

Molecular Dynamics Simulation of the Effects of Different Initial Water Content on Methane Hydrate Decomposition

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Abstract: Gas hydrate is mainly distributed in deep sea-floor sediments and permafrost regions. The water content of these sediments varies with the type of reservoir and affects the rate of hydrate decomposition. In this work, the decomposition process of methane hydrate under four different initial water contents was investigated by molecular dynamics simulation. The results were analyzed by the system conformation, radial distribution function (RDF), and mean square displacement (MSD), which revealed the microscopic mechanism of the effect of the initial water content on the decomposition rate of hydrate. The results demonstrate that the hydrate decomposition starts from the boundary to the middle, and the cage structure is destroyed layer by layer. Methane molecules continue to escape from the hydrate cages as the hydrate decomposes, and subsequent decomposition of the hydrate is inhibited when its solubility in water reaches saturation. The higher the initial water content is, the faster the decomposition rate of hydrate is. The movement distance of methane gas is affected by the initial water content. The higher the initial water content, the smaller the MSD of methane molecules.

Keywords: Water content; Decomposition rate; Gas migration; Molecular dynamics simulation

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1. Introduction

Gas hydrates are cage compounds formed by water molecules and guest molecules under certain temperature and pressure conditions, the guest molecules occupy intermolecular hydrogen-bonded water cages ^[1]. Under standard conditions, the decomposition of 1 m³ of natural gas hydrate can produce 164 m³ of natural gas ^[2]. The seabed is rich in natural gases, and the total amount of gas captured in the hydrate is about twice that of conventional fossil fuels ^[3]. Therefore, natural gas hydrate is considered a high-quality and reserve-rich clean energy source, which has a great prospect of meeting future energy demand and can effectively alleviate the energy problem. There are numerous problems in the process of hydrate extraction, and how to extract natural gas hydrates safely and efficiently has been the focus of many scholars.

The decomposition process of hydrate has received more and more attention from researchers. Hu *et al.*

^[4] investigated the disruption of the cage-type structure of methane hydrate by inorganic salts on the molecular level and compared the effect of different types of metal cations on the rate of hydrate decomposition. The results showed that the larger the charge and radius of the cation, the greater the rate of hydrate decomposition. Sun *et al.* ^[5] investigated the effect of ethanol concentration on the decomposition rate of methane hydrate and found that 40% ethanol concentration was most favorable for the decomposition of the hydrate. Myshakin *et al.* ^[6] simulated the relationship between cage-specific occupancy and the decomposition rate of hydrate and found that the existence of empty cages weakened the stability of hydrate and made it easier to decompose. There are fewer studies on the effect of water content on the decomposition rate of hydrate.

In this paper, the molecular dynamics method was used to simulate the decomposition process of hydrate under four different initial water contents. The change in the decomposition rate of hydrate and gas migration law was studied.

2. Simulation model and method

2.1. Molecular model

SI hydrate is a body-centered cubic structure with a spatial cluster of Pm3n and a unit cell structure of $2(5^{12})6(5^{12}6^2) \cdot 46\text{H}_2\text{O}$. Firstly, the SI methane hydrate model was constructed using Materials Studio, hydrogen atoms and oxygen atoms were placed according to the unit cell constant and absolute coordinates of structure I hydrate proposed by Takeuchi *et al.* ^[7]. The guest molecules were placed in the center of the crystal cavity, then a $3 \times 3 \times 3$ cell expansion was carried out, and the two sides were free water molecules. The initial configuration obtained is shown in **Figure 1**. The intermediate hydrate fraction contains 213 methane molecules and 1278 water molecules. The ratio of the number of free water molecules on both sides to the number of water molecules in the hydrate is used to define the initial water content, which is 23.55%, 33.41%, 45.15%, and 52.43% for the four simulations, respectively.

