MOLECULAR DYNAMICS SIMULATIONS OF CH₄ CLATHRATE HYDRATE DISSOCIATION ADJACENT TO HYDRATED SILICA SURFACES

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ABSTRACT
We use molecular dynamics simulations to study the decomposition of structure I CH₄ clathrate hydrate exposed to water. Simulations are performed for a hydrate + water system and two related cases with the hydrate adjacent to hydrate silica layers. The simulations are in the NVE adiabatic ensemble paying careful attention to the non-isothermal nature of the hydrate dissociation process. The effects of mass and energy transfer on the hydrate dissociation rate are studied. The effect of the silica surface on the dissociation rate and mechanism are studied. It is observed that the hydrate layer decomposes more quickly in simulations where it is in contact with silica. The implications on decomposition of the hydrate in hydrate reservoirs adjacent to sand sediments are discussed.

Keywords: gas hydrates, molecular dynamics, hydrate dissociation, reservoir models

INTRODUCTION
The mechanism and rate of methane hydrate formation and decomposition are important in optimizing industrial processes which use this material. Understanding the details of methane hydrate dissociation can help in designing optimal processes for methane extraction from natural methane hydrate reservoirs under the permafrost and ocean floor.

Molecular dynamics (MD) simulations of the dissociation of methane hydrate in contact with water phases have been performed. These simulations are usually carried out under the operation of a thermostat and at higher temperatures than the equilibrium hydrate – water – gas temperature.[1] We recently performed molecular dynamics simulations on methane hydrate dissociation under adiabatic, constant energy, constant volume conditions.[2] We believe that the heat released during hydrate dissociation and heat transfer from the liquid to the hydrate phase play crucial roles in mechanism and rate of the process and that isothermal simulations do not accurately account for this heat transfer.

In this work, we study the dissociation of methane hydrate in contact with a hydrated silica surface with NVE MD simulations. We are interested in studying the effect of the silica surface on the decomposition of methane hydrate as a first step in understanding the hydrate dissociation under real conditions.

COMPUTATIONAL METHODS
The molecular dynamics runs were simulated using DL_POLY program version 2.20. The intermolecular potential was computed by the

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following equation where the Lennard-Jones and Coulombic interactions are considered as the main contributors:

\[ V(r_{ij}) = \sum_{i \neq j} \left( 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \frac{q_i q_j}{4\pi \epsilon_{ij} r_{ij}} \right) \]

The force field parameters used in this work are summarized in **Error! Reference source not found.** and standard combination rules were used to calculate the Lennard-Jones parameters for the unlike pairs of atom species.

Table 1. Force field parameters: the atomic partial charges and Lennard-Jones parameters for united model for methane [3], EPM model for carbon dioxide, SPC/E model for water [4] and the force field of Lopes et al. for silica [5].

<table>
<thead>
<tr>
<th>Atom</th>
<th>( \epsilon / \text{kJmol}^{-1} )</th>
<th>( \sigma / \text{Å} )</th>
<th>( q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (CH(_4))</td>
<td>1.3650</td>
<td>3.6400</td>
<td>0</td>
</tr>
<tr>
<td>O (H(_2)O)</td>
<td>0.6502</td>
<td>3.1666</td>
<td>-0.8476</td>
</tr>
<tr>
<td>H (H(_2)O)</td>
<td>0</td>
<td>0</td>
<td>+0.4238</td>
</tr>
<tr>
<td>Si (SiO(_2)-bulk)</td>
<td>2.5104</td>
<td>3.9200</td>
<td>+1.08</td>
</tr>
<tr>
<td>O (SiO(_2)-bulk)</td>
<td>0.6364</td>
<td>3.1538</td>
<td>-0.53</td>
</tr>
<tr>
<td>O(SiO(_2)-surface)</td>
<td>0.6364</td>
<td>3.1538</td>
<td>-0.64</td>
</tr>
<tr>
<td>H(SiO(_2)-surface)</td>
<td>0.1925</td>
<td>0.4000</td>
<td>+0.32</td>
</tr>
</tbody>
</table>

A 3×3×6 unit cell replica of sI hydrate (\( a = 11.94 \text{ Å} \)) was prepared and methane molecules were placed at the center of the cages. Two reservoirs of water were added to the both sides of the hydrate phase along the \( z \)-direction such that the water reservoirs on each side were almost half the length of the hydrate phase. A row of water and methane molecules were eliminated from one end of the hydrate phase to make the hydrate phase symmetric along the \( z \)-direction. To equilibrate the system NVT followed by NPT simulations were performed for pressure relaxation. In these simulations, the hydrate phase was frozen to prevent decomposition. The system was allowed to dissociate in an NVE simulation by unfreezing the hydrate phase. Simulations of 1 and 2 ns overall time were performed. Using this protocol three sets of simulations were conducted at 283, 293 and 303 K. The time step of 1 fs and potential energy cutoff radius 15 Å were used in the periodic simulations. The set-up of the simulation is shown in Figure 1.

**RESULTS**

The system configurations at the end of the simulations at the three temperatures are given in Figure 2.

