Contribution ID: **228** Type: **Oral Presentation**

A novel DFT for associating fluids confined in nanopores and its application to water

Wednesday, 21 May 2025 12:50 (15 minutes)

A new free-energy functional is first proposed for inhomogeneous associating fluids. The general formulation of Wertheim's thermodynamic perturbation theory is considered as the starting point of the derivation. We apply the hypotheses of the statistical associating fluid theory (SAFT) in the classical density functional theory (DFT) framework to obtain a tractable expression of the free-energy functional for inhomogeneous associating fluids. Specific weighted functions are introduced in our framework to describe association interactions for a fluid under confinement. These weighted functions have a mathematical structure similar to the weighted densities of the fundamental-measure theory (i.e. they can be expressed as convolution products) such that they can be efficiently evaluated with Fourier transforms in a 3D space. The resulting free-energy functional can be employed to determine the microscopic structure of inhomogeneous associating fluids in arbitrary 3D geometry.

The new model is first compared with Monte Carlo simulations and previous DFT versions for a associating hard-sphere fluid against a planar hard wall in order to check its consistency in a 1D case. As an example of application in a 3D configuration, we then investigate the extreme confinement of an associating hard-sphere fluid inside an anisotropic open cavity with a shape that mimics a simplified model of zeolite. Both the density distribution and the corresponding molecular bonding profile are given, revealing complementary information to understand the structure of the associating fluid inside the cavity network. The impact of the degree of association on the preferential positions of the molecules inside the cavity is investigated as well as the competition between association and steric effect on adsorption.

Well-known for its ability to form oriented interactions that are hydrogen bonds, water belongs to the class of associative fluids. A SAFT-based DFT water model has been developed by using the new association functional as a perturbation of a Mie-monomer. We first employed the new model to investigate the behavior of water confined in slit-like nanopores made of graphitic surfaces for several configurations and thermodynamics conditions. The graphite - water - graphite system has already been studied with other SAFT-based DFT formulation such that it can be used to see the impact of the different SAFT-DFT frameworks on the density distributions and thermodynamics properties.

When crystallization occurs in a pore, the interactions between the crystal and the skeleton have led to the concept of "crystallization pressure". It has been supposed that the interaction should be mediated by the presence of a thin water fluid film located in between them. Hence, a ice - water - graphite system has then been studied with the new SAFT-based DFT formulation by considering the ice crystal as an external potential applied to the inhomogeneous water film. In this way, we could obtain the equilibrium distribution of water molecules confined into a slit-like nanopore consisting of an ice crystal on one side and a graphitic surface on the other side (see figure 1). Several configurations and thermodynamics conditions have been explored and the pressure of this inhomogeneous film has been analyzed.

Country

France

Acceptance of the Terms & Conditions

Click here to agree

Student Awards

Water & Porous Media Focused Abstracts

This abstract is related to Water

References

Primary authors: BARTHES, Antoine (Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France); Prof. GRÉGOIRE, David (Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France); Dr MIQUEU, Christelle (Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France)

Presenter: BARTHES, Antoine (Universite de Pau et de Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet, France)

Session Classification: MS13

Track Classification: (MS13) Fluids in Nanoporous Media