Methane Hydrate Nucleation: Chorography and Cadence from Molecular Simulations

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Abstract

Methane hydrates are ice-like solids that form at low temperatures and high pressures, with methane molecules encaged in a hydrogen-bonded water lattice. They have been of long-standing interest to the oil and gas industry because of their tendency to plug pipelines, as a resource in the vast seafloor hydrate sediment deposits, and recently in the containment of the Gulf oil spill. The control of hydrate formation in these and other situations can be guided by molecular level knowledge of the hydrate nucleation process. The nucleation of hydrates is a rare event that occurs in nanoseconds at a random location on a nanometer length scale, and thus a molecular understanding of the process has been difficult to obtain experimentally or by simulation.

By employing large-scale microsecond long molecular dynamics simulations, we have captured a mechanism for spontaneous hydrate nucleation, revealing an intricate cooperative dance between methane and water molecules \cite{Walsh2009}, and analyze the development of cage ordering during the process of hydrate nucleation. We discuss our findings with respect to different simulation system conditions (temperature, pressure) and system geometry (methane nanobubble and bulk methane). The system geometry is found to be important in affecting the concentration of methane in water and consequently inducing the probability of hydrate nucleation – a methane nanobubble causes hydrates to nucleate more readily, whereas nucleation in a bulk methane system requires longer times. By comparing different system geometries we also discuss possible roles for the interface in hydrate nucleation. Knowledge of the phase boundary, necessary for determining the subcooling driving force, was calculated by thermodynamic integration for the molecular potentials used \cite{Jensen2010}. Analysis of trajectories under different driving forces and geometries allowed an estimate of the nucleation rate as a function of methane concentration.

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References