

Surface free energy of a hard-sphere fluid at curved walls: deviations from Morphometric Thermodynamics

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We report molecular dynamics simulation results [1] for the surface free energy of hard-sphere fluid at cylindrical and spherical hard walls of different radii. The precision of the results is much higher than that in our previous study [Phys. Rev. E **86**, 060602 (2012)], allowing us to estimate the size of deviations from the predictions of Morphometric Thermodynamics (MT). We compare our results to the analytical expressions for the surface energy as a function of wall radius R and fluid density derived from the White Bear II variant of the Density Functional Theory, as well as to the leading terms of the virial expansion. For the cylindrical wall, we observe deviations from MT proportional to R^{-2} and R^{-3} , which are consistent with the available virial expressions. For the spherical wall, while the precision is not sufficient to detect statistically significant deviations from MT, the MD results indicate the range of densities for which the truncated virial expansions are applicable.

[1] R. L. Davidchack and B. B. Laird, J. Chem. Phys. **149**, 174706 (2018); J. Chem. Phys. **150**, 069901 (2019).