The size dependence of the vapour-liquid interfacial tension

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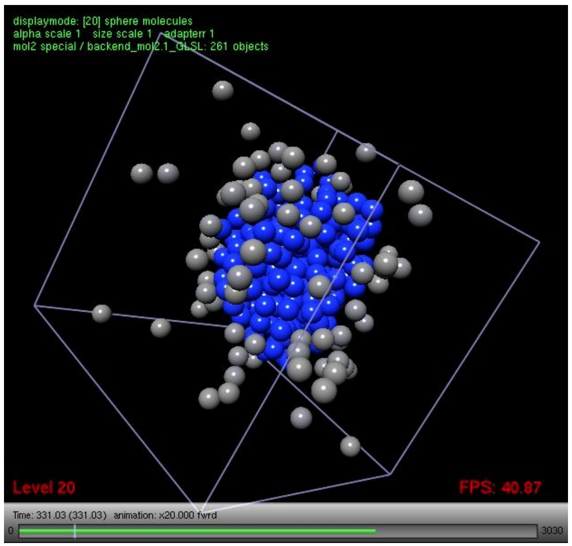
Computational
Molecular Engineering

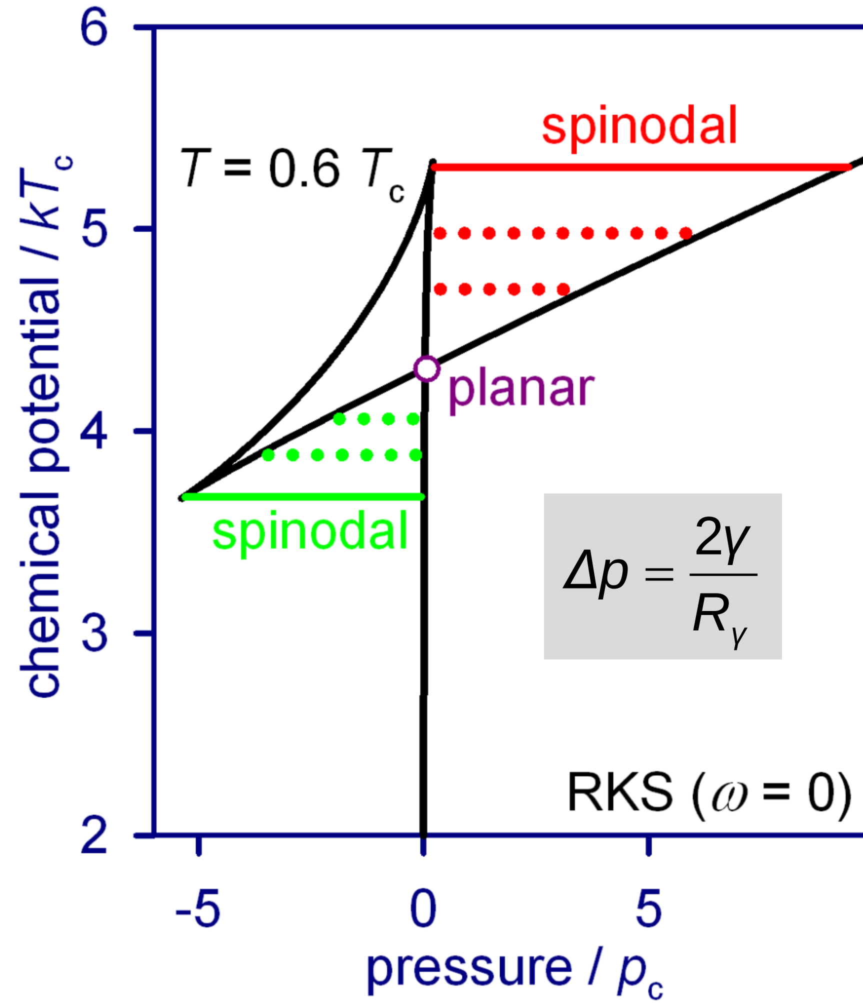
Curvature and fluid phase equilibria

- Droplet + metastable vapour
- Bubble + metastable liquid



