Pressures inside a nano-porous medium. The case of a single-phase fluid

Olav Galteland, Dick Bedeaux, Bjørn Hafskjold, Signe Kjelstrup

PoreLab, Department of Chemistry,
Norwegian University of Science and Technology

We define the pressure of a porous medium in terms of the grand potential and compute its value in a nano-confined or nano-porous medium, meaning a medium where thermodynamic equations need be adjusted for smallness. On the nano-scale, the pressure depends in a crucial way on the size and shape of the pores. According to Hill [1], two pressures are needed to characterize this situation; the integral pressure and the differential pressure. Using Hill's formalism for a nano-porous medium, we derive an expression for the difference between the integral and the differential pressures in a spherical phase α of radius $\hat{p}^{\alpha}-p^{\alpha}=\gamma/R$. We recover the law of Young-Laplace for the differential pressure difference across the same curved surface. We discuss the definition of a representative volume element for the nano-porous medium and show that the smallest REV is a unit cell in the direction of the pore in the fcc lattice. We also show, for the first time, how the pressure profile through a nano-porous medium can be defined and computed away from equilibrium.

We test the viability and validity of the pressure expression in the nano-porous medium using molecular dynamics simulations by studying two idealized models for nano-porous media, a single spherical grain and a lattice of spherical grains.

1. Terrell L. Hill, "Thermodynamics of Small Systems," New York: Dover, 1964.
2. S. Kjelstrup, D. Bedeaux, A. Hansen, B. Hafskjold, and O. Galteland, "Non-isothermal transport of multi-phase fluids in porous media. The entropy production," Frontiers in Physics, vol. 6, no. November, pp. 1–14, 2018.
3. S. Kjelstrup, D. Bedeaux, A. Hansen, B. Hafskjold, and O. Galteland, "Non-isothermal transport of multi-phase fluids in porous media. Constitutive Equations," Frontiers in Physics, vol. 6, no. January, pp. 1–12, 2019.
4. O. Galteland, D. Bedeaux, B. Hafskjold, and S. Kjelstrup, "Pressures Inside a Nano-Porous Medium. The Case of a Single-Phase Fluid," Frontiers in Physics, vol. 7, no. April, pp. 1–10, 2019.