

Decomposition and Diffusion of Methane Hydrate in Porous Medium Molecular Dynamics Simulation

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Abstract

This paper uses molecular dynamics simulation of methane hydrate decomposition and diffusion in porous media. This paper examines microscopic characteristics parameters of hydrate in porous media compared with pure hydrate, such as: density distribution, the radial distribution function(RDF), the diffusion coefficient and the mean square displacement(MSD) structural and dynamics properties of hydrate. We use NVT ensemble and NPT ensemble study decomposition and diffusion effects of methane hydrate in the silica surface. The purpose of this paper is to investigate the dissociation and diffusion mechanism of gas hydrates. Research showed that in the porous medium dissociation rate of hydrate is higher than the pure hydrate. So that under the specific pressure and temperature condition, the driving force of gas hydrate dissociation in porous media will be higher than that of pure methane hydrate.

Keywords: *Methane Hydrate; Molecular Dynamics; Diffusion Coefficient; in Porous Media*

1 INTRODUCTION

Gas hydrates are inclusion compounds where hydrogen-bonded water molecules encage appropriate guest molecules (such as CH₄, C₂H₆, C₃H₈, CO₂, N₂ and H₂) under suitable pressure and temperature conditions ^[1]. Gas hydrates are of interest to industry as they form in natural gas pipelines and petroleum wells, blocking the flow of fluid. Oil and gas companies are still seeking hydrate inhibiting chemicals which are economically and environmentally sound. The industrial interest in gas hydrates began with the discovery that hydrate formation could plug pipelines during the transmission of natural gas. A major task encountered by the petroleum industry is to decompose the hydrate plug formed in pipelines and other process equipments. Gas hydrates are also considered for energy storage and transportation purposes ^{[2]-[3]} as well as gas separation technology ^{[4]-[5]}. On the other hand, they are also considered potential energy resources because substantial amounts of natural deposits of predominantly methane hydrate are found in permafrost regions and continental margins. In addition, gas hydrates also have technological importance in gas transportation and storage ^{[6]-[7]}, gas mixture separation and CO₂ sequestration ^[8].

We use NVT ensemble and NPT ensemble study decomposition and diffusion effects of methane hydrate in the silica surface. The purpose of this paper is to investigate the dissociation and diffusion mechanism of gas hydrates. A series of molecular dynamics simulations are performed under isothermal conditions for the equilibrium interface between type I methane hydrate and porous media in the temperature T=280K in this paper. The structural, orientational and dynamical properties across the interface are analyzed and the likely mechanism of decomposition and diffusion effect is investigated at the molecular level.

2 THE INITIAL STRUCTURE MODEL

The initial positions of the oxygen atoms in hydrate lattice are obtained from X-ray diffraction experiment ^[9], and the

hydrogen atoms are then added in a random manner but consistent with Bernal-Fowler rule. It consists of 368 water molecules and 64 methane molecules in a simulation box of $2 \times 2 \times 2$ unit cell methane hydrate, as shown in Figure 1. Using the $1 \times 1 \times 2$ unit cell silica ZSM-11 zeolite model and the aperture size is $0.58 \text{ nm} \times 0.54 \text{ nm}$, as shown in Figure 2. This configuration is denoted as SiO_2 (ZSM-11 zeolite) in the text and is shown in Figure 3.

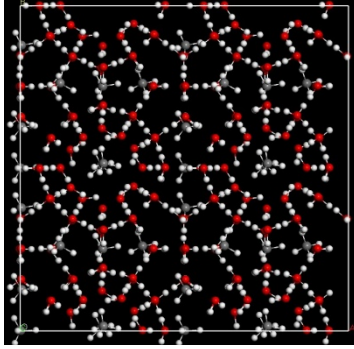


FIG 1. METHANE HYDRATES SIMULATION

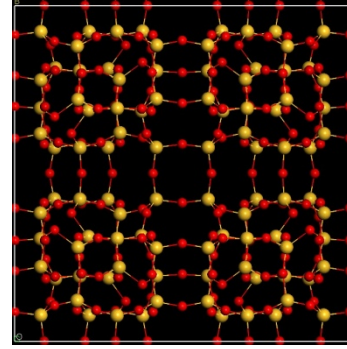


FIG 2. SiO_2 (ZSM-11 ZOLITE) SIMULATION SYSTEM USED IN THIS WORK.

