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Diverging Tolman's length and asymmetric interfacial density profiles in near-critical fluids¹ MIKHAIL ANISIMOV, HEATHER ST. PIERRE, DEEPA SUBRAMANIAN, University of Maryland, College Park — The surface tension of a curved surface behaves differently than that of a planar surface; however, the curvature correction to the surface tension - known as Tolman's length - is commonly ignored in practice. We show that asymmetric fluid phase equilibria result in diverging Tolman's length at the critical point with the amplitude of the divergence depending on the degree of asymmetry in fluid phase coexistence. The divergence of Tolman's length originates from the diverging critical fluctuations and does not exist in mean-field theories. However, the amplitude of this divergence (“intrinsic asymmetry”) can be obtained from an appropriate mean-field model. The asymmetry in phase equilibria is especially pronounced in ionic fluids and polymer solutions. In particular, Tolman's length in polymer solutions may become as large as the thickness of the interface, thus playing a significant role in behavior of micro droplets and confined polymer fluids.

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