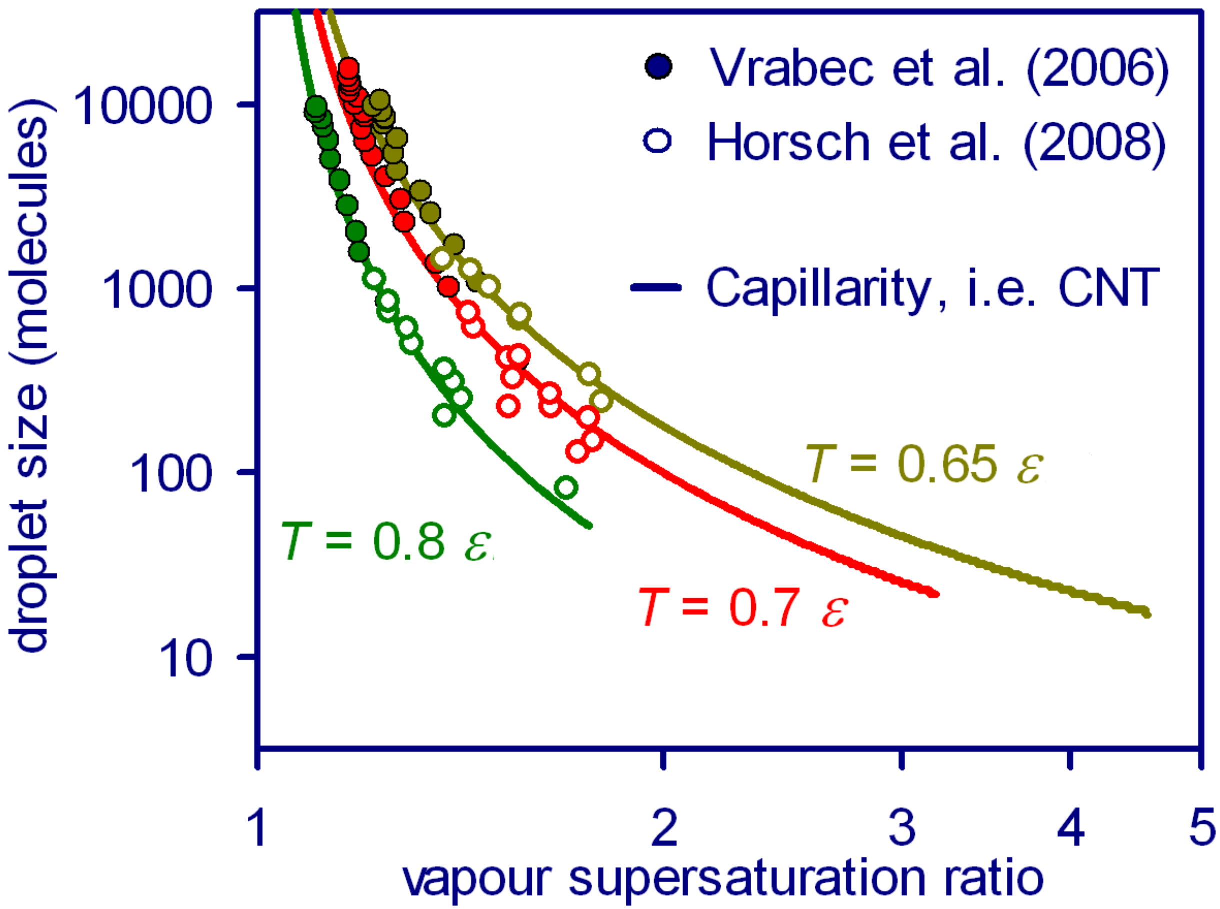
Spinodal limit: For the external phase, metastability breaks down.

Planar limit: The curvature changes its sign and the radius R_γ diverges.



Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets



Down to 100 molecules: Agreement with CNT ($\gamma = \gamma_0$).