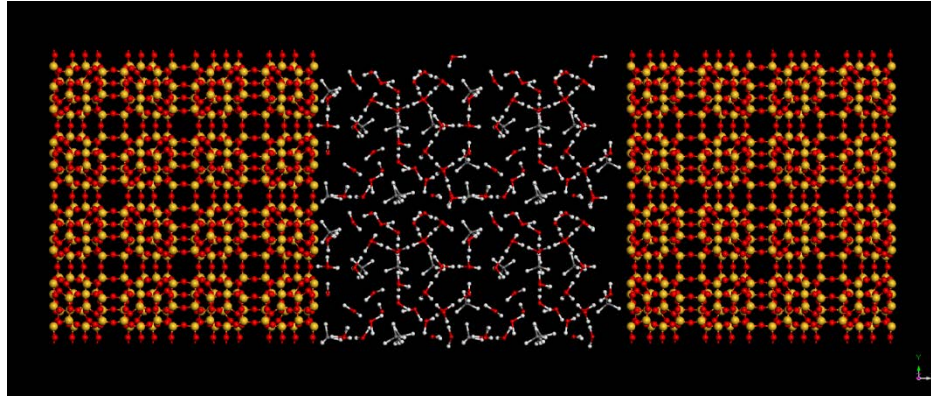


FIG.3. EQUILIBRIUM STRUCTURE OF THE HYDRATE- SiO_2 SYSTEM.

The rigid, three-center SPC/E potential model proposed by Berendsen^[10] is used for water-water interactions, in which each water has equilibrium O-H bond length of 1.0 \AA and H-O-H bond angle of 109.5° , in this work they are listed in Table 1. The SPC/E^{[11]-[14]} potential is expressed as

$$U(r_{mn}) = \sum_{m \neq n} \left\{ \frac{q_m q_n}{4\pi\epsilon_0 r_{mn}} + 4\epsilon_{mn} \left[\left(\frac{\sigma_{mn}}{r_{mn}} \right)^{12} - \left(\frac{\sigma_{mn}}{r_{mn}} \right)^6 \right] \right\}, \quad (1)$$

Where r_{mn} and $U(r_{mn})$ respectively molecules m and n the distance between the molecules and interaction potential, q_m refers to the charge on molecules m , ϵ_0 is the permittivity of free apace, ϵ_{mn} and σ_{mn} are the Lennard-Jones parameters. Methane molecules are treated as spherical particles, and Lennard-Jones potentials^{[15]-[17]} are used for methane-methane and water-methane interactions.

TABLE 1 INTERMOLECULAR POTENTIAL PARAMETERS FOR THE WATER MODELS USED IN THIS STUDY

Model	q_{H}/e	q_{O}/e	$l_{\text{OH}}/\text{\AA}$	$\angle\text{HOH}/^\circ$	μ/D
SPC	+0.82	-0.41	1.0	109.5	2.27

TABLE 2 LENNARD-JONES PARAMETERS USED IN THIS WORK

Atom	$\epsilon/\text{KJ}\cdot\text{mol}^{-1}$	$\sigma/\text{\AA}$
C-O	0.89	3.45
C-C(CH_4)	1.23	3.73
O-O(H_2O)	0.65	3.16
O-O(SiO_2)	0.63	3.158
Si-Si(SiO_2)	2.51	3.92

Long-range electrostatic interactions are handled by the Ewald summation method, and nonelectrostatic interactions are truncated at a distance of 11.0 Å. The equations of motion are integrated using the Leapfrog algorithm. The standard Lorentz-Berthelot combining rule is adopted for the methane-water nonelectrostatic interactions. The Lennard-Jones parameters of water and methane molecules used in this work are listed in Table 1 and Table 2. All molecular dynamics simulations are performed with periodic boundary condition using LAMMPS molecular dynamics software package ^[18].

Firstly, this hydrate sample is equilibrated using NPT molecular dynamics methods with periodic boundary conditions at pressure $p = 10\text{bar}$ ($1\text{bar} = 10^5\text{Pa}$) and temperature $T = 280\text{ K}$ and is found to be stable. The total simulation time is 500ps with a time step of 1fs, and 200ps is used for equilibration. Secondly, a further NVT simulation of the full system is run at each temperature for 1ns, after an equilibration period of 500ps.

