Theoretical investigation of methane hydrate nucleation kinetic from “water + gas” and “sea water + gas” mixtures

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Abstract. In this work we studied transition mechanics of a dynamic hydrogen bond network of water into a stable hydrogen bond network during gas clathrate hydrate formation process. For this purpose, we used Molecular Dynamic simulation methods and a bunch of home-made programs for determining structural properties during transition process. We have found that at certain conditions the network transformation process involves the whole system from the very beginning and could be considered as a collective effect, that results in high speed of hydrate formation.

1. Introduction
The issue of access to fresh water resources has become more important during the last few decades in many regions on our planet. Currently, only large-scale solutions are applicable is sea water desalination, because of its abundance and easy access. Numerous desalination techniques have been developed based on different basic principles and productivity/upkeep characteristics [1]. According to Xu et al. work [2] the most promising method is desalination using hydrate formation. This approach is very close to freezing technique that extracts fresh water from sea water by forming ice, because salt ions are not incorporated into ice structure. In the hydrate method, instead of water freezing, hydrates are formed from sea water. The main issue of this method is kinetics of hydrate formation and separation of obtained hydrate from brine [3].

Natural gas hydrates are crystalline solids composed of water and gas. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules [4]. Exact hydrate type depends on gas type, but the most common hydrate structures are cubic structure I (sI), cubic structure II (sII), and hexagonal structure (sH). Gases like methane, ethane form sI hydrates; propane, argon, nitrogen form sII hydrates; and sH structure is usually formed by large sized molecules like 1,2-dimethylecyclohexane, methylcyclohexane, etc. [2].

For utilizing hydrate desalination of sea water method, hydrate formation kinetics is the main limitation, especially in the presence of Na⁺, Cl⁻, Mg²⁺, SO₄²⁻, Ca²⁺, and K⁺ ions that are usually used as inhibitors. Understanding its underlying principles is very important for developing effective ways for fast and low-cost hydrate formation. Experimental study is very challenging due to nano- or even femto-second time resolution requirements for direct observation of nucleation processes [4].

Molecular level descriptions such as Molecular Dynamic (MD) simulations are the most relevant methods for studying formation kinetics even though they are still computationally challenging [5].

Gas hydrates nucleation process is the cornerstone for understanding overall hydrate formation kinetics. Despite long history of hydrate research, the nucleation and growth mechanism are still...
unclear due to the stochastic nature. There are two basic nucleation types: homogeneous and heterogeneous nucleation. In the case of homogeneous nucleation, new phase is formed directly from the origin phase by forming a critical nucleus that initiates steady growth of the new phase. This process is stochastic by nature. Before formation of critical nucleus, a new phase embryo fluctuates in size because of local thermodynamic parameters fluctuation. For real systems, homogeneous nucleation is unlikely to happen because of impurities and many other factors and heterogeneous nucleation is realized [6]. Heterogeneous nucleation occurs with help of a third phase, like phase interface or even impurity particle. From energy point of view, such formation way is more preferable than formation from a bulk phase, that results in greater nucleation speed [7]. Unfortunately, this nucleation mechanism is not well studied because of its complexity [8].

The hydrate growth from an embryo to a bulk phase is also the subject for extensive investigation. This issue has been studied by both experimental [9,10] and theoretical [11,12] methods but no solid-proof of one or another theory has been found.

In this paper we focused on heterogeneous nucleation mechanism. The process of transition of dynamic hydrogen bonds network of liquid water into a stable hydrogen bonds network of hydrate was studied. For this purpose, classical MD simulation methods and self-made helper programs were used for analyzing changes in structural and dynamic properties of hydrogen bonds network by the example of “water + methane” and “water + methane + salt ions of sea water” systems.

2. Calculation details

In this work we used a combination of classical Molecular Dynamic simulation methods implemented in the LAMMPS package [13] and the number of self-developed programs for structure analysis of hydrogen bonded network of water molecules, like hydrate cavities detection, bonded clusters detection, etc.

For MD simulation several simulation models were built. The first model consisted of 8000 water molecules with 1400 gas (methane) molecules. Such number of methane molecules was chosen in order to almost fully occupy hydrate if all water transits into a hydrate phase. The second smaller model was constructed from 1200 water molecules and 104 methane molecules; in this case only half of water molecules could transit into a hydrate phase. Every system was made in two variants: with and without hydrate seed. In the first model, 2×2×2 sI hydrate unit cells were selected as a seed, and in the second model the seed was constructed from conjugated large (5126) and small (512) cavities of sI hydrate. The 3rd and 4th models were similar to the first two ones, but with two salt ions: Na+ and Cl−, with concentration close to salt ion in sea water: one ion pair per 100 water molecules (due to very low concentration of Mg2+, SO42−, Ca2+, K+, these ions were not considered in our calculations); this gave 80 and 12 ion pairs for large and small systems, respectively.

For all modeling, four-point TIP4P/Ice water model are used [14]. This model is better for describing transition conditions between different phases of water (e.g. liquid water ↔ Ice Ih). Methane molecules were considered as one-point spherical particles with no charge with only van der Waals interaction [15]. Force parameters for salt ions (Na+ and Cl−) were taken from work [16, 17].