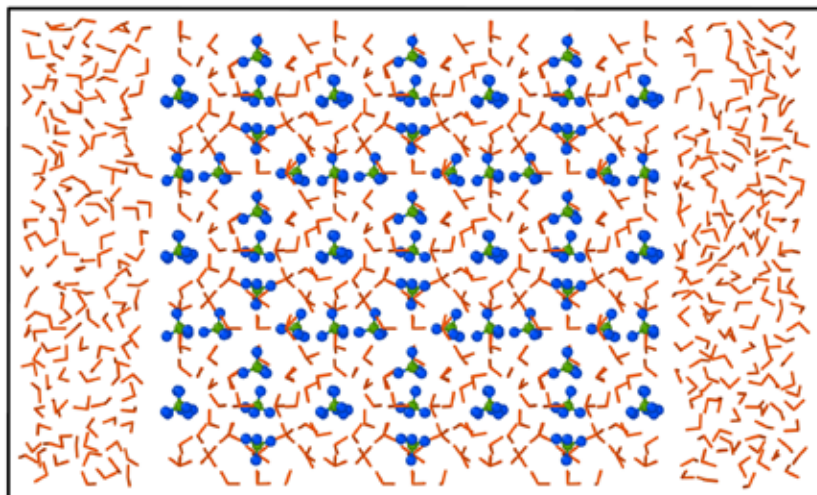


Figure1. Initial structure of methane hydrate

2.2. Force fields and simulation details

The OPLS-AA force field was chosen to describe the methane molecules, the water molecules were depicted by the SPC/E force field, and the water molecules were constrained by the SHAKE algorithm. The simulation system adopted periodic boundary conditions; the time step was 1fs. The long-range electrostatic force was calculated by the PPPM algorithm with an accuracy of 10^{-6} . The interaction forces between CH_4 and H_2O

molecules include the Lennard-Jones van der Waals force and the Coulomb force, and the potential energy interaction between the different atoms is determined by the Lorentz-Berthelot mixing rule. The Velocity-Verlet algorithm was used to solve Newton's equations of motion. The Nose-Hoover algorithm was used to maintain the temperature and pressure at constant values. Firstly, the conjugate gradient algorithm was used to minimize the energy of the system, and a relaxation step was performed using an NVT ensemble at 200 K for 500 ps. Hydrate decomposition was performed under the NPT ensemble with a simulation time of 1 ns.

3. Results and discussion

3.1. Conformation change

The decomposition process lasts for 0.3 ns. To analyze the structural changes during hydrate decomposition in-depth, the snapshots at 0.075 ns, 0.15 ns, 0.225 ns, and 0.3 ns of case 1 were taken to observe the decomposition process. **Figure 2** illustrates the hydrate morphology changes at four moments during the decomposition process. At 0.075 ns, the top and bottom water cages started to collapse, the half-cage structures on both left and right sides had been destroyed and the methane molecules had broken free from the water cages. At 0.15 ns, the cage structures in the middle portion had begun to be destroyed, and the complete water cages at the upper and lower ends had been destroyed. At 0.225 ns, the destruction of hydrate intensifies further. At 0.3 ns, the cage structure of hydrate had been destroyed completely, and methane gas molecules and water molecules were freely dispersed in the model. The decomposition of methane hydrate occurs firstly at the boundary and then progressively moves inward until the hydrate completely decomposes.