3 RESULTS AND DISCUSSION

This paper examines microscopic characteristics parameters of hydrate in porous media were compared with pure hydrate, such as: density distribution, the radial distribution function, the diffusion coefficient and the mean square displacement structural and dynamics properties of hydrate, analysis of the process of hydrate dissociation in porous media and its impact on the phase state.

In order to give the general features of the system configuration, snapshots of the configuration of methane hydrate dissociation process at $T = 280\text{K}$ are shown in Figure 4 and Figure 5.

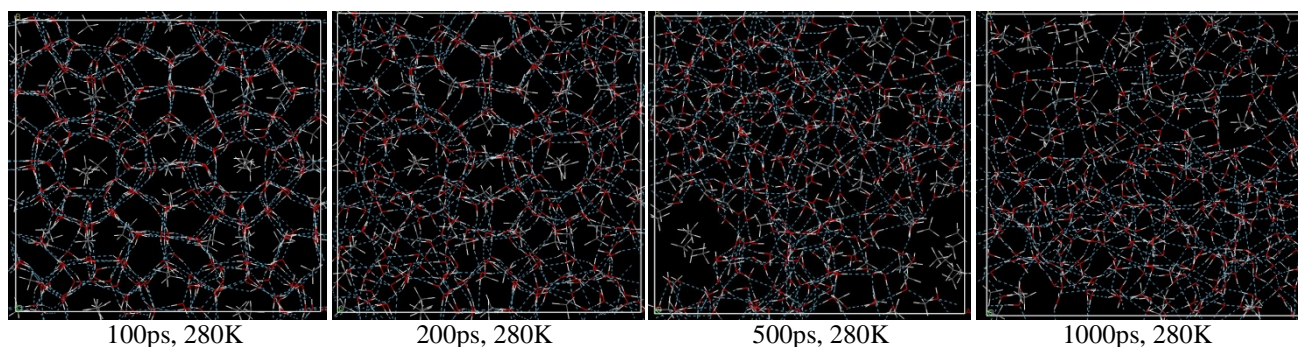


FIG 4.SNAPSHOTS OF THE CONFIGURATION OF METHANE HYDRATE DISSOCIATION PROCESS AT $T = 280\text{K}$.

