Gas hydrate nucleation from molecular simulations is a stochastic process, both in time-to-nucleation and in structuring of the incipient solids. Nevertheless, we observe some common phenomena among multiple molecular dynamics simulations of CH₄ and CO₂ gas hydrate nucleation and growth. In all cases, guest adsorption to hydrogen-bonded planar faces of cages and partial cages leads to cooperative hydrate growth, where adsorbed guest molecules protect the nascent solid while simultaneously encouraging the structuring of more cage-like hydrogen bonded networks around them. For both guests studied and across a range of thermodynamic conditions and interfacial geometries (50-4000 bar; 245-275 K; spherical, cylindrical, and slab gas phases), a specific set of seven cage types comprises 95% of all cages formed in the nucleated solids. This set of cages includes the 5₁^{12}_6^n subset (where n ranges from 0-4) as well the 4₁^{5}_{10}_6^n subset (where n ranges from 1-3), and these seven cages undergo simple interconversions via two mechanisms, both involving pairs of water molecules: insertions/removals and rotations. Such transformations are observed at the solid/solution interface as well as within the nucleated hydrate structures, and are possible mechanisms for the postulated annealing process from “amorphous” solids to crystalline hydrates. Although the nucleated solids lack long-range order, visible sI and sII motifs are observed in all simulations. In some simulations of CH₄ hydrate nucleation and growth in our larger systems (cubes of ~8 nm per edge), we observe the formation of multiple unit cells of sI hydrate adjacent to sII motifs; in these polycrystalline areas, the 5₁^{12}_6^n subset of cages occurs to the exclusion of the 4₁^{5}_{10}_6^n subset.

Keywords: Nucleation and growth mechanisms, adsorption, cage transformations, polycrystalline hydrate formation, templating mechanism