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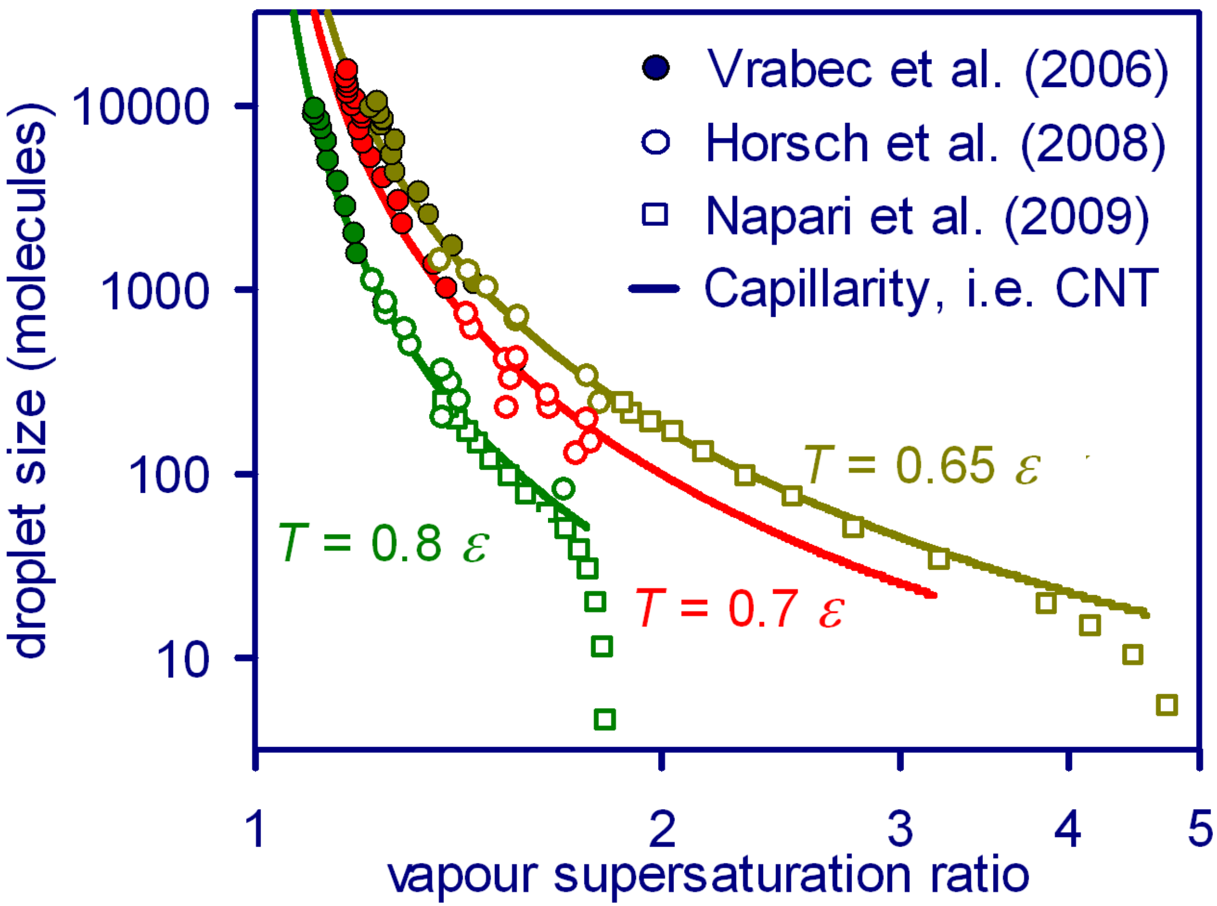


Down to 100 molecules: Agreement with CNT ($\gamma = \gamma_0$).

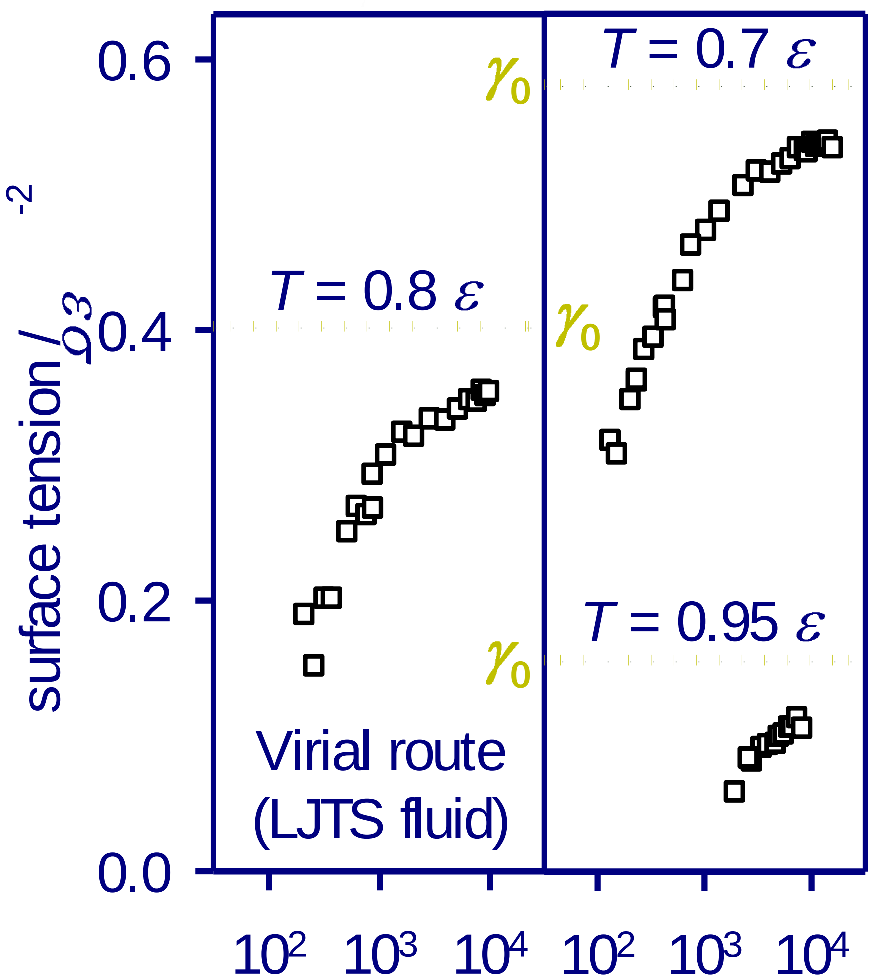
At the spinodal, the results suggest that $R_\gamma = 2\gamma / \Delta p \rightarrow 0$. This implies