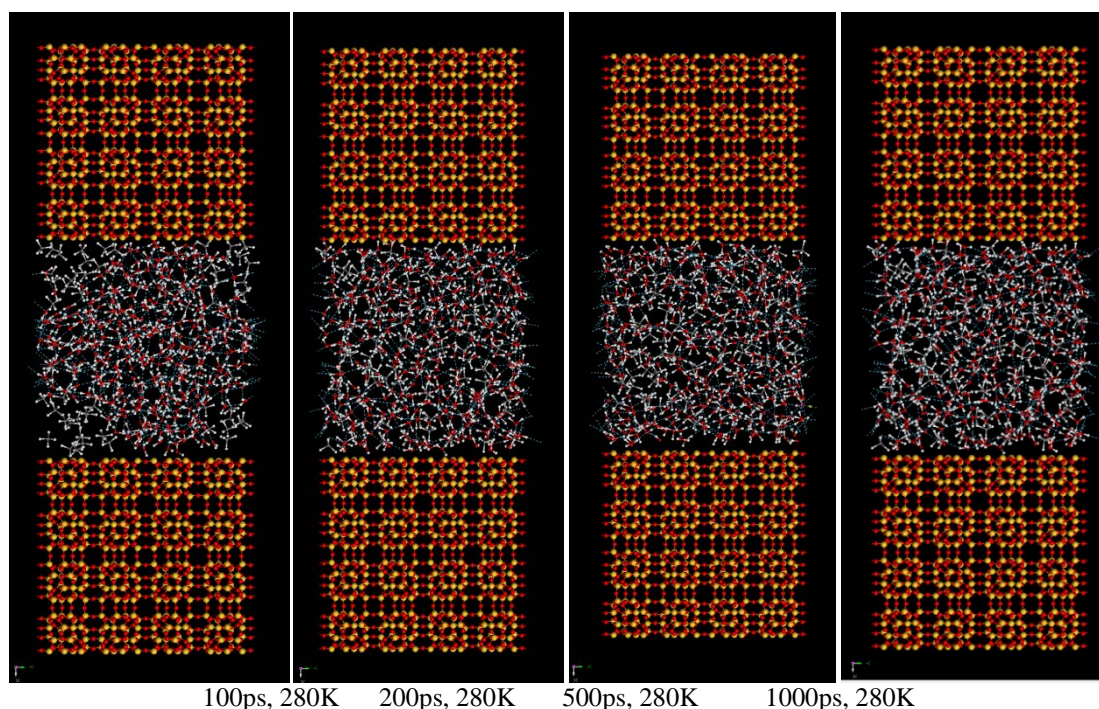


FIG 5.SNAPSHOTS OF THE CONFIGURATION OF METHANE HYDRATE DISSOCIATION PROCESS IN POROUS MEDIA AT $T = 280\text{K}$.

3.1 Structure Properties

1) Radial Distribution Function (RDF)

Radial distribution function (RDF) can be interpreted as the system area density (local density) and average density (bulk density) ratio. Around the reference molecule (r value is small) is different from the system, the average density of the area density, but when the distance to the reference molecule with an average density of the area density should be the same. When the r value is large, the value of the radial distribution function of the molecule should be close to 1. Dynamics calculation method of radial distribution function is shown as:

$$g(r) = \frac{1}{4\pi r^2 \delta r \rho} \frac{\sum_{t=1}^T \sum_{j=1}^N \Delta N(r \rightarrow r + \delta r)}{N \times T}, \quad (2)$$

Where N is the total number of molecular; T is the computer the total time (step); δr is the distance difference; ΔN is the number of molecules in between $r \rightarrow r + \delta r$.

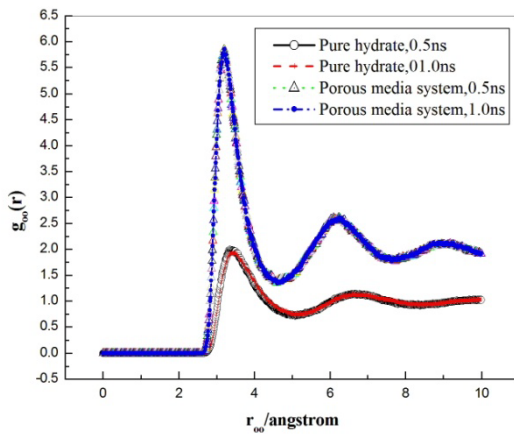


FIG 6. RDFs OF OXYGEN ATOMS IN DIFFERENT STAGES OF POROUS MEDIUM SYSTEM AND PURE HYDRATE SYSTEM IN THE WATER MOLECULES AT TEMPERATURE $T=280K$.

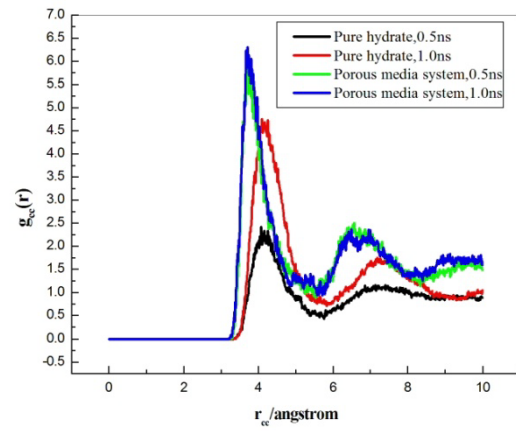


FIG 7. RDFs OF CARBON ATOMS IN DIFFERENT STAGES OF POROUS MEDIUM SYSTEM AND PURE HYDRATE SYSTEM IN THE WATER MOLECULES AT TEMPERATURE $T=280K$.

