SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: ES1405
STSM title: Elastic Properties of Hydrate Systems using Molecular Dynamics Simulations
STSM start and end date: 01/02/2019 to 15/02/2019
Grantee name: M. Dolores Melgar Freire

PURPOSE OF THE STSM:

The purpose of this STSM is to extend the application of a new method developed in our group to estimate the seismic velocities of geophysically relevant materials using Non-Equilibrium Molecular Dynamics to the particular case of different hydrate structures. This method consists in the creation of a perturbation and the study of its propagation. Moreover than the propagation velocity, the effects of this perturbation on the hydrate structure itself and the encapsulation of guest molecules were also studied.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

Different types of hydrate structures were studied during this STSM using Non-Equilibrium Molecular Dynamics Techniques.
The first part of this project was focused on methane hydrates. Both structures type I and II were studied. For both systems, a velocity perturbation was introduced in the system in order to analyse its propagation and to calculate the associated velocity both for longitudinal and transverse modes (P- and S- waves). A wide range of perturbation amplitudes were tested. To better understand the effect of this amplitude on the hydrate structure a Baez-Clancy analysis was performed, together with a more detailed cluster study (inspired by the work of Molinero) to determine how many of the large and small cages were recovered after the impact of the perturbation.
The second part consists in taking advantage of the methodology developed to understand the effects of the amplitude of the perturbation could have in the leaking of a type I hydrate structure with THF and H_2 or D_2 as guest molecules at different temperatures. The idea is to better understand the kinetics of that process using different perturbation amplitudes. For that, a simulation box half occupied by the hydrate and half empty was set and the system was let to evolve without any perturbation, to compare it with the wide range of amplitudes also tested. A Baez-Clancy analysis was performed for each simulation to calculate the number of water molecules that can be classified as hydrate, as well as the number of enclathrated guest molecucles. The simulations without perturbation are used as a point of reference to make a distinction between the effects of the vacuum and the effects of the perturbation itself.
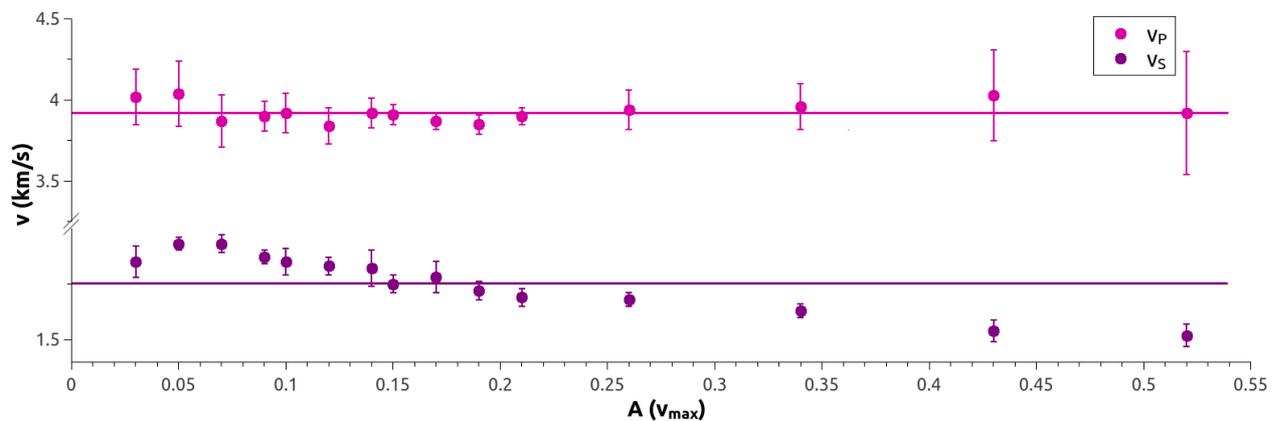

DESCRIPTION OF THE MAIN RESULTS OBTAINED

For the methane hydrate structures (sI and sII), a set of simulations where perturbations with different amplitudes and then the propagation velocity was calculated following the methodology developed last year in our group.

