantage of the possibility to calculate large and small cage occupancies, at equilibrium, for a wide range of temperatures and pressures. The manuscript is arranged as follows: in Section 2 we describe molecular models used in this work; Section 3 contains a description of the simulation setup; results from these simulations are presented in Section 4; concluding remarks are in Section 5.

## 2. Molecular model selection

Classical potentials are frequently used to model intermolecular interactions. For clathrate hydrates, such an approach is valid for temperatures above 150 K, below which it is necessary to consider quantum effects [42]. Among the classical potentials, a logical choice of water model for clathrate hydrate simulation is the four-site TIP4P/Ice forcefield (coarse-grained single-site water models offer computationally efficient alternatives, but require

parameterisation [26]). TIP4P/Ice was created with the intent to simulate the phase behaviour of liquid water and the various solid ice phases. Particular attention was made to match melting temperatures for $p < 2000$ bar to experimental observations [43]. Further work [44], with the TIP4P/Ice potential has shown it capable of simulating methane hydrate, which may form when liquid water is in equilibrium with united-atom Lennard-Jones methane [45]. Comparisons [46,47] with other TIP4P-like models, and with the SPC and SPC/E water models, found TIP4P/Ice to be superior in its prediction of three-phase liquid water-hydrate-methane vapour coexistence temperatures; giving the closest match to experimental work [4]. This appropriateness is attributed to an observed link between the accuracy of a water model's predictions for the ice melting point line and the three-phase coexistence boundary; there is a consistent offset in temperature between them [31,47]. Furthermore, it has been suggested that water models which closely match the melting point of ice also yield better predictions of cage occupancy in methane hydrate [34]. Similarly, simulations with other types of guest molecules, lend further support to the suitability of TIP4P/Ice for clathrate hydrate simulations [48,49].

For methane, three different coarse-grained, single site, molecular models are used: the TraPPE-UA Lennard-Jones potential methane; the OPLS-UA Lennard-Jones potential for methane [45], with $\varepsilon/k_B = 147.9457$ K; and a modified version of OPLS-UA methane, as used by Conde and Vega [46] for the simulation of methane hydrate that has the same $\sigma$ but differs in that $\varepsilon/k_B = 147.5$ K, as proposed by Guillot and Guissani [50]. Using this modified methane potential, together with TIP4P/Ice, Conde and Vega [46] obtained excellent agreement with experimental measurements of the three-phase liquid water-hydrate-methane vapour coexistence temperature [4]. Forcefield parameters for the molecular models mentioned above, and TIP4P-Ew water (as used in this work and by Henley and Lucia [1]), are given in Table 1. Lorentz–Berthelot mixing rules are used for the unlike interactions: $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$ [33,51].

## 3. Simulation details

Isobaric-isothermal Gibbs ensemble Monte Carlo simulations were performed with the MCCCS Towhee software package [52]. In this ensemble two simulation boxes are held at the same constant pressure $p$ and temperature $T$, while the total number of water and methane molecules across both boxes, is also constant ($N$). One box represents the methane hydrate crystal structure and the other the methane bulk phase. Snapshots of the two boxes are given in Fig. 1.

The initial configurations for the methane hydrate box were created by arranging 46 water molecules in an sI hydrate unit cell. This configuration was created using the data of Takeuchi et al. [53]. Their configuration was made for TIP4 water, so it was necessary to rescale the M site positions, to account for the differing O-M site separation distances in the TIP4P/Ice and TIP4P-Ew water models. This initial unit cell was then replicated to form a $2 \times 2 \times 2$ cubic system comprising eight unit cells, to give a total of 368 water molecules. The initial domain length of the cubic methane hydrate box is 24 Å along each Cartesian axis. Initial cage occupancies are set to 100% by placing a single methane molecule at the centre of each cage, to give a total of 64 methane molecules in the hydrate box. Tests were also performed for initial configurations with zero or 32 methane molecules in the hydrate box, and results were found to be identical when equilibrated with the methane bulk box. Initially, the methane bulk box contains 500 methane molecules and is also cubic, with an initial domain length of 60 Å along each Cartesian axis.