PhD GRANT

ÉCOLE DOCTORALE SCIENCES EXACTES ET LEURS APPLICATIONS - ED 211 / NATURAL SCIENCES DOCTORAL SCHOOL

Avenue de l'université BP 1155 64 013 PAU Cedex – France

PhD SUBJECT

TITLE: Crystallization of water in nanoporous materials and its induced impact on the solid matrix

ABSTRACT:

Confinement of water in nanopores affects its freezing temperature, the crystal structure, the glass transition temperature. When crystallization occurs in a nanopore, the interactions between the crystal and the solid skeleton are complex. They have led to the concept of "crystallization pressure" whose exact form has been rather controversial (e.g. over simplified) in the literature. One reason is that the crystal to solid skeleton interaction should be mediated by the presence of a thin fluid film (a few nanometer thick) located in between them. The accurate kinetics and thermodynamic description of this three components system remain to be elucidated. The aim of the thesis is to generalize a SAFT-DFT formalism to study the crystallization of water due to confinement, to describe the liquid-like water film occurring between crystals and surfaces during confined crystallization, and to compute the involved crystallization pressures. The crystal growth and the influence of the different parameters (pore size, functionalization of the surface…) on nucleation and crystal growth will be also investigated.

Keywords :

Water. Porous materials. Crystallization. Density Functional Theory. Statistical Thermodynamics.

WORKING CONDITIONS

Laboratory : Laboratory of Complex Fluids and their Reservoirs (LFCR), UMR 5150
Site web : https://lfc.univ-pau.fr/

PhD Director: Christelle Miqueu (Associate professor HDR, LFCR, UPPA)
PhD co-Director: David Grégoire (Full professor, LFCR, UPPA)

Principal location : LFCR, Geomechanics and Porous Media team, Anglet, FRANCE

Start : 01/10/2020	**Duration:** 3 years

Employer: Université de Pau et des Pays de l'Adour (UPPA)

Monthly salary before taxes : 1907€ (encompassing 32h teaching activities/years)

HOST LABORATORY PROFILE

The LFCR is a joint research unit attached to the UPPA, the CNRS and TOTAL. LFR is a research unit which research goes from the nanometer to hundreds of kilometers, from the nanosecond to a million years, from the physics and chemistry of interfaces, through the thermodynamics of fluids under flow, to reservoir geology, geomechanics and geophysics. The G2MP (Geomechanics / Porous media) group focuses on the mechanical behavior of porous media, fluid-solid couplings and the general transport properties in these media. The group develops both experimental characterization and modeling activities using digital simulation tools at different scales. Its current activities focus essentially on: (1) understanding fluid behavior in microporous networks, (2) poro-mechanical modeling of micro- and meso-porous media and the transition from the nano-scale to continuum mechanics, (3) understanding relations and couplings between permeability and damage, (4) storage and separations of gases by adsorption.

NewPores research project presentation

NewPores is an international hub dedicated to the mechanics and physics of porous materials, which intends to answer to new Energy and Environment challenges. This is a joint effort of the group on Geomechanics and Porous Materials (G2MP) of the Laboratoire des Fluides Complexes et leurs Réservoirs at E2S UPPA (France), the Centre for Sustainable Engineering of Geological and Infrastructure Materials (SEGIM) at Northwestern University (USA), the University of Vigo (Spain), the Technical University of Madrid (Spain) and University of Liège (Belgium).

MISSION – PRINCIPAL ACTIVITIES

I. Scientific context

Water confined in nanoporous materials has focused many attentions due to its vast number of technical applications and scientific fields such as geosciences, biology, nanotribology… (Zangi, 2004; Giovambattista, 2012). Confinement of a fluid at the nanoscale can lead to changes in both its structural and dynamical properties caused by the high interactions between the fluid and the surfaces. Hence, confinement of water in nanopores affects its freezing temperature, the crystal structure, the glass transition temperature… (Zangi, 2004). Whenever phase changes are expected, *e.g.* precipitation of salt in the fluid phase, a complex crystal-solid skeleton interaction occurs. This interaction leads authors to the concept of "crystallization pressure" (Scherer, 2004) whose exact form has been rather controversial (e.g. over simplified) in the literature. One reason is that the crystal to solid skeleton interaction should be mediated by the presence of a thin fluid film (a few nanometer thick) located in between them. The accurate kinetics and thermodynamic description of this three components system remain to be elucidated.

