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Call for Thesis subjects for 2020/2021

RESEARCH SUBJECT TITLE:

Pulling hard on heavy water:
properties at negative pressure to explain water anomalies

Name of the laboratory: **Institute of Light and Matter**
Website: http://ilm.univ-lyon1.fr/?&lang=2

Name of the research team: **Liquids and Interfaces**
Website: http://ilm-perso.univ-lyon1.fr/~fcaupin/indexeng.html

Name of the supervisor: Frédéric CAUPIN
University / Institution: Université Claude Bernard Lyon 1
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Doctoral School: Physics and Astrophysics (PHAST)

Lab Language: English/French

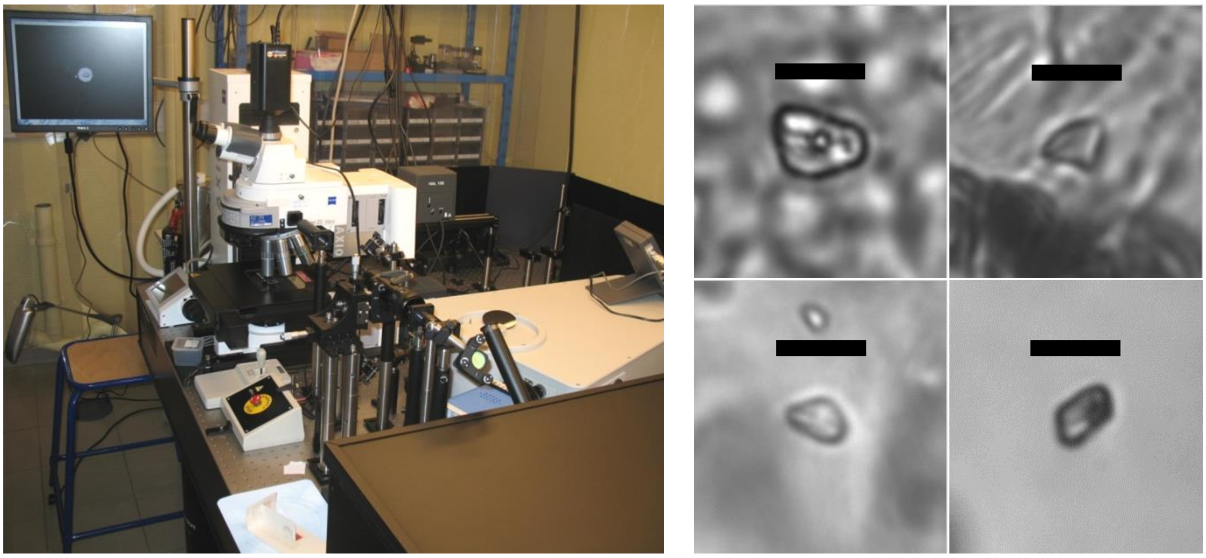
Minimum language level required:
- English: fluent
- French: beginner

Abstract:
Despite being an everyday liquid, water is regarded as the most anomalous [1]: it expands upon cooling below 4 °C, or flows more easily when mildly pressurized. An hypothesis proposed 28 years ago [2] to explain these counter-intuitive behavior is still highly debated [1,3]. Water might exist in two liquid states, which would differ by the local arrangement of the molecules. However, the two liquids would separate only at very low temperature, and thus, up to now, experiments were not able to detect this transition, despite record-low temperatures reached with liquid water (-43°C [4,5]).

In order to decide between the available theoretical scenarios, we investigate metastable liquid water, in the frame of the French-German project *H2D2OX*. The proposed doctoral work focuses on water at negative pressure, generated by cooling water at constant volume. The samples are a few µm droplets trapped into a quartz crystal, synthesized by the group of Max Wilke in Potsdam. We measure

the sound velocity in the liquid with Brillouin spectroscopy, from which we reconstruct the equation of state. We have reached -140 MPa in water, and discovered a new anomaly [6]: a maximum in isothermal compressibility along isobars. This anomaly is a necessary condition for the validity of two scenarios for water. These two theories also predict that the famous line of density maxima (at 4 °C at ambient pressure) should reach a turning point at P<0 (maximum temperature). In our experiment, we see the line becoming more vertical but, unfortunately, we could not reach the putative turning point with light water because of unavoidable nucleation of the vapor (cavitation).

Our project is to repeat the same study on heavy water. Because water and heavy water have nearly equal surface tensions, we expect cavitation to occur at similar pressures. In contrast, extrapolations from the equation of state at positive pressure suggest that the turning point of the line of density maxima occurs at less negative pressure. The long-sought turning point might thus become observable in our experiment. Raman and X-ray spectroscopy will also be used to investigate the vibrational and structural features of water at negative pressure.



Experimental setup and examples of inclusions studied (scale bar = 7 µm)

Keywords: water, negative pressure, metastability, thermodynamics, spectroscopy.

Expected duration of the thesis: 36 months

References:
[1] Gallo *et al.*, *Chem. Rev.* **116** 7463 (2016)
[2] Poole *et al.*, *Nature* **360** 324 (1992)
[3] Debenedetti et al., *Science* **369**, 289–292 (2020)
[4] Sellberg *et al.*, *Nature* **510** 381 (2014).
[5] Goy *et al.*, *Phys. Rev. Lett.* **120** 015501 (2018).
[6] Holten *et al.*, *J. Phys. Chem. Lett.* **8** 5519 (2017).