# Bubble nucleation in liquids confined in nanopores.

Joel Puibasset*[1]

[1]Interfaces, Confinement, Matériaux et Nanostructures – Centre National de la Recherche Scientifique : UMR7374, Centre National de la Recherche Scientifique – France

## Résumé

1 Introduction

The extreme confinement of fluids in nanopores strongly affects their properties, which has measurable consequences even at the micrometre scale. One can cite the effect of surface chemistry or corrugation, local curvature, pore morphology, or any other nanometre-scale property of the surface. Molecular simulation is a powerful route to address such issues since it takes into account the relevant fluid/fluid and fluid/substrate interactions at the atomic scale. The present study focuses on cavitation in bulk and confinement.

2 Discussion

An interesting issue is the out-of-equilibrium pore emptying, in particular in the case of the so-called inkbottle pores that are connected to the outside only through narrow channels. Focusing on the molecular simulation of fluids confined in chemically disordered pores, we will show how the heterogeneities induce the appearance of metastable states, and how these states can be used to study cavitation in inkbottle pores. The simulations are compared to the classical nucleation theory, through the direct evaluation of the nucleation rate and the barrier height. The results are relevant to experiments showing that in such pores desorption proceeds via liquid fracture (cavitation).

A second interesting feature concerns the bubble size distribution. From a statistical point of view, the bubble nucleation barrier W(s) is related to the equilibrium bubble size distribution p(s) through the Boltzmann factor p(s)_˜EXP(-W(s)/kT). In principle, p(s) is measurable in equilibrium molecular simulations. However, we will show that, in practice, the quantity that can be obtained from simulations is the distribution of the *largest* nucleus pL(s) and not of *all* nuclei p(s). We will show how few mathematics help to rigorously transform pL(s) into p(s). This opens new routes to the calculation of nucleation barriers in realistic thermodynamic conditions.

Figure 1: bubble size distributions: black symbols: pL(s) as given by biased simulations; blue symbols: the expected p(s); red line: mathematic transformation of pL(s) into p(s).

References

(1) Puibasset, J., Adsorption/Desorption Hysteresis of Simple Fluids Confined in Realistic Heterogeneous Silica Mesopores of Micrometric Length: A New Analysis Exploiting a Multiscale Monte Carlo Approach, *J. Chem. Phys.* 127, 154701 (2007).

---

*Intervenant

(2) Puibasset, J., Adsorption-Induced Deformation of a Nanoporous Material: Influence of the Fluid–Adsorbent Interaction and Surface Freezing on the Pore-Load Modulus Measurement, *J. Phys. Chem. C* 121, 18779-18788 (2017).

(3) Puibasset, J., Cavitation in Heterogeneous Nanopores: The Chemical Ink-Bottle, *AIP Adv.* 11, 095311 (2021).

(4) Puibasset, J., A General Relation between the Largest Nucleus and All Nuclei Distributions for Free Energy Calculations, *J. Chem. Phys.* 157, 191102 (2022).

(5) Puibasset, J., Are nucleation bubbles in a liquid all independent?, *J. Mol. Liq.* accepted (2023).