$$\lim_{R_\gamma \to 0} \gamma = 0,$$

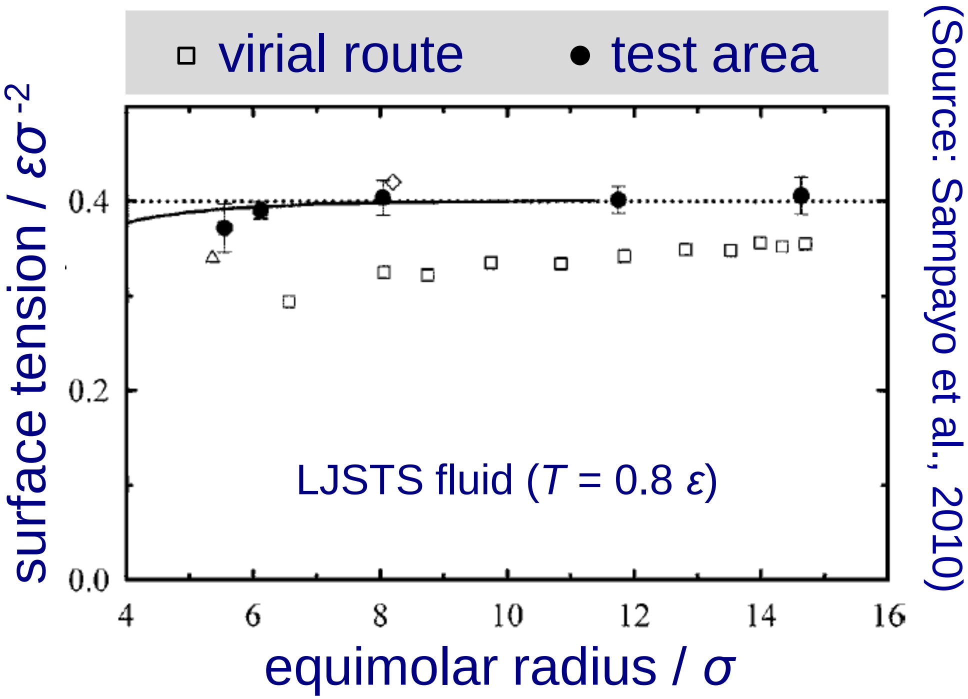
as conjectured by Tolman (1949) …

Surface tension from molecular simulation

Integral over the pressure tensor



Test area method:
Small deformations of the volume



Mutually contradicting simulation results!

Analysis of radial density profiles

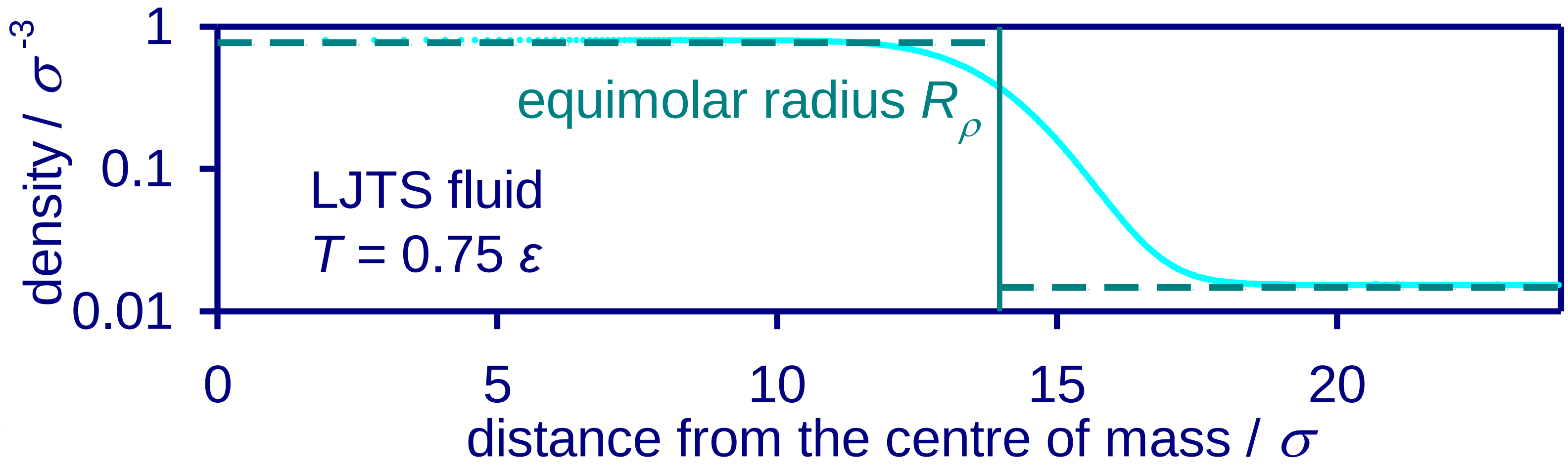
The thermodynamic approach of Tolman (1949) relies on effective radii:

- Equimolar radius R_ρ (obtained from the density profile) with

$$\Gamma = \int_0^{R_\rho} dR\, R^2 \left[\rho(R) - \rho'\right] + \int_{R_\rho}^{\infty} dR\, R^2 \left[\rho(R) - \rho''\right] = 0$$

- Laplace radius $R_\gamma = 2\gamma/\Delta p$ (defined in terms of the surface tension γ)

Since γ and R_γ are under dispute, this set of variables is inconvenient here.