**Figure 1.** The initial configurations of the methane hydrate + water systems.

**Figure 2.** The configurations of the methane hydrate + water systems at the end of simulations.

An order parameter was used to probe the structure of the water phases at different times during the simulation. Baez and Clancy [6] defined the order parameter based on the ideal 104.25° tetrahedral angle for hydrogen bonding in the solid water phases as follows,

\[ F_{3,j} = \frac{1}{2} \left( \cos \theta_{jik} \cos \theta_{jik} + \cos^2 104.25 \right) \]

with

\[ F_{3,j} = \begin{cases} 0.1 & \text{liquidwater} \\ 0.0 & \text{solidwater (ice, hydrate)} \end{cases} \]

For each water molecule, the \( F_{3,j} \) order parameter is calculated for all oxygen atoms within a spherical shell of radius 3.5 Å (the first
peak in the RDF of O-O in liquid water phase). The $\theta_{ijk}$ is the angle between triplets of oxygen atoms in this shell with the $i$th atom being in the center. This parameter measures deviation from the tetrahedral arrangement of oxygens in its solid state of water (ice and hydrate).

To analyze the structure of the phases, the system was subdivided into 12 layers in the $z$-directions, each ~12 Å in thickness, as shown in Figure 3. The $F_3$ for all of the oxygens in a layer were averaged ($F_{3,\text{avg}}$) and are plotted in Error! Reference source not found.. The $F_{3,\text{avg}}$ refers to the order parameter averaged over all of the oxygen atoms present in the system. The increase of $F_3$ for a layer from a value from 0.02-0.04 to ~0.1, represents the melting of that layer.

At 283 K no dissociation occurs. However, in Figure 3 it is observed that the layers at the interface are partially disordered and on average contain both hydrate phase and liquid phase components. Their order parameter of $F_3 \approx 0.04$ is closer to the hydrate configuration ($F_3 = 0.02$) than that of the liquid water phase. At higher temperatures, 293 and 303 K, Figure 3 shows that the dissociation proceeds in a stepwise manner. The layers of hydrate closer to the interface start to dissociate and after they have reached a certain percentage of collapse (as characterized by $F_3 \approx 0.8$), the decomposition of the next inner layer begins. The decomposition of hydrates is endothermic.

In Figure 4 we observe that as the layers of hydrate dissociate, the temperature drops and consequently the rate of decomposition of the next inner hydrate layers decreases. This is known to be a problem in the hydrate reservoirs where a depressurization technique is used to extract methane from hydrate deposits and remove excess pressure on the decomposing hydrate phase.

**SIMULATIONS WITH SILICA LAYERS**

Two different scenarios are considered. In the first case, shown in Figure 5 top panel, the hydrate phase is directly in contact with the hydrated silica surface and in the second case, a ~3 Å thick confined layer of water is allowed to penetrate between the hydrate phase and silica surface.

To study the decomposition of the hydrate confined by the hydrated silica phase, simulation parameters similar to the decomposition of hydrates in bulk water was used. The atoms of the silica slabs are frozen.

Figure 3. The change with time of the order parameter for the different layers in the simulation of the methane hydrate in contact with water at three different initial temperatures. The hydrate is seen to decompose in a stepwise fashion with the outer layer decomposing before the inner layers start to dissociate.
Figure 4. The temperature profile for the simulations of the hydrate-water dissociation as a function of time. At initial temperatures higher than 283 K, the hydrate decomposes and a temperature drop is observed.

The $F_3$ order parameter for the water and hydrate phases where calculated for the confined simulations. The order parameters at 303 K for the different molecular layers along the $z$- and $y$-directions for the simulation where the hydrate phase is directly in contact with the hydrated silica phase are shown in Figure 6. The dissociation is seen to occur relatively quickly in this configuration with subsequent hydrate layers quickly decomposing. The incommensurability of the silica and hydrate layer at the interface likely destabilizes the hydrate and promotes dissociation.

Figure 5. The initial set-up for simulations with the presence of a hydrated silica surface. The upper panel shows the configuration with no water layer between the silica surface and the hydrate and the lower panel shows the set-up with water layers separating the hydrate from the silica layer.

Figure 6. The $F_3$ order parameter for the water and hydrate phases as a function of time for different layers along the $z$-direction (top) and $y$-direction (bottom) of the simulation box at 303 K and direct contact of the hydrate phase with the silica surface with no bound water layer.

In the simulations with a layer of water molecules between the hydrate and silica surfaces, the hydrate dissociation occurs more slowly than the case with the hydrate in direct contact with the silica phase, but the dissociation is still faster than an unconstrained hydrate phase. Dissociation of hydrate in the presence of silica is faster compared to bulk conditions. This is consistent with the observation that hydrate formation conditions in small pores shift to higher pressure and lower temperature and therefore at a specified $P$ and $T$, the driving force for decomposition of hydrate in the pore would be higher compared to the bulk condition.
The presence of a layer of water between the silica surface and hydrate phase stabilizes the hydrate. This is because the dissociation with no bound water layer resulted in complete decomposition of the hydrate block after 1 ns of simulation. For the case of the simulation with the bound water between the silica and hydrate phases, at least three intact cages remain after 1 ns simulation time (see Figure 7).

Unlike the dissociation of the hydrate phase in contact with water alone, the dissociation process in the presence of silica does not proceed in a stepwise manner. Hydrates also begin to dissociate from the sides in contact with the silica surface. In fact, the hydrate phase decomposes like a shrinking core.

Further analysis of the hydrate decomposition of in the presence of silica will remain for future work.

REFERENCES


