

## Insight into the Nucleation of Ethane Hydrate from Molecular Simulations

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As a structure I crystal former, ethane hydrates share fundamental nucleation concepts with methane hydrates, beginning with the formation of coordinated guest clusters in water. However, while methane demonstrates total occupancy of structure I, which contains two  $5^{12}$  and six  $5^{12}6^2$  cages in its unit cell, ethane will only infrequently occupy the  $5^{12}$  cages. Indeed, observations from molecular dynamics simulation studies reveal that there exist differences in both the cage type distributions and cage occupancy between methane and ethane hydrate nucleation. Occupied  $5^{12}$  cages dominate methane hydrate nucleation, while ethane hydrates have been found to predominately form  $4^{15}10^6$  cages as both the first and most common cage structure. While the  $4^{15}10^6$  cage appears to provide a more comfortable fit for the ethane molecule than the  $5^{12}$  cage, the orientation of the coordinate guest ethane molecule appears to be restricted inside the  $4^{15}10^6$  cage. These  $4^{15}10^6$  cages do not represent thermodynamically stable structures, and thus are not observed to occur in the crystal structure. However, these kinetically favored cages have been observed to readily undergo transformation into different thermodynamically favored cage structures, such as  $5^{12}$  or  $5^{12}6^2$  cages. These results have been obtained from a number of NPT molecular dynamics simulations of water and ethane, starting from phase separated systems corresponding to a bulk water and bulk ethane phases.