P-T Diagram of Elastic Moduli of CH_4 and CO_2 Hydrate

J. JIA[1,2,*], Y. LIANG[1], S. MURATA[1], T. TSUJI[2], T. MATSUOKA[1]

[1]Graduate School of Engineering, Kyoto University, Kyoto 615-8540, Japan

[2]International Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University, Fukuoka 819-0395, Japan

* Presenting author: jia.jihui.45c@st.kyoto-u.ac.jp

Gas hydrate is considered to be an important potential future energy, and elastic properties of pure hydrate are crucial for evaluating elastic wave velocity of hydrate-bearing sediment in order to monitor the distribution of hydrates occurred in the formation in industry. Meanwhile, understanding the difference of elastic properties between methane (CH_4) and carbon dioxide (CO_2) hydrate induced by different "guest" molecules facilitates calibration of geophysical observation (P-wave velocity) with regard to Carbon Capture and Stroratge (CCS). In this paper, Molecular Dynamics (MD) simulations were performed to determine the elastic constants of CH_4 and CO_2 hydrate at one hundred pressure-temperature (P-T) data points, respectively. Elastic moduli of the hydrate aggregate were evaluated using Voigt-Reuss-Hill model. The P-T range covers the conditions of arctic permafrost and marine sediments where natural gas hydrate occurs. On the basis of the P-T diagrams, elastic wave velocities of hydrate-bearing sediments can be estimated so as to evaluate the formation situations in real time during natural gas production or CCS.

Interestingly, the shear modulus and Young's modulus of the CO_2 hydrate increased anomalously with increasing temperature, whereas those of CH_4 hydrate decreased regularly with increase in temperature. It indicates that the thermal effect can enhance the rigidity of CO_2 hydrate, which has been rarely reported with regard to the crystalline materials. Based MD simulations results, we ascribe this anomaly to the kinetic behavior of the linear CO_2 molecule. The aspherical shape of the cage limits free rotational motion of the CO_2 molecule at low temperature. With increase in temperature, the CO_2 molecule can rotate easily and fully, which will enhance the stability and rigidity of the CO_2 hydrate. This work provides a key database for the elastic properties of gas hydrate to monitor the distribution of CO_2 and CH_4 hydrate in the field when CO_2 replaces CH_4 from gas hydrate deposits, and molecular insights into stability changes of CO_2 hydrate from high temperature of approximately 280 K to a low decomposition temperature of approximately 100-120 K.