PRF#: 58024-ND6
Project Title: Role of Methanol in Methane Clathrate Formation
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Research Progress:

Methane clathrate is formed by methane molecules trapped within a crystal water structure similar to ice. It can occlude pipelines posing a serious danger for the petroleum industry. Methanol injection into gas transmission lines has been widely used to prevent the undesirable formation of these structures. The atomic mechanisms accounting for this inhibiting effect of methanol are not well understood. Moreover, there is evidence that methanol at low concentration and very low temperature could promote (instead of inhibiting) the formation of methane clathrates. This project is providing an understanding at the atomic level of the role of methanol in methane clathrate formation through extensive all-atom molecular dynamics simulations. This methodology allows us to probe nanometer length-scales and microsecond time-scales required to study clathrate formation. We anticipate that the mechanistic insights provided by this project will enable rational designs of new and more efficient clathrate inhibitors.

Milestones achieved during this project:

1. We have developed a software that computes different quantities related to the formation of clathrates, including 5^{12}, $6^2 5^{12}$, and $6^4 5^{12}$ cages, as well as the F_4 dihedral order parameter. We have publish a paper (Computer Physics Communications **244**:385–391 (2019)) describing how different quantities are computed within the code (see **Figure 1**) and the code has been shared with the community as open source software.

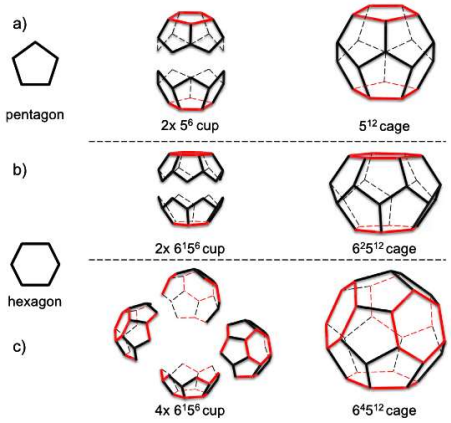

Figure 1—Schematic representation of how 5^{12}, $6^2 5^{12}$ and $6^4 5^{12}$cages are computed in a hierarchical manner. First, all *non-distorted* five- and six-folded rings made by connecting first-neighbor water molecules are computed. Second, five- and six-folded rings are analyzed to compute 5^6 and $6^1 5^6$ cups. At last, cages are computed by studying the connectivity of these cups.

2. We have developed protocols to simulate the homogeneous nucleation of methane clathrates for system made of methane+water as well as methane+water+methanol at different temperatures. In this protocol, we use random initial position and velocity for all molecules.

3. Using these protocols, boxes containing methane, methanol and water molecules were prepared and simulated at 50 MPa and different temperatures. **Figure 2** shows how the number of 5^{12} cages increases as a function of time in simulations performed in the absence and presence of methanol at 230 K and 270 K. The vertical red line in the different panels corresponds to the average time required to nucleate twelve 5^{12} cages. These simulations show that at 270 K methanol increases the time required to nucleate methane clathrates whereas at 230 K this molecule shortens the nucleation time. This inhibiting effect of methanol at 270 K is well documented in the literature and is the reason why methanol is injected in pipelines during the transport natural gases. There is evidence that methanol can promote clathrate formation at temperatures below 250 K, however, this effect is still under debate and its molecular mechanism remains unknown.

4. Currently, our lab is investigating the molecular mechanisms accounting for methanol inhibiting/promoting effect on clathrate formation.

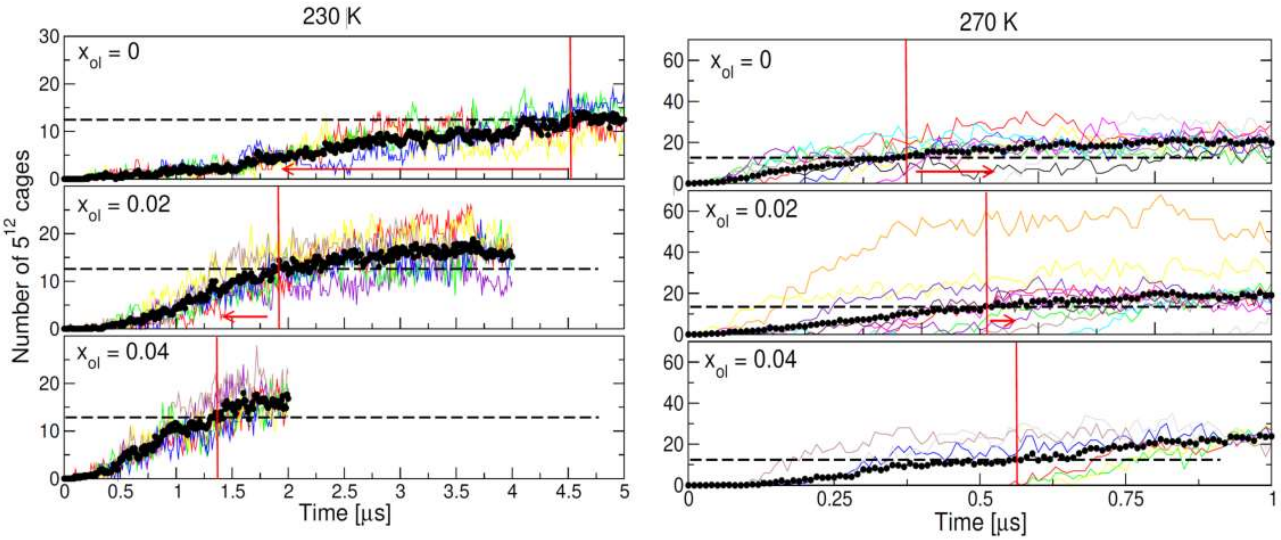

Figure 2—Nucleation of methane clathrates at 230 K (left panels) and 270 K (right panels) in solutions without methanol (first row) and containing a methanol mole fraction x_{ol} of 0.02 (second row) and 0.04 (third row). Simulations performed using different initial conditions are represented by different colored lines. Black dots correspond to the average over all simulations performed under the same conditions of temperature, pressure, and methanol concentration. Red arrows show the effect of methanol on the time required to nucleate 12 methane

Impact of the research on the PI's career:

This project opened a new research venue in the PI's lab with focus on natural gases and the design of small molecules to inhibit/promote clathrate formation. New collaborations with more senior researchers in the broad field of petroleum research were forged in this process. Moreover, this year the PI was able to secure NSF funding. The proposal submitted to NSF uses a methodology very similar to one developed in this PRF-project. Thus, it is safe to say that without the work carried out in this project, it would have been difficult to secure NSF funding.

Impact of the research on students' career:

This project allowed one PhD student to dedicate himself full-time in research activities for the whole year. This student defended his thesis in Fall 2019 and he is now working as a post-doctoral fellow at NYU. Another PhD student and an undergraduate student were supported by this project during the summer. Both students continue to work in the Dias lab during the academic year while taking courses. Thus, this project allowed these graduate and undergraduate students to immerse themselves in research while benefiting from a convivial atmosphere where seniors students train juniors ones under the guidance of the PI.