From Figure 6, it can be seen that RDFs of oxygen atoms in different stages of porous medium system and pure hydrate system in the water molecules at temperature $T=280K$. For a stable type I hydrate crystal, there are two distinct peaks in the radial distribution functions of oxygen atoms $g_{oo}(r)$. The first maximum peak is located at 3.365\AA . The first peak represents the distribution of the neighboring particles, and hence it is known that the nearest oxygen atoms are separated from each other at a distance of around 3.365\AA . There are two distinct peaks located at 3.185\AA and 6.205\AA for porous media system at $280K$ and run time $t=0.5ns$ and $4ns$, which indicates the existence of tetrahedral hydrogen bonding structures of water molecules in methane hydrate, the second maximum peak in $g_{oo}(r)$ is almost horizontal. As can be seen from the graph, the second characteristic peak of the radial distribution function of oxygen atoms of porous medium system is increased obviously than that of pure hydrate system, indicated that the hydrate crystal has been decomposition. Similarly, as can be seen from Figure 7, the second characteristic peak of the radial distribution function of oxygen atoms of porous medium system is increased obviously than that of pure hydrate system, indicated that the hydrate crystal has been decomposition.

From the above discussion it can be concluded that under the same conditions, affected by the decomposition of methane hydrate in porous media, the hydrate dissociation rate in the decomposition process is greater than the pure hydrate.

3.2 Density Distribution

$$L_x L_y \int_{-L_z/2}^{L_z/2} \rho_i(z) dz = N_i, \quad (3)$$

Where $\rho_i(z)$ is the number density of atom i at a distance z , N_i is the total number of atom i in the simulation box,

and L_x , L_y and L_z are the box sizes along x , y and z directions, respectively. z to molecular density distribution is an important characteristic that it is sensitive to small changes in the adjacent interface architecture.

From Figure 8 it can be observed that is mainly the hydrate phase at 0.5ns, indicated that the hydrate begins to decomposition. With the hydrate dissociation produce methane and water at 1ns. With the simulation time, because of the effects of in porous medium the hydrate phase to the gas phase and liquid phase advance.

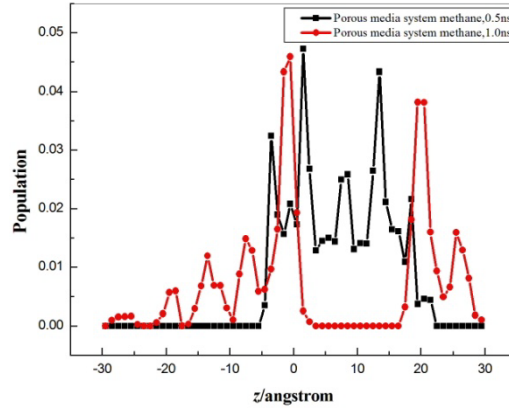


FIG 8. Z DENSITY PROFILES OF METHANE MOLECULES AT 280K AND RUN TIME T=0.5NS AND 1NS.

3.3 The Dynamics Properties

1) Mean Square Displacements (MSD)

Mean square displacements (MSD). MSD is a measure of the average distance a molecule travels over some time interval and can be used to represent the amplitude of the thermal vibration of a molecule, which is defined as:

$$MSD = R(t) = \left\langle \left| \vec{r}(t) - \vec{r}(0) \right|^2 \right\rangle, \quad (4)$$

The average type in parentheses said. Based on statistical principle, as long as there are enough number of molecules, calculate long enough, the system of any moment can be as the zero point of time, the calculation of average value should be the same. Type can be obtained by:

$$MSD = R(t') = \left\langle \Delta^2 r(t') \right\rangle = \frac{1}{N} \sum_{i=1}^N \left\langle \left| \vec{r}_i(t' + t_0) - \vec{r}_i(t_0) \right|^2 \right\rangle, \quad (5)$$

Where $R(t')$ is the mean square displacement, and $\vec{r}_i(t_0)$ is the position of molecule i in the system at run time t_0 , where the summation is over all the finite system containing N identical molecules.

From Figure 9, it can be seen that the in-slab MSDS perpendicular to the surface of water and methane molecules in porous medium system and pure hydrate system at temperature $T=280K$. As can be seen from the graph, the in-slab MSDS perpendicular to the surface of water and methane molecules in porous medium system and pure hydrate system are increasing with time increasing, while the mean square displacement of the methane and water molecules in porous medium system increasing rate with time is obviously higher than that of pure hydrate. Based on the above discussion, we conclude that the dynamical properties of water molecules show continuous transition from hydrate phase to gas and liquid phase across the quasi-liquid layer.

