CO clathrate hydrate stability with pressure : a DFT approach

Master 1 CompuPhys - Project Lab
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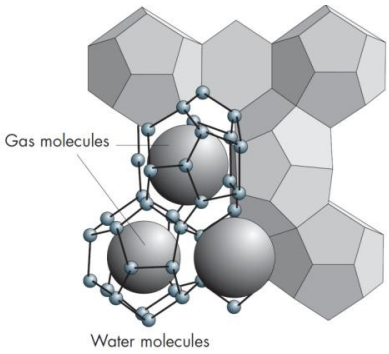

Under specific conditions of pressure and temperature, the mixing of water and gas molecules can lead to the formation of nanoporous crystalline solids called clathrate hydrates. These compounds are made by a tetrahedral network of water molecules (“host”) forming cages inside of which gas molecules (“guest”) are encapsulated. Naturally abundant on Earth, gas hydrates can be observed on permafrost regions (Alaska, Siberia), on ocean floors and are generally expected to exist on icy celestial bodies (comets and planets of the solar system). 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.

After a bibliographic research in the gas hydrates field, the student will study the **energetic properties of CO gas hydrates** for two crystallographic structures (sI and sII). Indeed, experimental results show that CO gas hydrate is initially formed in the cubic sI structure and after few days transforms into the cubic sII structure. The sI structure would be kinetically promoted at the early synthesis stage whereas the sII structure would be thermodynamically favored thanks to a double filling of large cages. Previous studies showing the structural stability of sII hydrate were already performed. Nevertheless, the effect of pressure on the gas hydrate stability still remain to be studied. Calculations will be performed on both structures by using a density functional theory (DFT) code with appropriate exchange-correlation functionals and considering various CO occupancy in cages. For every CO concentrations, effect of unit cell volume will be assessed and the role of pressure on CO gas hydrates properties will be deduced. Finally, the so-called convex hull approach will be used to deal with CO clathrate hydrate stability.

Key words: clathrate hydrates, DFT/AIMD calculations, diffusion coefficients

Numerical tools: VASP software, Python/Bash scripts

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