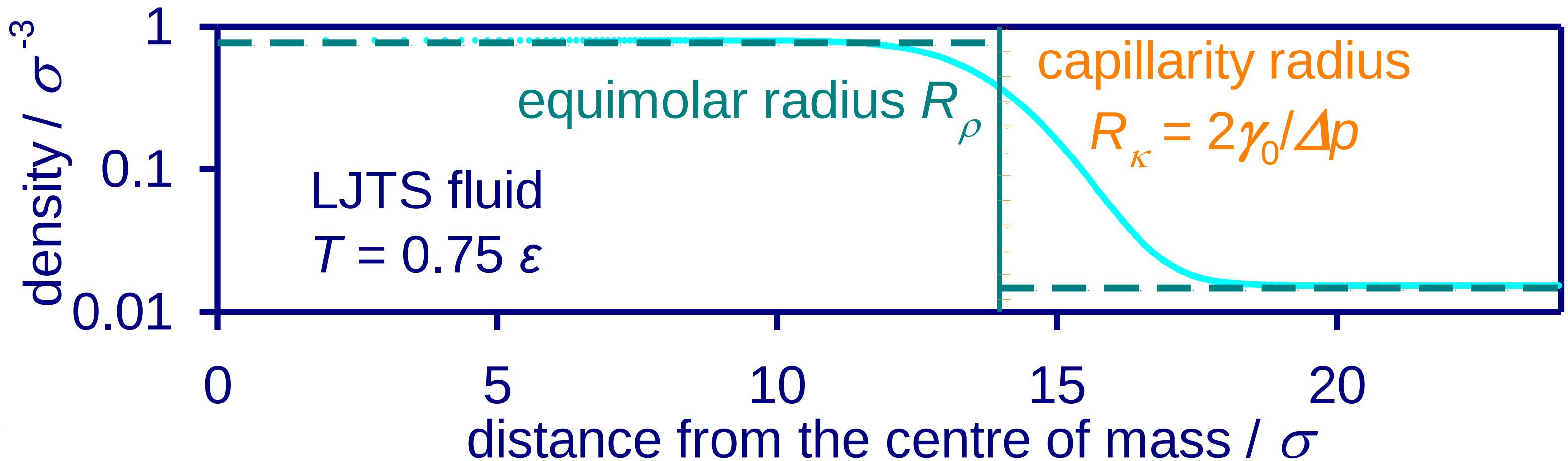


Analysis of radial density profiles

Various formal droplet radii can be considered within Tolman's approach:

- Equimolar radius R_ρ (obtained from the density profile)
- Capillarity radius $R_\kappa = 2\gamma_\infty/\Delta p$ (defined by the planar surface tension γ_∞)
- Laplaceradius $R_\gamma = 2\gamma/\Delta p$ (defined by the curved surface tension γ)

The capillarity radius can be obtained reliably from molecular simulation.



Approach: Use $\gamma/R_\gamma = \Delta p/2$ instead of $1/R_\gamma$, use $R_\kappa = 2\gamma_0/\Delta p$ instead of R_γ.

The Tolman equation

Tolman theory in R_ρ, R_γ, and $1/R_\gamma$

Tolman length:

$$\delta = R_\rho - R_\gamma$$

Tolman equation:

$$\left(\frac{\partial \ln R_\gamma}{\partial \ln \gamma}\right)_T = 1 + \left(\frac{2\delta}{R_\gamma} + \frac{2\delta^2}{R_\gamma^2} + \frac{2\delta^3}{3R_\gamma^3}\right)^{-1}$$

First-order expansion:

$$\gamma = \gamma_0 - 2\delta_0\gamma_0 \frac{1}{R_\gamma} + O\left(\frac{1}{R_\gamma^2}\right)$$

The Tolman equation in terms of R_κ

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Tolman theory in R_ρ, R_κ, and γ/R_γ

Excess equimolar radius:

$$\eta = R_\rho - R_\kappa$$

Tolman equation:

$$\left(\frac{\partial \ln \gamma R_\gamma^{-1}}{\partial \ln \gamma}\right)_T = \frac{3}{2}\left(1 - \left[\frac{\eta\,\gamma R_\gamma^{-1} + \gamma_0}{\gamma}\right]^3\right)^{-1}$$