**Seismic velocities for sI:**
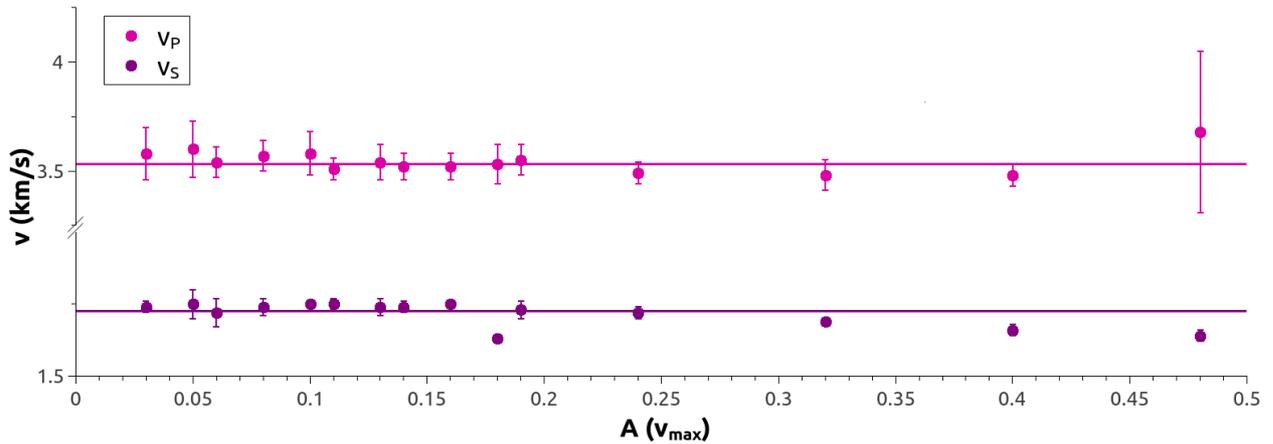
Seismic velocities for sII:

The seismic velocities calculated for both longitudinal and transverse modes are not dependent on the perturbation amplitude, although the amplitude plays a role regarding the conservation of the