Theoretical Study on the Stability of Methane Hydrates

Fernando Alvarez-Ramírez, Isidoro García-Cruz, Yosadara Ruiz-Morales [C, S] and Ascención Romero-Martínez
Programa de Ingenieria Molecular, Instituto Mexicano del Petróleo, México D.F., México

Ab initio molecular dynamics, using the NVT ensemble and the DMol^3 method, were carried out to determine the stability of type II methane hydrates as a function of the methane content, temperature, and pressure. As a starting crystalline structure we considered the crystalline unit cell, which is cubic with a symmetry PM-3N (OH-3), IT number 223, and contains 46 water molecules. Different methane contents were considered, and for each, the average energy variation of the cell was calculated as a function of its size, i.e. as a function of its volume and at a constant temperature. Several different temperatures were considered and the pressure was calculated with the equation $P = -\partial E/\partial V$, where E is the average energy at the given cell volume (V) and at the given temperature. It is found that the potential energy minimum is shifted to higher cell sizes as the content of methane molecules is increased. The fluctuation in the formation or disappearance of hydrogen bonds along the molecular dynamics was analyzed. It is observed that the amount of individual water molecules is increased as the size of the cell increases and the pressure decreases with the concomitant reduction of hydrogen bonding. In this case the water molecules behave more as individual entities, like liquid water, than a solid crystalline cumulus. The inverse behavior is observed as the volume of the cell is decreased and the pressure increases.