PRF#: 58024-ND6
Project Title: Role of Methanol in Methane Clathrate Formation
Principal Investigator Name, Affiliation: Cristiano L. Dias, The New Jersey Institute of Technology, University Heights, Newark (NJ) 07042

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 of the inhibiting effect of methanol are not well understood. Moreover, effects of methanol at low concentration and very low temperature remain under debate. This project is addressing these knowledge gaps through extensive all-atom molecular dynamics simulations in order 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 the reporting period include:

1. Development of software that computes different quantities related to the formation of clathrates, including 5^{12} and $5^{12}6^2$ cages, and the F_4 dihedral order parameter. The input of this software is the atomic positions of oxygen and hydrogen atoms of water molecules in *gro* format. Currently, we are writing a manuscript describing how different quantities are computed within the code (see **Figure 1**) and the code is being prepared to be shared with the community as open source software. We anticipate that this software will be used as a template code that will be optimized by research groups for their specific needs. To the best of our knowledge, there is no commercial or open source software to analyze water cages. This implies that, currently, researchers have to write their own codes from scratch which is time consuming given the complexity of the operations required to compute clathrate cages. Thus, we believe that making our code publicly available as open source software will positively impact our research community. We expect that the software and the manuscript will be submitted for publication November 2018.

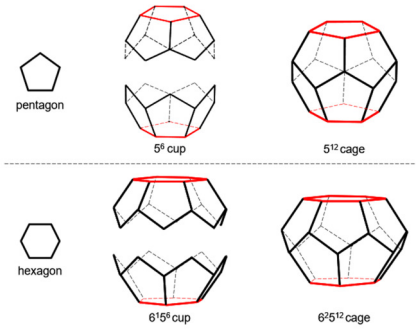

Figure 1—Schematic representation of how 5^{12} and $6^2 5^{12}$ cages are computed in a hierarchical manner. First, we compute all *non-distorted* five- and six-folded rings (i.e., pentagons and hexagons) made by connecting first-neighbor oxygen atoms. Second, five- and six-folded rings are analyzed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

2. Developments of protocols to perform all-atom molecular dynamics simulations of homogeneous nucleation of methane clathrates for system made of methane+water as well as methane+water+methanol. Using these protocols, boxes containing methane, methanol and water molecules were prepared and simulated at 50 MPa and three temperatures (i.e., 270, 250, and 230 K). For these simulations, we used a methane mole fraction of x_m=0.056 and three mole fractions for methanol x_{ol}=0, 0.02, and 0.04. The number of TIP4P-ice water molecules in these boxes was 3335, 3305, and 3191, respectively. As an example of the outcome of these simulations, we show in **Figure 2** how the number of 5^{12} cages increases as function of time in seven simulations performed in the absence of methanol (panel a) and at a methanol mole fraction of x_{ol}=0.02 (panel b) at 270 K. From these simulations, we compute the average time required for five clathrates to nucleate irreversibly in the absence ($\langle t_n \rangle = 154 \pm 75$ ns) and presence ($\langle t_n \rangle = 331 \pm 174$ ns) of methanol. Despite the large uncertainty in the computed nucleation time, these simulations are already showing that even at small mole fraction, methanol inhibits the formation of clathrates at 270 K. Additional simulations are being performed to provide better estimates for these average nucleation times. In panels *c* and *d* **of Figure 2**, we show atomic representations of 5^{12} and $6^2 5^{12}$ cages at different times for simulations performed in the absence and presence of methanol, respectively. Simulations performed at 250 and 230 K are not shown here.

Irreversible clathrate formation at these temperatures requires simulations to be performed for 2 and 4 μs, respectively.

3. Analysis of our simulations in the absence of methanol is confirming results from the literature. In particular, we find that isolated water cages are rare and they have a short life-time at 270 K. Thus, the formation of clathrates requires a critical nucleus size to be formed with several methane molecules at close proximity from each other—see **Figure 2c,II**. At 230 K, we find that isolated cages become more stable and occur more frequently.

4. Currently, our lab is investigating the molecular mechanism of methanol in inhibiting clathrate formation at different temperatures.

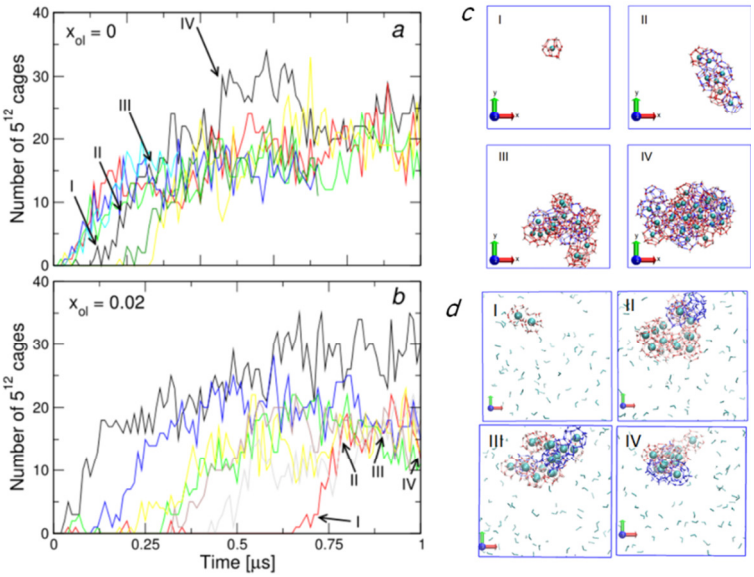

Figure 2—Homogeneous formation of methane clathrate at 270 K and 50 MPa. Time dependence of the number of 5^{12} cages formed in seven independent simulations (a) in the absence of methanol and (b) at a methanol mole fraction of 0.02. Atomic representations of 5^{12} (in red) and $6^2 5^{12}$ (in blue) cages are shown at different instant of time for one particular simulations in (c) pure water and (d) methanol solution. Licorice and van der Waals representations are used for methanol and methane, respectively. The simulation box is represented as a blue square.

Impact of the research on the PI's career:

This research project has had a positive impact on the career of the PI. In particular, the PI was promoted to Associate Professor this year. Also, this research project has opened a new research venue in the PI's lab with a focus on natural gases and the design of small molecules to inhibit clathrate formation. Results from this research project are being used as preliminary results for a new research proposal to be submitted to NSF.

Impact of the research on students' career:

This proposal has had a positive impact on the research of students in the PI's lab. It has enabled one PhD student to dedicate itself full-time to this project. Moreover, this PhD student is supervising undergraduate and high school students under the guidance of the PI. Thus, the PhD student is training to become a mentor while undergraduate and high school students are being introduced to a scientific career.