Molecular properties of clathrate hydrates using modern machine learning approaches

PhD position – Institut UTINAM (Besançon - FRANCE)

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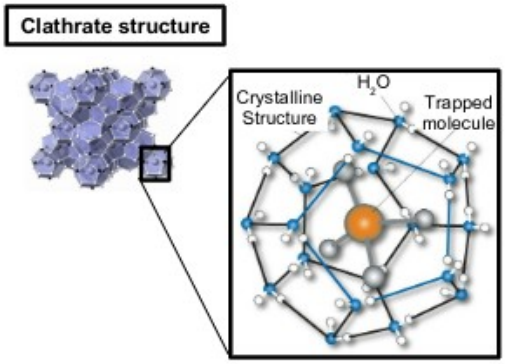
Clathrate hydrates (or gas hydrates), are ice-like non-stoichiometric inclusion compounds composed of water molecules self-assembled into cages and stabilized by the presence of small guest atoms or molecules encapsulated within the water host lattice (cf. Figure) [1]. Appropriate pressure (millibars to several hundred bars) and temperature (lower than 300K) conditions are required to form gas hydrates naturally occurring on Earth in deep ocean regions and in permafrost (Siberia, Alaska, Arctic) mainly as methane hydrates. This natural occurrence makes them relevant for many geophysical and astrophysical applications. Therefore, research studies on gas hydrates have steadily expanded nowadays toward a broad area ranging from molecular sciences to geosciences.



Schematic view of cages in clathrate hydrate [2]

The storage and transport of gas in the form of gas hydrates constitutes an important and promising research area. Indeed, gas (like CH_4, CO_2, H_2, ...) stored in hydrate form is a safe storage mode (soft thermodynamics conditions), environmentally friendly, with robust stability and high energy density [3-5]. Improving storage conditions requires a better understanding of the molecular properties according to thermodynamics conditions (pressure, temperature) and compositions (quantity and nature of the trapped gaz). Molecular simulations using density functional theory (DFT) are well suited for studying the molecular properties of gas hydrates, but can be computationally demanding especially for investigating the properties of many systems under conditions close to the experience. However, combined with machine learning (ML) approaches, ML-DFT is a powerful tool in computational materials science nowadays [6]. The **PhD position falls in this research context and aims at investigating the molecular properties in clathrate hydrate using a combination of DFT and ML simulations**. In the context of gas storage applications, the main objectives of the thesis will focus on the following two points and using training database from DFT calculations:

- prediction of the enthalpy of formation for a wide variety of gas hydrate composition (pure and mixed);
- generation of force-field potentials (MLFF) usable in classical molecular dynamics simulation to extract transport coefficients. These coefficients will be used in a Kinetic Monte Carlo (KMC) program to evaluate solid-state diffusion of gas molecules on a larger time scale.

Key words: clathrate hydrates, DFT/AIMD calculations, machine learning/evolutionary algorithms, KMC simulations.

References:

[1] Sloan E. D. et al., *Clathrate Hydrates of Natural Gases*, 3rd ed. Taylor & Francis-CRC Press: Boca Raton, FL (2008).

[2] Marboeuf U. et al., *A model of cometary nucleus taking into account all phase changes of water ice: amorphous, crystalline, and clathrate*, EPSC Abstracts 6, EPSC-DPS2011-840, (2011).

[3] Yang L. et al., *Enhanced clathrate hydrate phase change with open-cell copper foam for efficient methane storage*, Chem. Eng. J. **440**, 135912 (2022).

[4] Veluswamy H.P. et al., *Hydrogen storage in clathrate hydrates: current state of the art and future directions*, Appl. Energy **122**, 112-132 (2014).

[5] Gupta A. et al., *Hydrogen Clathrates: Next Generation Hydrogen Storage Materials*, Energy Storage Mat. **41**, 69-107 (2021).

[6] Fielder L. et al., *A Deep Dive into Machine Learning Density Functional Theory for Materials Science and Chemistry*, Phys. Rev. Mat. **6**, 040301 (2022).