Initial systems were constructed by multiplying single water molecule by the required number of times, then methane particles and, if required, the salt ions pair were randomly placed in modeling cell volume. Then it was initially optimized at a pressure of 1 bar and a temperature of 283 K for 2 ns, because at these conditions hydrate formation is not expected. At this optimization process for systems with a seed, the whole seed was treated as a rigid body to preserve it for production run. The final modeling of water systems was conducted at a fixed temperature of 270 K and three different pressures: 1, 100 and 1000 bar. Modeling of system evolution continued until the lack of significant changes for more than 50 ns. Pressure and temperature were controlled by Nose-Hoover thermostat-barostat [18, 19] with the following dumping parameters: 100 fs (for temperature) and 1000 fs (for pressure).

For finding and characterizing cavities that form during hydrate nucleation process we used the following algorithm: as the first step we searched through all water molecules and found all places
with the nearest distance to water molecule of more than 2.5 Å; then checked connectivity of all surface molecules by hydrogen bonds that form a shell around these small bubbles, and finally determined what type of particles contains this shell: water, methane or salt ion. All hydrate cages should obey Euler’s rule for polyhedral: \( E + 2 = F + V \), the number of Edges \((E)\) plus 2 equals the number of Faces \((F)\) plus the number of Vertices \((V)\). So it is easy to classify all required cavity types; for example small \(5^{12}\) cavity consists of 20 water molecules connected by 30 hydrogen bonds, and large \(5^{12}6^2\) consist of 24 water molecules connected by 36 hydrogen bonds. Overall connectivity of all water molecules by hydrogen bonds has been also calculated and analyzed.

3. Results and Discussion

In this paper we studied two models with different sizes. The large model was used for observing the collective effect of transformation of hydrogen bond network. The small one was applied for hydrate dynamic formation, because for smaller system it was easier to achieve long modeling time.

The large system was modeled at 270 K and relatively high pressure of 1 kbar to be sure that hydrate formation did take place. Since gas was mixed well in the water phase, we minimized the induction time significantly. At these conditions we observed volumetric transition of dynamic hydrogen bonds network of liquid water into a stable hydrogen bonds network of one of hydrate-like structures. Unlike classical homogeneous nucleation where critical embryo steadily grows and fills up the whole volume, in our case we observed formation of small \(5^{12}\) cages, as more energy favorable cavity types, filled up with methane molecules in different parts of the modelling volume. The lifetime of small cages was growing in time. It should be noted that these small cages were not connected to each other at the beginning, but eventually they formed many middle-sized clusters, at the same time formation of large \(5^{12}6^2\) cages occurred around small cages. At that moment it became possible to discuss hydrate formation.

![Figure 1](image1.png)

**Figure 1.** The large system snapshots with only water molecules forming proper \(5^{12}\) small \(sI\) hydrate cages. Snapshot \((b)\) was taken after 10 ns after snapshot \((a)\).

Fig. 1 shows the large system snapshots with only water molecules that form proper small \(5^{12}\) cages (connected with 30 hydrogen bonds water molecules cages near the plane faces). Apparently, the formation of this cavity types occurs in the whole volume and is not localized in a certain point. Therefore, the hydrate formation process at these conditions could be considered as a collective effect of hydrogen bond network of water molecules. Moreover, the formation of small cavities is a spontaneous process and their lifetime is limited, that causes almost complete recombination of the cavities clusters; so, there is more than one hydrate formation origin, and formation process involves reconfiguration of entire hydrogen bond network. Fig. 1a and 1b contains snapshots at two sequential
time steps with an interval of 10 ns. For the case of the same sized system with hydrate seed the similar collective effect is not that evident, and new cavities formation is localized around the seed. Most likely it happens because this behavior is more energy favorable.

![Figure 2](image.png)

**Figure 2.** Time dependence of small and large hydrate cavities during methane hydrate formation at 50 and 1000 bar.

The small systems were used for analyzing time dependent changes of structural parameters like the number of different cavities. In this work we focused only on large $5^{12}6^2$ and small $5^{12}$ cavities, because only these cavity types indicate a hydrate presence/absence. Fig. 2 presents the dependence of the number of small and large hydrate cavities on time for methane hydrate. A smoothed dependence for 50 and 1000 bar pressure only is presented. At 1 atm cavity formation process exists as well, but life time of these cavities is very limited. Small cavities formation starts earlier than formation of large cavities because small cavities are more energy favorable. In $sI$ hydrate structure, relation of large and small cavities is 3:1, in contrast to our systems during formation. This behavior is associated with the large number of hydrate-water interface water molecules in relation to hydrate phase water molecules: thermodynamic condition fluctuation distorts or even destroys large cavities. For this graph we have chosen a very strict criterion and counted only “proper” cavities. Therefore, only part of all cavities may be considered “stable,” and a notable part of large cavities appears to go beyond the limit of our observation. For example, some surface level cavities could lose one of their water molecules and retain it later in time, in other words these “improper” cavities are stable except for one water molecule. Nevertheless, the strict criteria indicate rapid hydrate grows. Introduction of the seed hydrate in this case just slightly increases the number of formed cavities, but reduces the “rapid growth” time interval.

**Conclusions**
In the presented work we described and analyzed methane hydrate formation process from “water + gas” system at different conditions. We have found that it is possible to achieve volumetric recombination of dynamic hydrogen bond network into the stable hydrogen bond network of hydrate. This recombination process has stochastic origin and does not localize. Hydrate formation process is connected with cavities formation, the small cavities are formed first, and they help to form the large cavities. Moreover, small cavities can recombine to large ones.

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