II. Objectives, working environment and work plan

Classical Density DFT has been widely recognized as one of the most efficient methods for theoretical study of both confined fluids and freezing/melting transitions in simple fluids as well as in colloidal dispersions (Neuhaus et al. 2014). In particular, important progress was made when the Fundamental Measure Theory (FMT) was proposed and used in the DFT frameworks as FMT is naturally suitable for fluids and solids (Rosenfeld, 1989). DFT is able to describe freezing/melting transitions within a unified theoretical framework, unlike classical equation-of-state approaches that use different models for coexisting phases. The key point is that DFT directly expresses the thermodynamic potential of the system -whatever the phase- in terms only of the one-body density profiles. Originally and in many works, the anisotropic solid density field is approached by as a sum of Gaussians centered at the fixed lattice sites of a given Bravais lattice but in recent works, unconstrained crystallization has also been obtained (Archer and Malijevsky 2016, Lutsko and Lam 2018). However, it should be noted that none of these works deals with the crystallization of water, whether in a homogeneous phase, on a heterogeneous surface or confined in a porous medium. The principal reason of this should be that the application of DFT to water requires to combine the DFT framework to a powerful thermodynamic model for water instead of using simple classical interaction potentials (such as hard-sphere, Lennard-Jones…). It has been done recently to study the behavior of water confined in slit pores with a coupled DFT-SAFT approach (Malheiro *et al.* 2014, Miqueu and Grégoire 2020).

The aim here is to generalize a SAFT-DFT formalism to study the crystallization of water due to confinement. First, a static DFT formalism will be developed. It will be used in particular to describe the liquid-like water film occurring between crystals and surfaces during confined crystallization, and to compute the involved crystallization pressures. The impact on the solid skeletons will be analyzed. In a second time, a dynamic DFT formalism, inspired from the works of Neuhaus and co-workers, will be developed to study the crystal growth and to assess the influence of the different parameters (pore size, functionalization of the surface…) on nucleation and crystal growth.

References

- Archer, A. J. and Malijevský, A. (2016) Crystallization of soft matter under confinement at interfaces and in wedges, *Journal of Physics: Condensed Matter*. IOP Publishing, 28(24), 244017.
- Giovambattista, N., Rossky, P. J. and Debenedetti, P. G. (2012) Computational Studies of Pressure, Temperature, and Surface Effects on the Structure and Thermodynamics of Confined Water, *Annual Review of Physical Chemistry*. Annual Reviews, 63(1), 179–200.
- Lutsko, J. F., & Lam, J. (2018). Classical density functional theory, unconstrained crystallization, and polymorphic behavior. *Physical Review E*, *98*(1), 012604.
- Malheiro, C. *et al.* (2014) 'Nonlocal Density Functional Theory and Grand Canonical Monte Carlo Molecular Simulations of Water Adsorption in Confined Media', *The Journal of Physical Chemistry C*. 118(43), pp. 24905–24914.
- Neuhaus, T., Härtel, A., Marechal, M., Schmiedeberg, M., & Löwen, H. (2014). Density functional theory of heterogeneous crystallization. *The European Physical Journal Special Topics*, *223*(3), 373-387.
- Rosenfeld, Y. (1989) Free-energy model for the inhomogeneous hard-sphere fluid mixture and density-functional theory of freezing, *Physical Review Letters*. 63(9), 980–983.
- Scherer, G. W. (2004). Stress from crystallization of salt. *Cement and concrete research*, *34*(9), 1613-1624.
- Zangi, R. (2004) Water confined to a slab geometry: a review of recent computer simulation studies, *Journal of Physics: Condensed Matter*, 16(45), S5371–S5388.
- Miqueu, C. and Grégoire, D. (2020). Estimation of pore pressure and phase transitions of water confined in nanopores with non-local density functional theory. *Molecular Physics*, https://doi.org/10.1080/00268976.2020.1742935 .

REQUIRED SKILLS

The candidate should hold a Master degree in Physics, Statistical Physics, Mechanics, Materials or a similar field. Previous experience with theoretical developments, porous materials or thermodynamic modeling at molecular scale is an asset. The candidate should have a strong interest in performing numerical work in a multi-disciplinary team. Proficiency in English is mandatory.

CRITERIA USED FOR THE CANDIDATE SELECTION

Selection process steps:
- Establishment of the selection committee.
- Evaluation of the applicants cv's.
- Interview with the selected candidates and ranking.

Criteria used in selection of the candidate:
- The candidate's motivation, scientific maturity and curiosity.
- Candidate's knowledge in physics, mechanics, thermodynamics, chemical engineering.
- Candidate's marks and rankings in M1 and M2.
- French proficiency for teaching in Bachelor's degree

APPLICATION FORM

Send an e-mail containing:
- a CV
- a cover letter detailing candidate's motivations
- candidate's MSc marks and ranking
- any letters of recommendation
- contact details for 2 possible academic or industrial referees

Dead-line for application :	**16/07/2020**

CONTACTS AND APPLICATIONS

e-mail : christelle.miqueu@univ-pau.fr