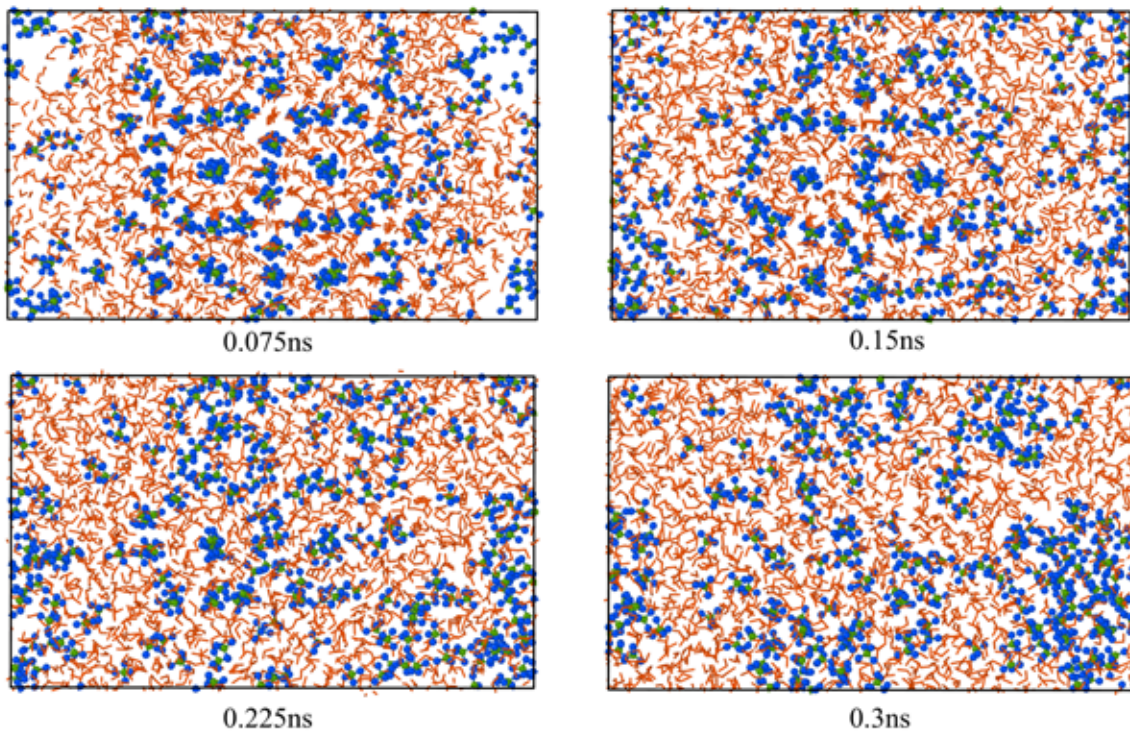


Figure 2. Structure morphology changes

3.2. Decomposition rate

Figure 3 shows the RDF variation curves between oxygen atoms. The RDF of 0.001 ns, 0.05 ns, 0.1 ns, 0.15 ns, 0.2 ns, 0.25 ns, and 0.3 ns were selected to analyze the decomposition rate of hydrate. There are

several relatively obvious characteristic peaks in the curves at 0.001 ns. During the period from 0.001 ns to 0.05 ns, the characteristic peak decreased greatly, indicating that the hydrate was very unstable in the initial stage of decomposition. In this stage, the hydrate structure became more perturbed and the positions of the water molecules changed greatly in a short time. With the progress of decomposition, the hydrogen bonds between water molecules were gradually broken, the distance between oxygen atoms gradually increased, and the characteristic peak gradually decreased. The peaks of the RDF curves of the four simulations gradually decreased, but the peaks in the last moments were different. The first characteristic peaks at 0.3 ns of the four simulations were 3.94, 3.8, 3.73, and 3.56, and the peak sizes were as follows: case 1 > case 2 > case 3 > case 4, which was the opposite of the initial water content of the simulations. As the water content increased, the first characteristic peak at the end of decomposition decreased, indicating an increasing decomposition rate of hydrate. The main reason is that methane gas gradually escapes from the water cage during the decomposition of hydrate. The subsequent decomposition of the hydrate will be inhibited due to the excessive methane gas dissolved in the water. The higher the initial water content, the smaller the inhibitory effect.

