

Investigation of the growth of methane clathrate hydrates using molecular simulations

Contact: ANTOINE PATT, post-doctoral fellow at the UTINAM Institute

E-mail: antoine.patt@univ-fcomte.fr - Office: 311 C

Clathrate hydrates are inclusion compounds made of hydrogen bonded water molecules forming a network of cages stabilized by encapsulated gaseous molecules[1]. These crystalline water-based solids are thought to be ubiquitous on Earth, especially on the ocean floor and within the surface layer of the so-called permafrost, where methane is mainly trapped. The estimations of the amounts of gas stored in clathrates indicate that they are significantly greater than those from all the other sources of fossils fuels. Thus, clathrate hydrates are viewed as a potential energy resource for the future. This very fact implies that clathrate hydrates are also at the heart of environmental concerns regarding the release of methane (which is a potent greenhouse gas) in the atmosphere. Hence, understanding the mechanisms underlying the formation and stability of these crystalline structures is of great importance if we are to either exploit this resource or prevent it from collapsing and contributing directly to climate change.

The thermodynamics and equilibrium properties of clathrate hydrates have been extensively and efficiently studied since the 1950's. Experiments, statistical physical models and molecular simulations agree on countless situations, especially in the description of phase equilibria. However, studying the kinetics of clathrates is less straightforward given the stochastic nature and the great mass and heat transfers typical of the nucleation process of hydrates for example. The exact model describing the molecular mechanisms leading to the formation of clathrates is still to be developed. Obviously, molecular simulations constitute a powerful tool to investigate such dynamical properties (among others) by accessing scales unreachable to the experiments and without some limitations used in theoretical thermodynamic models.

Numerical studies of clathrates nucleation are quite demanding and often require sophisticated methods in order to yield any significant results. However, a first step in this direction can be achieved by investigating the growth process arising once a critical nucleus of hydrate has formed. This kind of study still requires to master the key features of molecular simulations (especially molecular dynamics) and thus constitutes a strong introduction to these numerical methods along the analyses necessary to translate computational results into physical interpretation. Moreover, this study is also an insight into the molecular physics behind water, particularly in its solids forms, which is nowadays a very active research field despite the apparent simplicity of the water molecule.

The student undertaking this laboratory project will first spend time learning from the literature about clathrate hydrates (and other solid forms of water), the statistical physics behind the phenomenon of enclathration, the kinetics and nucleation of hydrates but also about molecular simulations. The practical part of the project will aim at simulating the growth of a methane hydrate to understand the characteristics of this process and understand how to enhance or to prevent it. If time allows it, the student will confront themselves to the simulation of hydrates homogeneous nucleation or at least work at bridging their previous growth simulations to possible nucleation ones.

In terms of numerical tools, the student will use a general purpose simulation software already written (for obvious reasons), but its use and all the analyses will require them to write many scripts and programs, in the programming language they want.

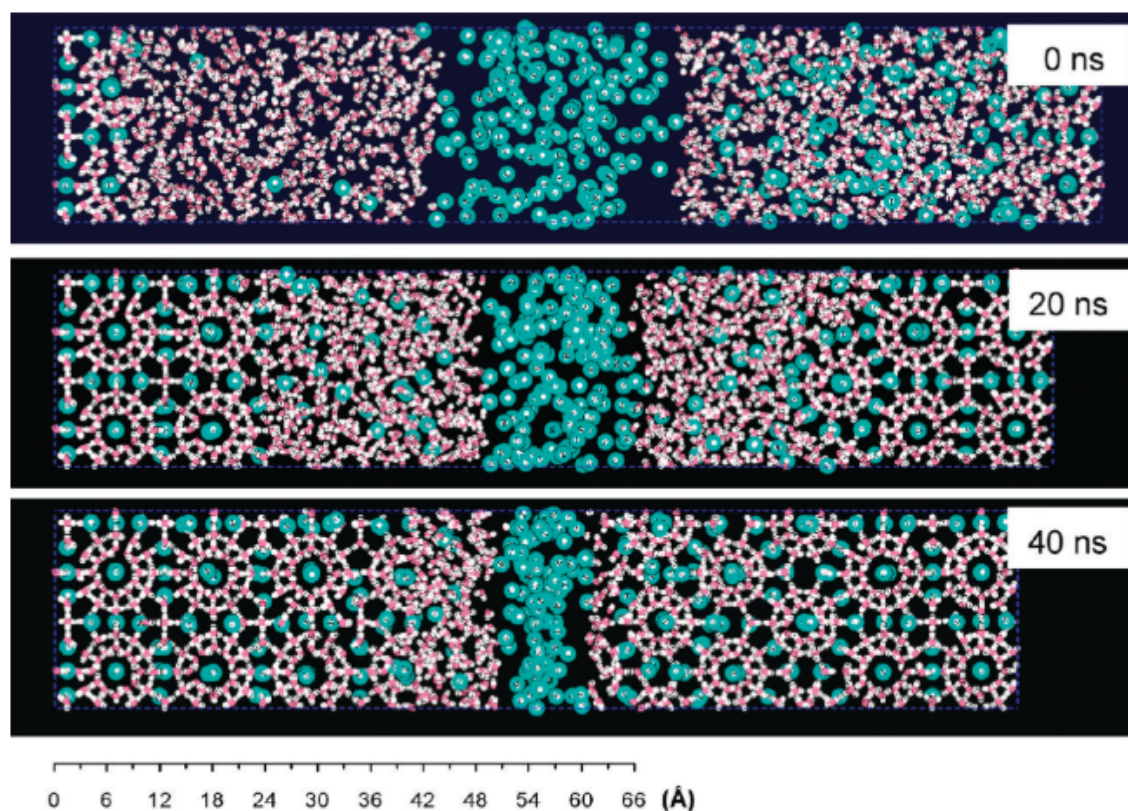


Figure 1: Snapshots taken from a methane hydrate growth simulation at 60 MPa and 260 K, from the work of Tung *et al.*[2].

References

- [1] Sloan, E; Koh, C. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press, FL, 2008.
- [2] Tung, Y.-T.; Chen, L.-J.; Chen, Y.-P.; Lin, S.-T. *J. Phys. Chem. B* **2010**, *114*, 10804-10813.