*Invited Contribution from AIChE Area 1a*

**Elucidating the Nucleation Mechanism of Clathrate Hydrates of Soluble Guest Molecules**

Ryan DeFever and Sapna Sarupria [C, S]

*Chemical and Biomolecular Engineering, Clemson University, Clemson, SC, U.S.A.*

*ssarupr@clemson.edu*

Clathrate hydrates are a solid phase composed of guest molecules entrapped in a lattice of polyhedral water cages. The guest molecules are generally light gases, such as methane or carbon dioxide. Currently active research on applications of clathrate hydrates ranges from energy and flow assurance to gas storage. Many such applications of clathrate hydrates require a firm understanding of the mechanism of hydrate formation. The birth of the hydrate phase occurs from a supersaturated liquid solution of water and guest molecules through an activated process called nucleation. Hydrate nucleation is inherently a molecular-level phenomenon, occurring on length- and time-scales that are difficult to probe with current experimental techniques. Though the length and time-scales of hydrate nucleation appear well-suited to study through molecular simulation, in most cases the associated activation barrier is large, and nucleation is a rare event in simulations. Correspondingly, in straightforward simulations most of the computational power is expended waiting for the nucleation event to happen rather than simulating the nucleation events of interest. To overcome these challenges, we use a technique called forward flux sampling (FFS) to generate over one thousand nucleation trajectories. We focus on the nucleation of clathrate hydrates of soluble guest molecules. Accurate committor probabilities were calculated for over 150 configurations generated with FFS. Through this we comprehensively characterize the transition state and are able to discuss the mechanism of hydrate nucleation for soluble guest molecules. This is the first study with such detailed and extensive study of hydrate nucleation of soluble guest molecules. We conclude by investigating how our proposed nucleation mechanism applies to mixed hydrate systems with two types of guest molecules. The extensive simulations required to study hydrate nucleation have motivated further work in developing novel sampling methods with improved efficiency. We will also discuss some of our recent developments in this area.