

Appraising the Surface Thermodynamics of Nanoscopic Liquid Drops: From a Mechanical to a Quantum Description

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The focus of our study is an in-depth investigation of the mechanical and quantum features associated with the surface tension and thermodynamics of nanoscopic liquid drops. The behaviour of drops of quantum Lennard-Jones (LJ) fluids is investigated with classical Canonical Monte Carlo (MC-*NVT*) and with path-integral Monte Carlo (PIMC) simulations, and the test-area (TA) method is used to determine the surface tension of the spherical vapour-liquid interface. As the quantum nature of the system (characterized by the de Broglie thermal wavelength, λ_B) becomes more significant, the average density of the liquid drop decreases, with the drop becoming mechanically unstable at large wavelengths. As a consequence, the surface tension is found to decrease monotonically with λ_B , vanishing altogether for dominant quantum interactions. The surface tension is therefore wavelength-dependent and quantum effects can be significant leading to values which are notably lower than the classical thermodynamic limit, particularly for smaller drops. Marked quantum effects are therefore unmasked for the surface thermodynamics of nanoscopic liquid drops. A significant decrease in the liquid density and surface tension is found even for weak quantum interactions. Unsurprisingly quantum effects are large in the case of the macroscopic planar interface for values of λ_B corresponding to hydrogen or helium at the low temperatures of vapour-liquid coexistence. Large quantum effects are, however, also found for small drops of molecules with quantum interactions corresponding to water, ethane, and carbon dioxide even at ambient conditions. The resulting reduction in the free-energy barrier of a nucleating cluster (compared to that assumed in classical nucleation theory) has important implications for the description of the nucleation kinetics of liquid drops and of bubble formation. This implies that drops would form at a much greater rate than is predicted by the classical theory [1].

References

1. S. Contreras, C. Avendaño, A. Gil-Villegas, and G. Jackson, *J. Chem. Phys.*, 160 (2024). <https://doi.org/10.1063/5.0196501>