First-order expansion:

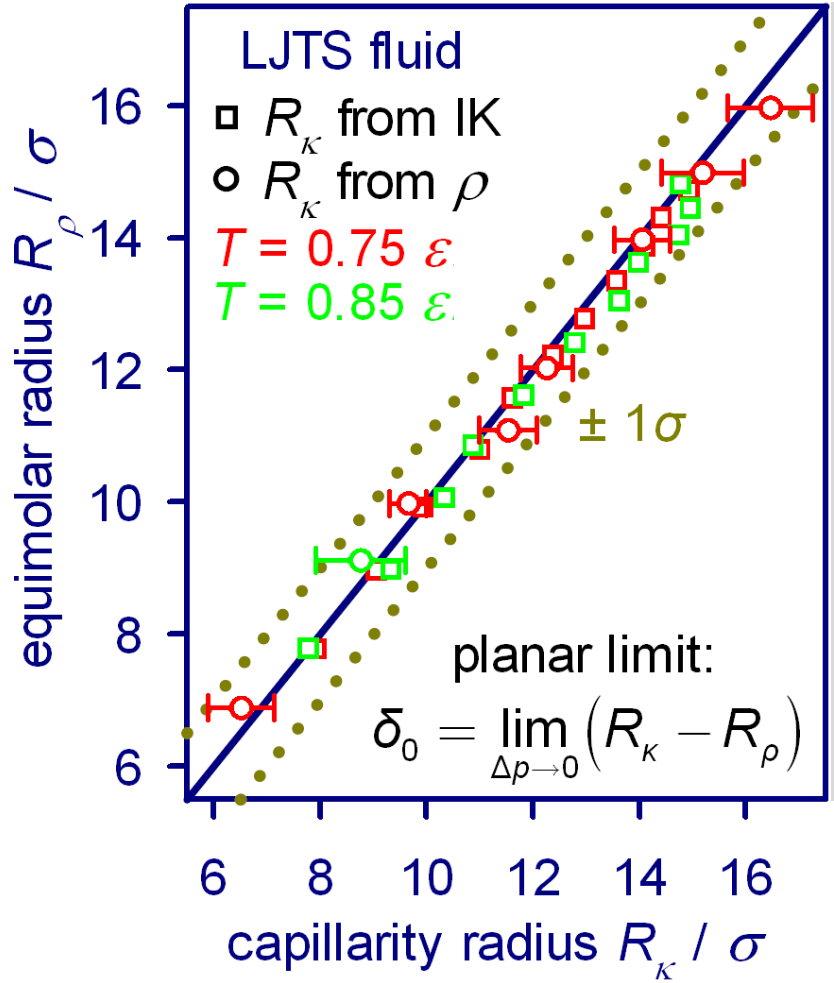
$$\gamma = \gamma_0 + 2\eta_0 \frac{\gamma}{R_\gamma} + O\left(\frac{\gamma^2}{R_\gamma^2}\right)$$

How do these notations relate to each other?

$$\eta_0 = \lim_{\Delta p \to 0}\left(R_\rho - \frac{\gamma_0}{\gamma R_\gamma^{-1}}\right) = -\lim_{\Delta p \to 0}\left(R_\rho - \frac{\gamma}{\gamma R_\gamma^{-1}}\right) = -\delta_0$$