hydrate structure. For small amplitudes, the structure can be recovered after the perturbation, but for larger amplitudes the structural damage is irreversible.
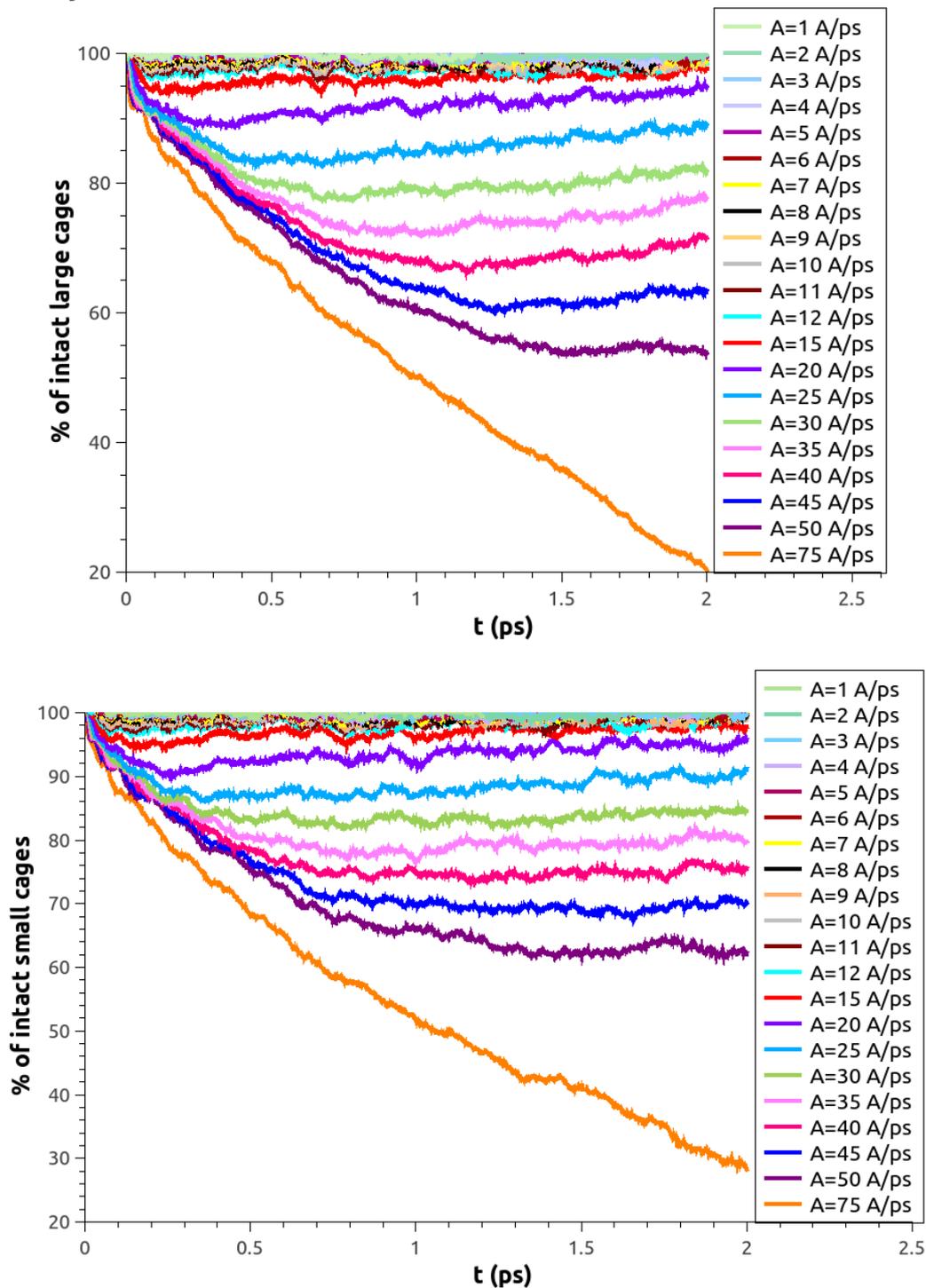
**Baez-Clancy analysis for sI:**
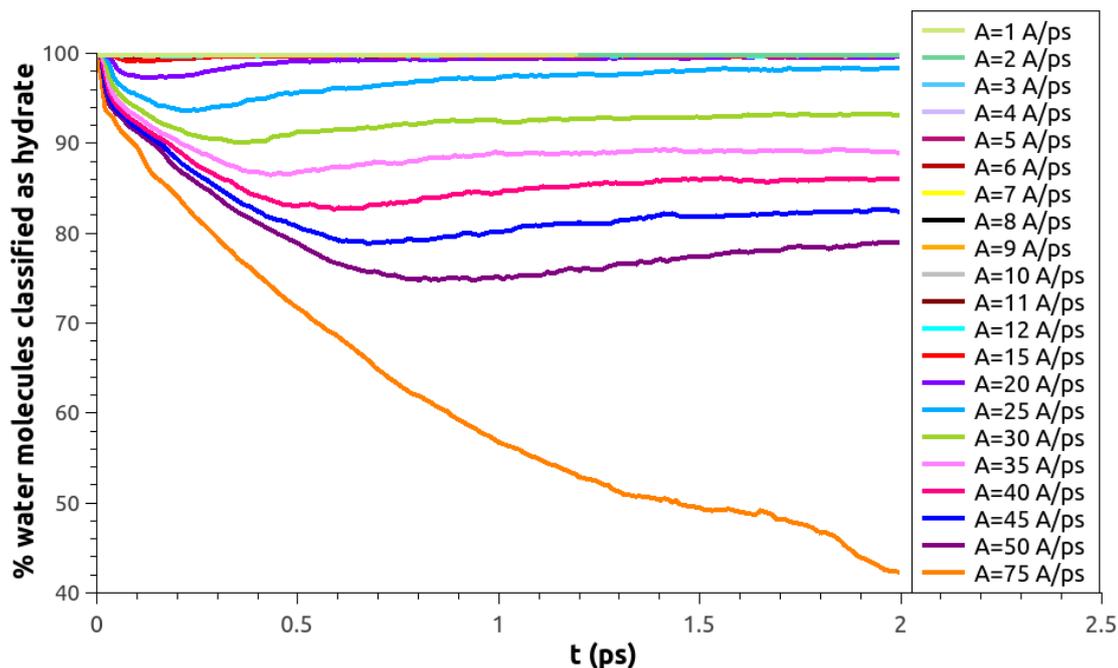
Baez-Clancy analysis for sII:
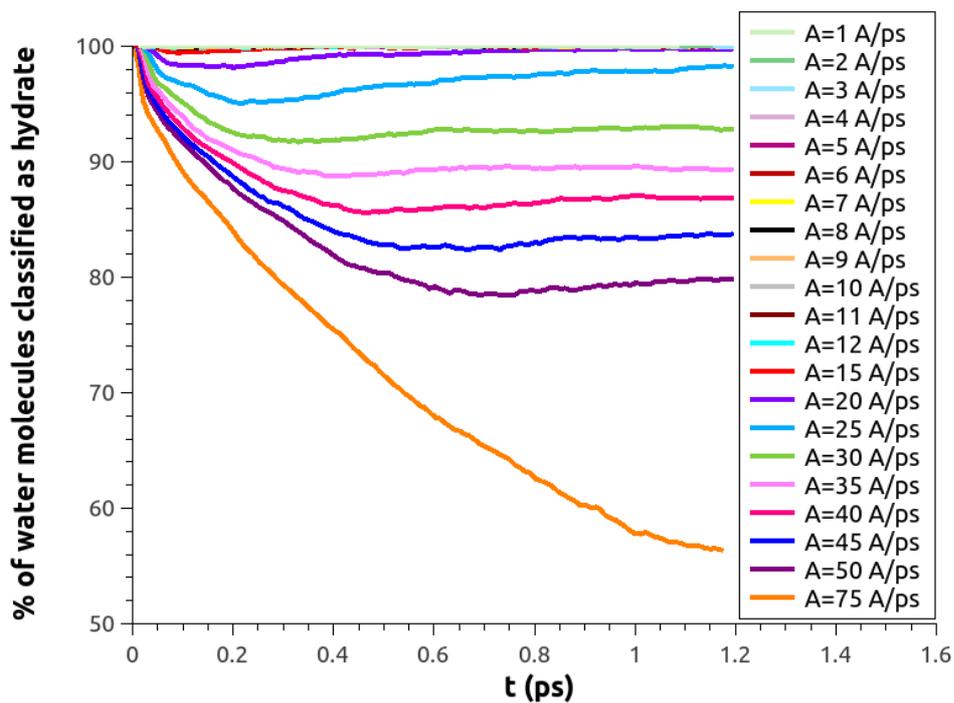
This Baez-Clancy results were consistent with a cluster analysis inspired by the work of Molinero. This consists in counting how many large and small cages exist at each time-step.
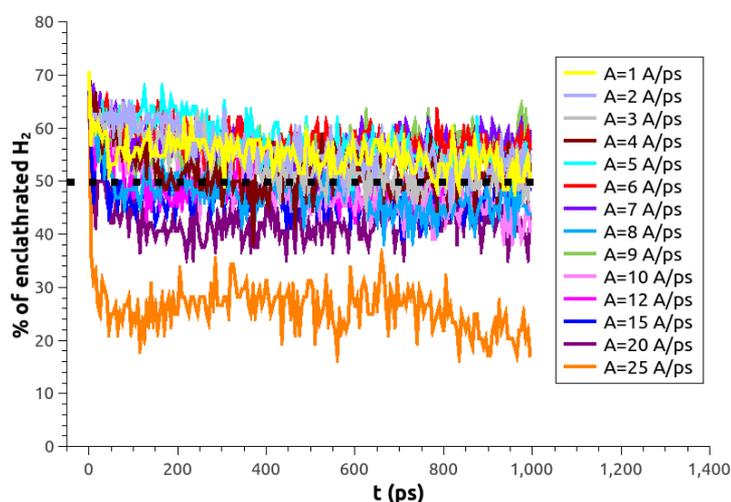
Cluster analysis for sI:

