On the Tolman Length Puzzle: A Comparative Study of Interfacial and Bulk-Pressure Routes for Sign and Critical Scaling

Luis A. Pascual [a], Lamberto Díaz Damacillo [b], Leonardo Di G. Sigalotti [b], Gerardo Odriozola [b]

a) Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, 09340 CD México, Mexico
b) Área de Física de Procesos Irreversibles, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Azcapotzalco, Av. San Pablo 180, 09340, CD México, Mexico

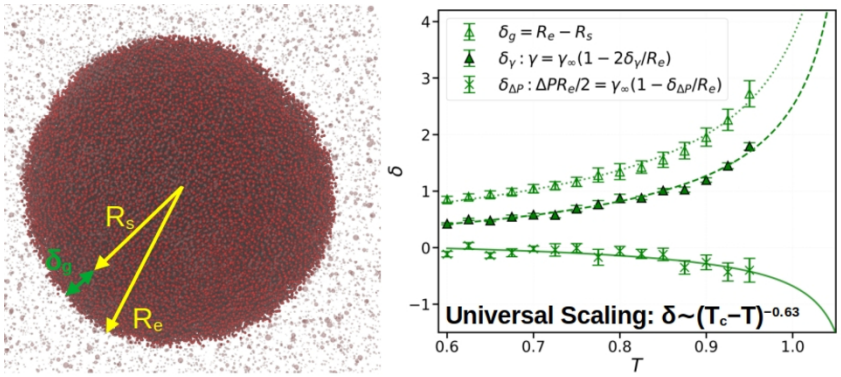
godriozo@azc.uam.mx

The Tolman length, δ, a fundamental parameter describing the curvature dependence of surface tension, remains contentious due to persistent discrepancies in its sign and magnitude. In this work, we systematically investigate these inconsistencies for a truncated and shifted Lennard-Jones fluid ($r_c = 2.5$) using molecular dynamics simulations. We evaluate δ through three distinct methodologies: the geometric difference, $\delta_g = R_e - R_s$, the surface tension expansion, δ_γ, and the bulk-pressure route, $\delta_{\Delta P}$. To address the non-uniqueness of the pressure tensor, we implement a discretized Irving-Kirkwood contour with K sampling points, finding that $K \geq 3$ is required for numerical consistency in interfacial-based routes.

Our results show that interfacial definitions (δ_g, δ_γ) are consistently positive, with δ_g being approximately twice as large as δ_γ across all studied conditions. In contrast, the bulk-pressure route yields a small negative Tolman length, $\delta_{\Delta P} \approx -0.03$ at $T = 0.8$. Both the δ_γ and $\delta_{\Delta P}$ frameworks exhibit a remarkable dual self-consistency: they quantitatively recover the planar surface tension $\gamma_\infty(T)$ for all K as curvature vanishes, while capturing the expected qualitative trends for critical point shifts and droplet vapor pressure via the modified Kelvin equation. This dual consistency helps explain the historical difficulty in reaching a consensus on the sign of δ.

We suggest that the bulk-pressure route is more robust, as it is independent of the discretization parameter K and avoids numerical integration across the anisotropic interfacial region. Finally, we found that all δ definitions exhibit temperature dependence consistent with the universal scaling $\delta \sim (T_c - T)^{-\nu}$, with the 3D Ising critical exponent $\nu = 0.63$.

Keywords:
Tolman length, Molecular dynamics simulation, Nanoscopic droplets, Surface tension, Pressure tensor, Lennard-Jones fluid



(Left) Simulated liquid droplet illustrating equimolar, Re, and surface of tension, Rs, radii. (Right) Tolman length, δ, from geometric, δg, surface tension expansion, δγ, and bulk-pressure, δΔP, routes vs. temperature (T), showing universal scaling near Tc.