Extrapolation to the planar limit

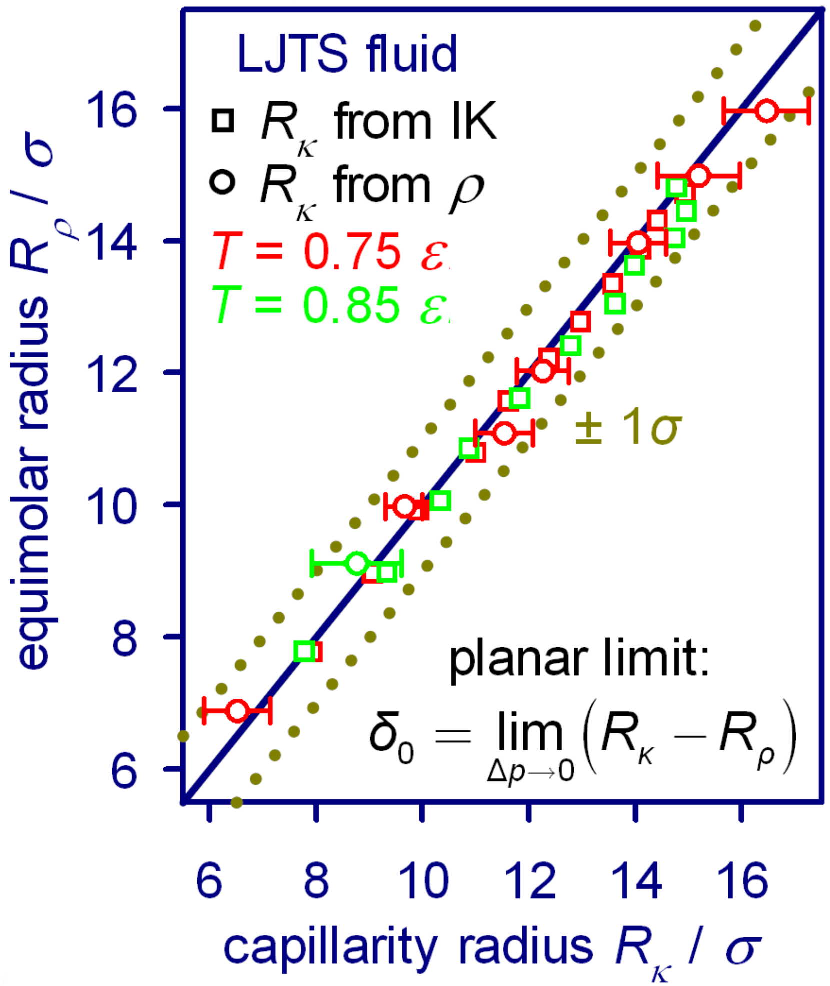
Radial parity plot



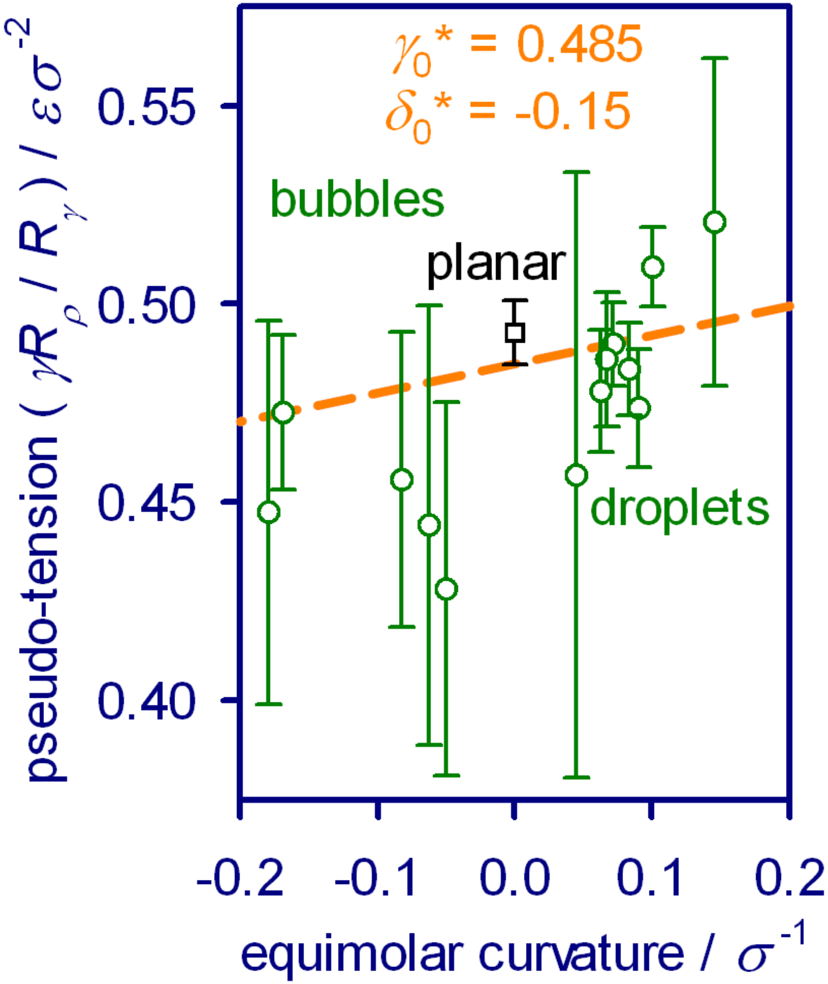
- The magnitude of the excess equimolar radius is consistently found to be smaller than σ / 2.
- This suggests that the curvature dependence of γ is weak, i.e. that the deviation from γ_∞ is smaller than 10 % for radii larger than 10 σ.
- This contradicts the results from the virial route and confirms the grand canonical and test area simulations.

