Guest-Host Interactions in Mixed CH_4 – CO_2 Hydrates: Neutron total scattering and computational modeling

Combined neutron total scattering and computational modeling are used to study gas hydrates with guest molecules of pure CH_4, pure CO_2 and mixed CH_4-CO_2. The goal of this work is to understand inter-molecular interactions between the guest molecule and the water lattice and how they impact the atomic structure and stability of gas hydrates This knowledge helps in predictions of how deposits will respond to changing environmental conditions caused by: climate change, drilling and CH_4 harvesting, and CO_2 sequestration. Total scattering measurements were conducted at the Nanoscale-Ordered Materials Diffractometer (NOMAD) at the Spallation Neutron Source at Oak Ridge National Laboratory to collect both neutron Bragg diffraction patterns and pair distribution functions (PDFs). Computational modeling of the hydrates includes classical molecular dynamics (MD) simulations to understand energetics and dynamics of the system and reverse monte carlo (RMC) modeling to refine structures against the total scattering data. Tools to aid in seamless transition between the two computational methods (MD and RMC) are enabled via the ICE-MAN: Integrated Computational Environment-Modeling analysis for Neutrons software development project. Pair distribution functions (PDFs) and three-dimensional density distributions provide insight into the changes in guest orientation and interactions with the host hydrate framework as a function of guest composition. From the MD work, the experimentally observed isotropic orientation of CH_4 molecules in both small and large cages is confirmed and the description of the anisotropic orientation of CO_2 molecules in the large cage is confirmed and further enhanced. Also from simulations, in mixed hydrates, the presence of CH_4 alters the orientation of CO_2, an indication that the interactions between guests, either direct (guest-guest), or mediated through interactions with the host (host-guest), are an important phenomenon in these systems for understanding stability and water lattice changes with respect to different guest molecules.