A New Non-Local Classical DFT Formulation for Confined Mie Fluids

Thomas Bernet [C, S]
Department of Chemical Engineering, Imperial College London, London, United Kingdom, United Kingdom
t.bernet@imperial.ac.uk

We present a free free-energy functional to explicitly take into account pair correlations between molecules in inhomogeneous fluids. The framework of classical density functional theory (DFT) is used to describe variations in the density of molecules interacting with a Mie potential (a generalized Lennard-Jones potential). The version of the statistical associating fluid theory developed for the Mie potential (SAFT-VR Mie) is selected as a reference for the homogeneous bulk limit of the free energy of the DFT model. We make note of the importance of having an accurate representation of the free energy thus formulate: the theory is formulated following the Barker-Henderson high-temperature expansion to find an inhomogeneous equivalent of the SAFT-VR Mie free energy as a functional of the local density. In order to undertake adsorption studies, a non-local DFT version is considered, with specific weighted densities describing the neighborhood effects of molecules. The computation of these quantities is made possible in three-dimensional space, for any pore geometry, with repulsive or attractive walls. We showcase examples to assess the adequacy of the new functional, revealing a very good agreement with molecular simulations. The new DFT-SAFT model is well-adapted to describe realistic complex confined systems, extending the SAFT EoS to model the adsorption in confined media.

The example of a fluid confined in a cylindrical pore with continuous wall is considered to assess the effects of a wall curvature on the fluid-density distribution and adsorbed quantities. The approach also can be used to deal with explicit surfaces and roughness. The density profile of a fluid around a single fixed molecule is a specific example of this formulation, which can be used to reproduce the radial distribution function of a Mie fluid. This case is a reference test to show the validity of the approach with non-ideal walls.