

Novel rapid order transmission mechanism in the heterogenous nucleation of gas hydrates

David T. Wu^{1,2,3}, Dalip Kumar² and Shiang-Tai Lin²

¹*Institute of Chemistry, Academia Sinica, Nangang, Taiwan*

²*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan*

³*Chemistry & Chemical Engineering Departments, Colorado School of Mines, Golden, CO, USA*

Gas hydrates have been of long practical interest due to their ubiquitous formation in cold pressurized water, e.g., in oil and gas pipelines, where they present a major problem in flow assurance, or on the sea floor where they represent a vast potential energy resource. They are also of fundamental interest as a generic behavior of water structuring in response to small hydrophobic guest molecules. The nucleation of gas hydrates has thus been of interest not only for applications but also as a model system for multicomponent, multiphase nucleation, where the role of transport and interfaces, and accompanying temporal behavior, play a heightened but not fully understood role.

We investigated the nucleation of methane hydrate in the presence of ice (Ih) at initial CH₄ concentrations from 3 to 10 mole % at 250 K and 50 MPa by molecular dynamics. The initially growing ice accumulated CH₄ molecules near the advancing interface and promoted formation of short-lived partial hydrate cages at the ice surface. This transient hydrate-like order propagated rapidly away from the surface by a novel order transmission mechanism leading to nucleation near but not on the surface. The growing ice front thus acted to enhance the rate of hydrate nucleation. The Van-Hove space-time correlation function was used to distinguish the role of molecular diffusion from the transmission of order via different molecules.