The reason of the irreversibility of the structural damage is the triggering from a certain amplitude of the formation of a methane nanobubble in the systems, which makes impossible the recovery of the structure after the perturbation. This is shown in the growing shoulder before the first peak that appears in the carbon-carbon radial distribution function (RDF).
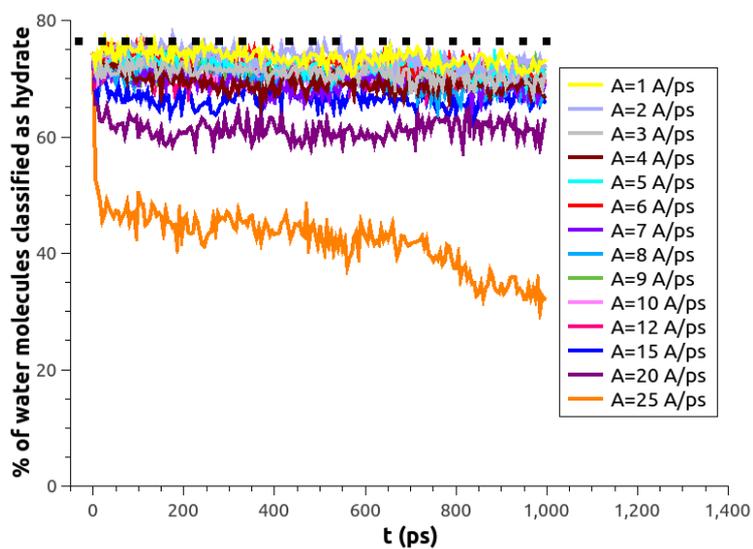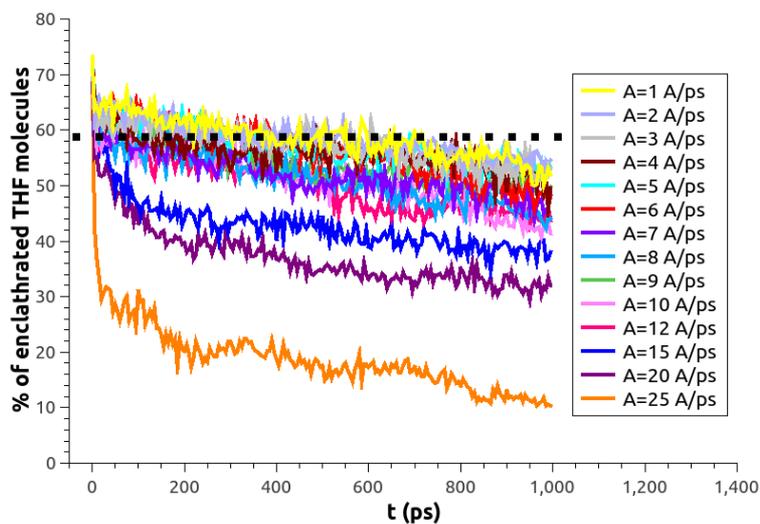
C-C RDF for sI:
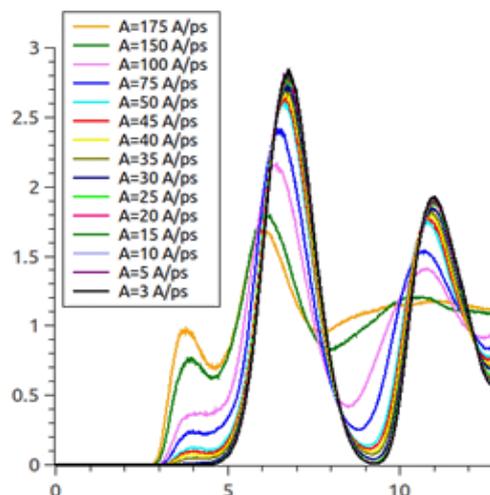
For the hydrate structure I with THF and H2 as guest molecules, different simulations were performed in order to have a better understanding of the kinetics of the leaking process of H2. These include different temperatures (T=80 K, 100 K, 110 K, 140 K, and 180 K) and the substitution of H2 by D2. For all of them, half of the simulation box was empty and the other half occupied by the hydrate structure. Then a set of longitudinal perturbations with different amplitudes were tested trying to favour the extraction of the small guest molecules. Again, Baez-Clancy analyses were carried out to calculate the number of enclathrated molecules and the number of water molecules forming an hydrate structure. For high temperatures, the most of the guests molecules (both large and small) are found outside the hydrate structure and only half of the water molecules can be classified as hydrate. This happens at the very beginning of the simulation and it is independent of the perturbation amplitude, which indicates that is caused by the vacuum and not triggered by the perturbation. The same occurs when H2 is substituted by D2, but in this case the effect is even more dramatic, although, again, not depending on the perturbation. In contrast, for H2 systems at lower temperatures, there is an effect of the perturbation amplitude on the number of guest molecules enclathrated, as well as in the hydrate structure itself.

 Baez-Clancy analysis for the THF-H2 sI hydrate structure (dotted line indicates the final percentage for the simulation where no perturbation was introduced):