2) Diffusion Coefficients

Molecular diffusion coefficient used to describe the motion of the molecules, said unit time moved all orientation of statistical average, according to Einstein's law of diffusion is:

$$\lim_{t \rightarrow \infty} \langle R(t') \rangle = 6Dt, \quad (6)$$

Where, D is the particle diffusion coefficient. So when the time is very long, MSD the time of slope is the $6D$.

From Figure 10, it can be seen that the in-slab diffusion coefficients perpendicular to the surface of water and methane molecules in porous medium system and pure hydrate system at temperature $T=280\text{K}$. As known from the reference, diffusion coefficient of methane molecules in pure hydrate is higher than that of water molecules, but can be obtained from the above, the diffusion coefficient of methane and water molecules in the porous medium system significantly increased, and the diffusion coefficient of methane molecular diffusion coefficient increases significantly higher than that of the water molecule. This is because in the porous medium, when the temperature is higher than the freezing point, the mass transfer resistance of water molecules decreased, thus resulting in a substantial increase in diffusion coefficient of water molecules.

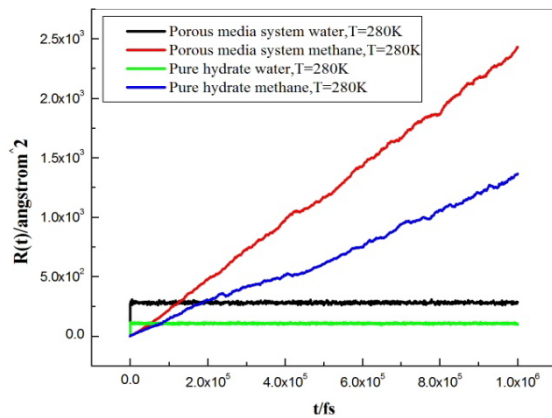


FIG 9. THE IN-SLAB MSDS PERPENDICULAR TO THE SURFACE OF WATER AND METHANE MOLECULES IN POROUS MEDIUM SYSTEM AND PURE HYDRATE SYSTEM AT TEMPERATURE $T=280\text{K}$.

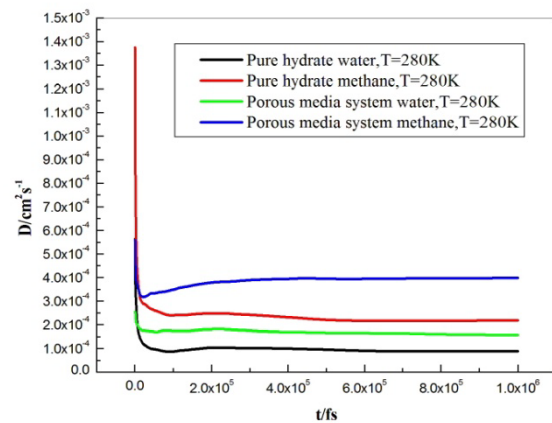


FIG 10. THE IN-SLAB DIFFUSION COEFFICIENTS PERPENDICULAR TO THE SURFACE OF WATER AND METHANE MOLECULES IN POROUS MEDIUM SYSTEM AND PURE HYDRATE SYSTEM AT TEMPERATURE $T=280\text{K}$.

4 CONCLUSION

In the simulations with a layer of methane hydrate in SiO_2 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. For the case of the molecular dynamics simulation of decomposition and diffusion of methane hydrate in porous media between the silica and hydrate phases. Dissociation of hydrate in the presence of silica is faster compared to the pure methane hydrate. 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 pure methane hydrate.

From the results of the present simulations, we make several observations that are relevant to the proper modeling of the methane hydrate decomposition process in a reservoir. First, decomposition goes in a series of steps where rows of clathrate decompose one after another. Second, simultaneous release of methane gas from decomposing rows of the clathrate hydrate leads to the formation of methane micro-bubbles in the water phase. Diffusion of released methane gas from the hydrate surface is not homogenous and the solution phase will not necessarily remain isothermal over short time periods. Extracting an activation energy from the temperature dependence of the rate constant is problematic because the hydrate dissociation rate constant captures many non-equilibrium effects, including heat and mass transfer, during the decomposition process which makes it to be set up-dependent and non-transferable.

The effects of mass and energy transfer on the hydrate dissociation rate are studied. The effects 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. Further analysis of the hydrate decomposition of in the presence of silica will remain for future work.

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