Exploring the kinetics and the free energy landscape of clathrate formation

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Gas hydrates are one of the major carbon carriers in Deep Ocean, and play a substantial role in energy recovery, global climate change, and gas storage/transportation. While significant, the key mechanisms through which hydrates form remain controversial. Here we present a computational study to overcome the major limits of theoretical understanding of hydrate formation. We developed a conceptually simple, yet computationally effective order parameter [1], on the basis of topological analysis of the hydrogen bond network, to drive and characterize hydrate nucleation. The order parameter is inclusive on various nucleation pathways, allowing identifying and verifying nucleation mechanisms with sufficient statistics. The quality of the order parameter has been strictly verified by the p_B histogram analysis, which indeed shows its close representation to the real reaction coordinates. We have integrated the order parameter into the forward flux sampling method [2], and successfully investigated hydrate formation under the thermodynamic condition where spontaneous nucleation becomes too difficult in direct simulation. By combining both the forward and backward samplings, we have also obtained the free energy landscape of hydrate nucleation, which clearly shows its non-classical nature. Remarkably, the obtained ensemble of nucleation trajectories include not only the nucleation pathways that are consistent with the proposed two-step mechanism, but also those “one-step” nucleation events that lead to the direct formation of crystalline hydrates. The diversity of the identified nucleation pathways demonstrates the complexity of hydrate nucleation, and sheds new light on the crystallization mechanism of hydrates.

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(2) Allen, R. J.; Frenkel, D.; Wolde, Ten, P. R. Simulating Rare Events in Equilibrium or Nonequilibrium Stochastic Systems. J Chem Phys 2006, 124 (2), 024102.