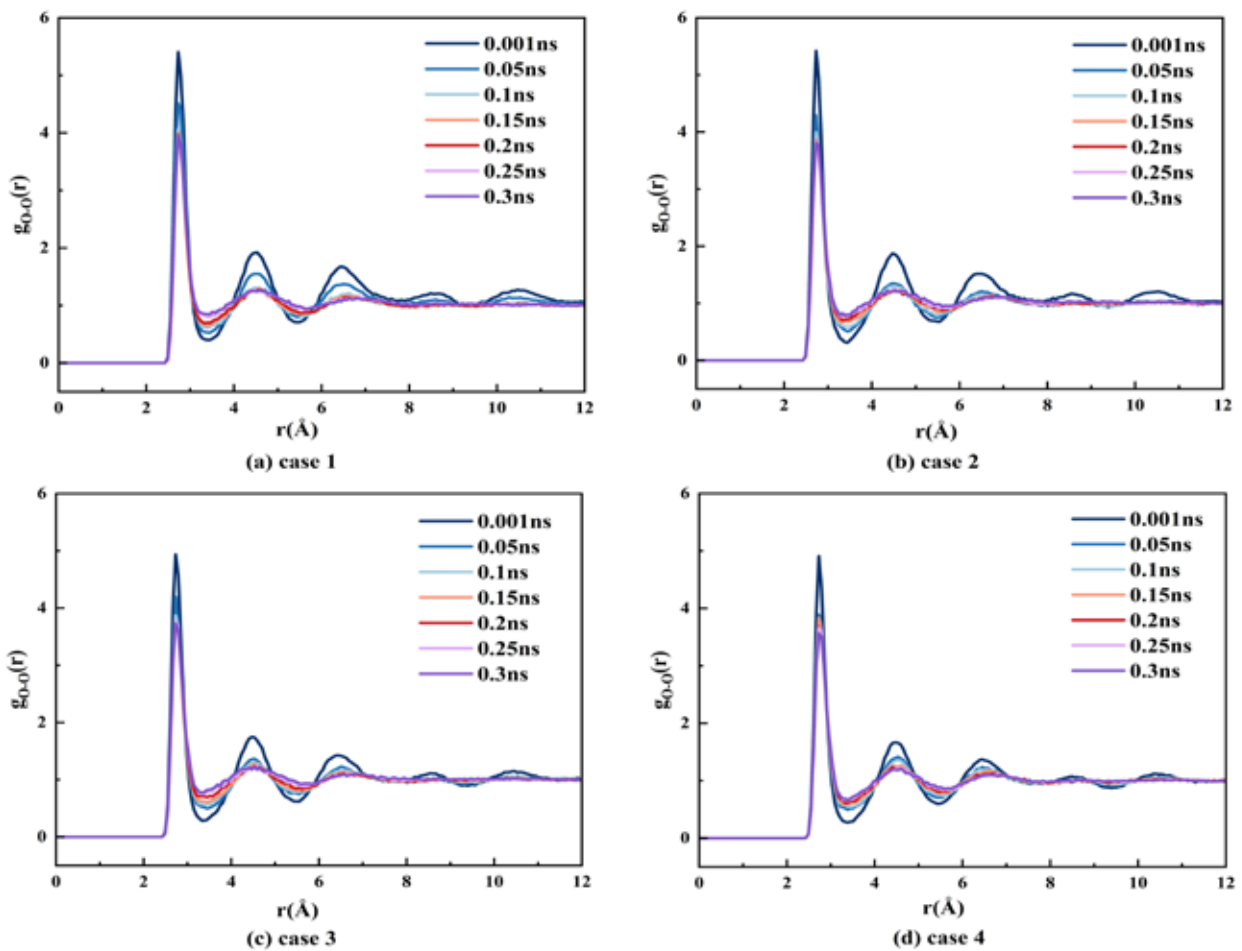


Figure 3. RDF change of oxygen atoms

3.3. Gas transport

The MSD represents the average distance of the spatial position of the molecules in the system that deviate from their initial positions. The MSD change of methane molecules during hydrate decomposition is shown in Figure 4. The MSD of methane increased slowly before 0.15 ns and increased rapidly between 0.15 ns and 0.3 ns. At the beginning of decomposition, methane molecules are trapped in the hydrate cage with little change

in MSD. As the hydrate decomposes, the gas gradually escapes from the hydrate cage, and the MSD changes greatly. After the decomposition is completed, the methane molecules completely break free from the shackles and begin to move freely, so the MSD of the methane molecules increases rapidly. The initial water content of the four simulations increases gradually, but the MSD decreases gradually. The larger the initial water content, the stronger the hydrogen bonding between free water molecules and water molecules produced by hydrate decomposition, which restricts the diffusion of the methane molecules.

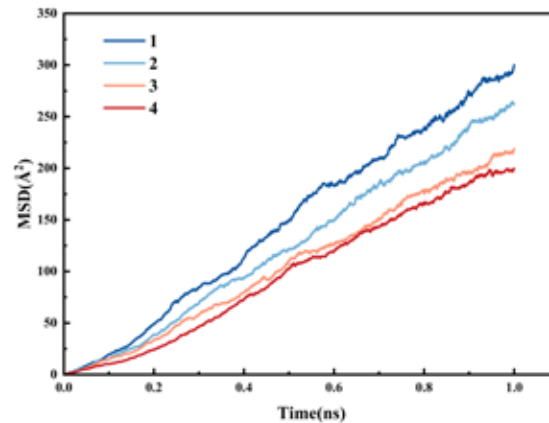


Figure 4. MSD of methane molecules

4. Conclusion

The results showed that the decomposition process of hydrate proceeded layer by layer from the edge to the center. The higher the initial water content, the more gas dissolved in water, and the less inhibition effect on hydrate decomposition. The decomposition rate of hydrate increases with the increase of initial water content. With the decomposition of hydrate, the motion distance of methane molecules gradually increases. The changes in MSD are also affected by initial water content. The higher the initial water content, the smaller the MSD of methane molecules.

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Disclosure statement

The authors declare no conflict of interest.

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