

A new route to evaluate the curvature dependence of the surface tension of vapour-liquid interfaces by molecular simulation

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The Tolman equation [1]

$$\frac{\gamma_0}{\gamma} = 1 + \frac{\delta}{\gamma} \Delta p + O(\Delta p^2), \quad (1)$$

expresses the surface tension γ of a nanodroplet in terms of the surface tension of the planar interface γ_0 , the pressure difference between the coexisting fluid phases Δp and the Tolman length δ , defined as the deviation between two characteristic radii

$$\delta = R_e - \frac{2\gamma}{\Delta p}, \quad (2)$$

the equimolar radius R_e and the Laplace radius $2\gamma / \Delta p$. At present, however, a striking disagreement prevails regarding the magnitude of the Tolman length and even its sign. In case of droplets, Tolman expected δ to be positive [1]. Nonetheless, more recent studies found δ to be negative [2] or equal to zero [3], while others claim that its sign is curvature dependent itself [4]. Thereby, only the mutual inconsistency of the employed assumptions and methods has been proven, while nothing quantitative is truly known about δ and the dependence of γ on the droplet radius. In the present work, the curvature dependence of the surface tension is related to the excess equimolar radius η , defined by

$$\eta = R_e - \frac{2\gamma_0}{\Delta p}, \quad (3)$$

i.e. by the deviation between the equimolar radius R_e of a droplet and its Laplace radius according to the capillarity approximation ($\gamma = \gamma_0$). In line with an interpretation of the Tolman approach in the planar limit, i.e. $\Delta p \rightarrow 0$, recently proposed by van Giessen and Blokhuis [2], Eqs. (1) to (3) imply that the Tolman length and the excess equimolar radius converge to values of equal magnitude and opposite sign

$$\lim_{R_e \rightarrow \infty} \eta = - \lim_{R_e \rightarrow \infty} \delta, \quad (4)$$

as the radius increases. The surface tension of nanodroplets can thus be discussed by following a new route that relies exclusively on calculations, e.g. by molecular simulation, of the density profile (yielding R_e) and the chemical potential (yielding Δp). This avoids the intricacies of computing γ by means of a pressure tensor or effective variations of the surface area, as required by other molecular simulation methods. Here, droplets of the truncated-shifted Lennard-Jones (TSLJ) fluid are considered using molecular dynamics (MD) simulation in the canonical ensemble, with equimolar radii ranging between 6 and 16 times the size parameter σ . From an analysis of these simulations, the deviation of the equimolar radius from capillarity (and, by consequence, the magnitude of the Tolman length) is found to be smaller than 0.5σ , cf. Fig. 1, which is consistent with data from previous work [5]. Other methodical approaches, which have led to contradicting claims in the past, are critically discussed.

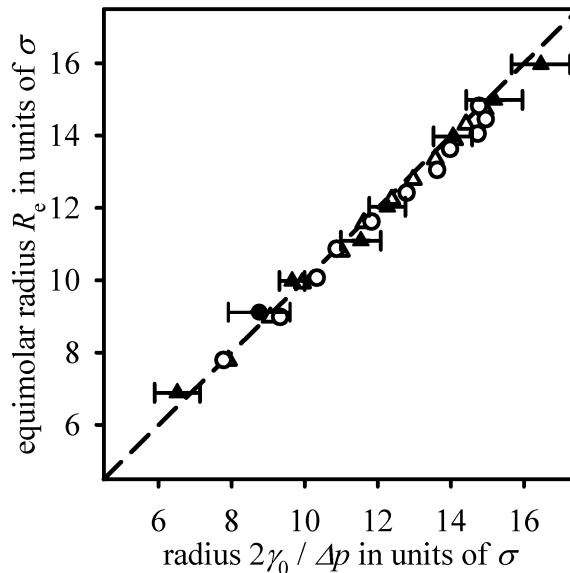


Figure 1. Parity plot of the equimolar radius R_e with respect to the radius expected from the capillarity approximation, from the present canonical MD simulations of the TSLJ fluid at the temperatures $T = 0.75$ (\blacktriangle) and $0.85 \varepsilon / k_B$ (\bullet), where ε is the energy parameter of the pair potential, in comparison with results of Vrabc *et al.* [5] at $T = 0.75$ (\triangle) and $0.85 \varepsilon / k_B$ (\circ). Deviations from the diagonal (—) correspond to η which in the planar limit evaluates to $-\delta$.

References.

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