

博士論文（要約）

**Molecular Scale Simulation of Fluid-Hydrate-Mineral
Interactions with Application to Petroleum Engineering**

（流体 - ハイドレート - 鉱物相互作用の分子スケールシミュレ
ーションとその石油工学への応用）

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論文の内容の要約

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(流体-ハイドレート-鉱物相互作用の分子スケールシミュレーションとその石油工学への応用)

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Fossil fuel, like oil and gas, are important resources for industry and society in past and future decades. CO₂ emission from fossil fuel consumption can cause global warming. CCS (carbon dioxide capture and storage) and gas hydrate resource development are expected as technologies for realizing a low-carbon society. Understanding the molecular-scale interactions between geofluids and mineral, and between geofluids and hydrates has a practical significance since they underlie all the natural and industrial processes. Molecular simulations are powerful tools to detect interfacial interactions and adsorption structures at the molecular scale, which are difficult to determine by traditional research methods. In this thesis, I performed molecular scale simulations: (1) to understand the underlying mechanism of the CO₂-induced swelling of the non-swelling kaolinite clay mineral; (2) to determine the phase diagram of simple methane and ethane sl hydrate, and (3) to identify the underlying mechanism of sl/sII hydrate growth and hydrate structural transition.

First, geofluid-mineral interactions are studied for CCS. CO₂-geosequestration is a promising and feasible technique for greenhouse gas mitigation. To improve the CO₂ storage efficiency and develop monitoring techniques, it is important to know how CO₂ interacts with the connate water and minerals in subsurface rocks. Molecular scale simulations of the CO₂-water-kaolinite system were performed by using molecular dynamics (MD) and grand canonical Monte Carlo (GCMC). I proposed a new swelling mechanism in kaolinite, a typical non-swelling clay. This supplements the swelling mechanism besides hydration and osmotic effects. The results emphasize the importance of the different wettabilities of the two kaolinite surfaces and the synergistic actions of CO₂ and water in the adsorption behavior. The magnitude of the strain change induced by CO₂ adsorption can be significantly greater than that caused by pore-pressure changes alone. This result has academic and engineering significance because it supports the technology of detecting the CO₂ invasion region of CCS, and can be used to monitor CO₂ leakage in wellbore by measuring the formation strain.

Second, the simple hydrate (with methane and ethane as guest molecule) phase boundary

are studied. The natural gas from hydrate is well-known as an unconventional energy resource and has begun to open its promising future for the world. Since methane and ethane are two major compounds of natural gases, gas hydrate formed from these gases are of practical importance. Molecular dynamics simulation was carried out in the system of Hydrate-Liquid Water-Vapor (H-Lw-V) to predict the phase-boundary curve (three-phase equilibrium line). I succeeded in reproducing the phase boundary for simple methane and ethane sl hydrate with a new combination of water and hydrocarbon models. Especially, I overcame the difficulty for ethane sl hydrate phase boundary in the intermediate pressure area where ethane's phase behavior is complicated. The result can help to understand hydrate stability in marine area and has possibility to improve our estimation accuracy in hydrate reserves. Besides, more studies with similar method are expected in the future study where long-chain molecules (like propane or other hydrocarbon) and even organic matters (like resin) exist in system, with possibility to detect the subtle molecular interactions in the system.

At last, the unique structural transition phenomenon in methane-ethane binary system was studied. Previous works have shown that both pure methane and ethane form sl hydrate, however their mixture may form sII hydrate at certain composition. However, many details remain ambiguous. Here, I studied the hydrate structural transition. Molecular simulations were conducted focusing on the hydrate growth regularity and molecular-scale analysis. I studied the structural characteristics of the hydrate transition, finding the importance of 15-hedron as bridging role. Then I investigated the influence from pressure, temperature and methane mole fraction. It was demonstrated that within the simulation conditions, lower temperature and higher pressure is in favor of sl hydrate growth. Moreover, the methane mole fraction in certain area can facilitate the sII hydrate growth over sl. The underlying mechanism of this hydrate transition phenomenon was later explained by adsorption preference difference between methane and ethane at interfaces and cages, and by the formation energy difference of sl and sII hydrate systems with different methane/ethane occupancy. These results are fundamental possessing academic and engineering significance for natural hydrate development in the reservoirs with mixed gas hydrate structures. The study is also important for the development of the hydrate kinetics inhibitor and anti-agglomerate in flow assurance engineering.

In summary, the interactions among clay (kaolinite), water, and methane / ethane / CO₂ were studied through molecular simulations and experiments. Meanwhile, with the above findings, we demonstrate the possible application to petroleum engineering, for providing a concrete theoretical background, yet practical means, in the monitoring technique (namely, to monitor the CO₂-adsorption-induced strain) in CO₂-geosequestration; and for providing new insights on the development of the hydrate deposits containing natural gas mixtures, where sl and sII hydrates coexist.