THE DISJOINING PRESSURE IN A DROPLET ON A SPHERICAL SOLID PARTICLE: DFT RESULTS

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The effects of internal inhomogeneity of a thin spherical liquid droplet formed on a wettable solid particle are manifested through the appearance of its disjoining pressure [1]. For a flat thin liquid film between a solid substrate and undersaturated vapor, the disjoining pressure is defined as the difference in the normal component of the pressure tensor in the film and the bulk pressure in the liquid phase at given chemical potentials and temperature. However, because the normal component of the pressure tensor in the liquid film with curved interfaces depends on the location inside the film, it is not completely clear how to define the disjoining pressure for such films. It is possible to use a thermodynamic route [1] and to take the disjoining pressure in spherical films to be the same as in flat films of the same thickness. A rigorous analysis of the mechanical equilibrium condition of a curved wetting liquid film on a solid substrate established a relationship [2] between the normal component of the pressure tensor inside the curved film in the vicinity of the solid substrate, the Laplace pressure of the film, and the difference in bulk pressures in the liquid and gas phases for given molecular chemical potentials. This relation can be considered as a mechanical route to find the disjoining pressure. However, it was still unclear how close to the solid core one should to choose the local value of the normal component of the pressure tensor and how the thermodynamic and mechanical routes for the disjoining pressure are consistent in reality.

We have shown here that the answer can be found with the help of the density functional theory (DFT) for a Lennard-Jones fluid with the Carnahan-Starling hard-sphere contribution. Using the square-gradient variant of the DFT at different values of the condensate chemical potential, we have found density profiles for thin spherical liquid films around the solid core and the density peak in the vicinity of the core, which exceeds the bulk value for the liquid density and weakly depends on the value of the condensate chemical potential. Our analysis of the profiles for density and normal and tangential pressure in the central part of the thin droplet on a solid core demonstrates overlapping of surface layers of solid-liquid and liquid-vapor interfaces. We have shown that the disjoining pressure for a flat thin liquid film on a solid substrate in the undersaturated vapor can be related to the disjoining pressure in small spherical droplets on completely wettable solid cores in supersaturated vapor found through the thermodynamic and mechanical routes. The disjoining pressure of the spherical liquid films depends on the internal and external radii of the film.

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