Interpolation to the planar limit

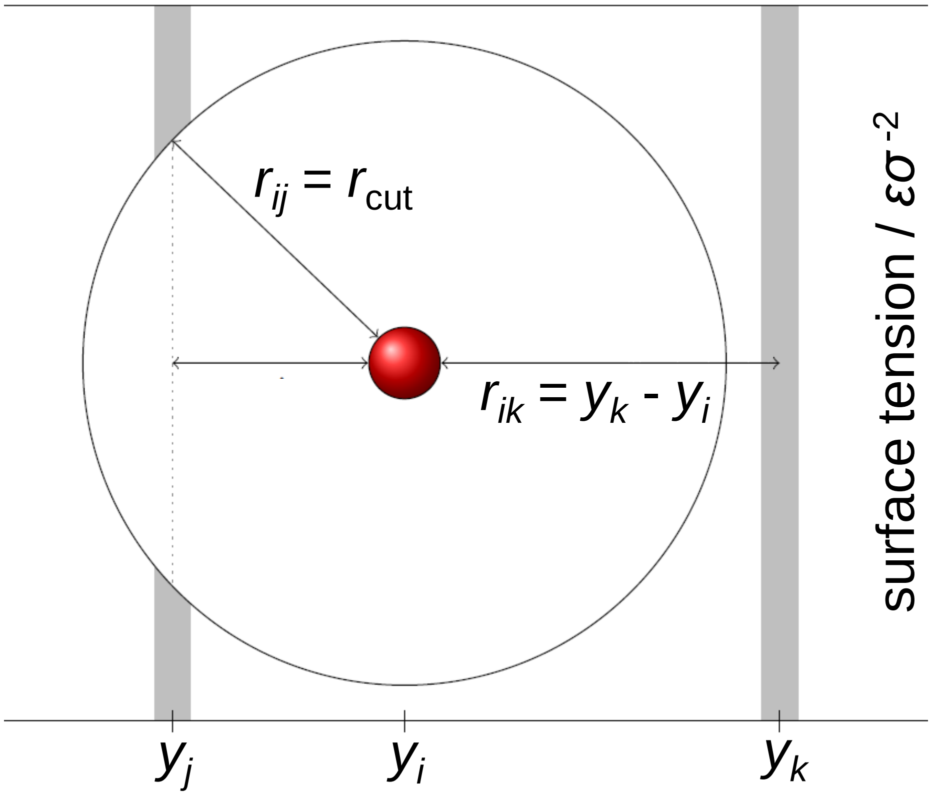
Radial parity plot



Nijmeijer diagram

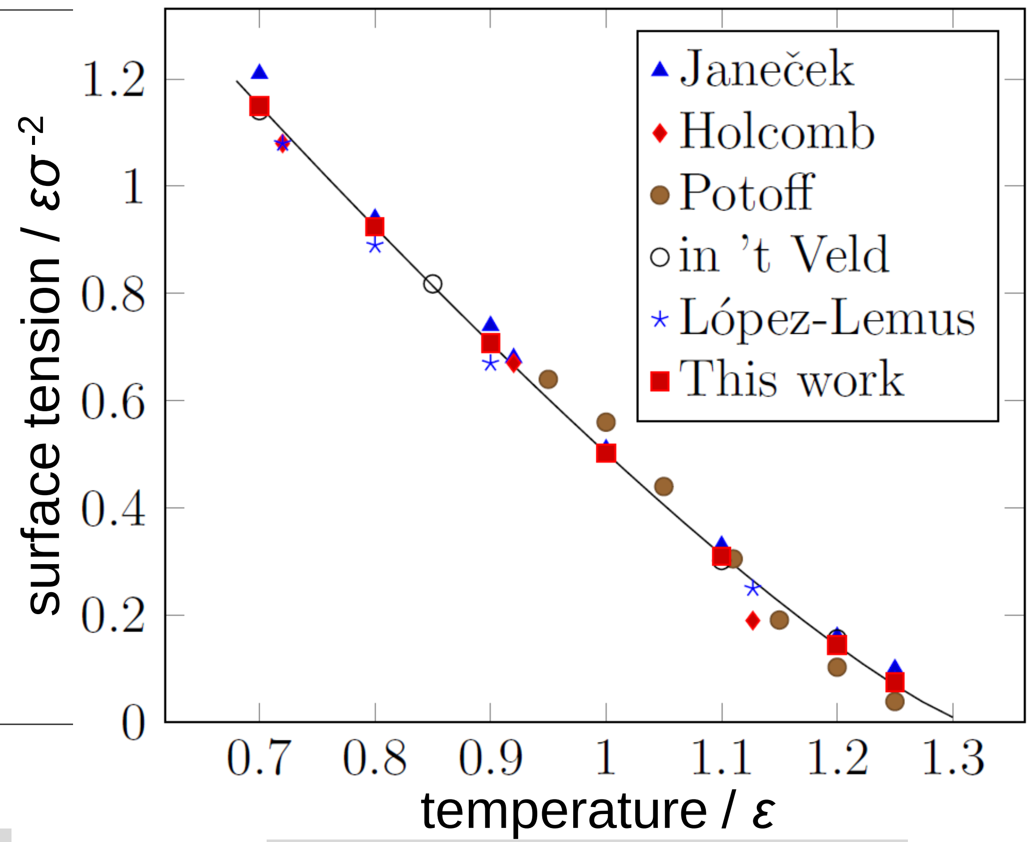


Simulation of planar vapour-liquid interfaces



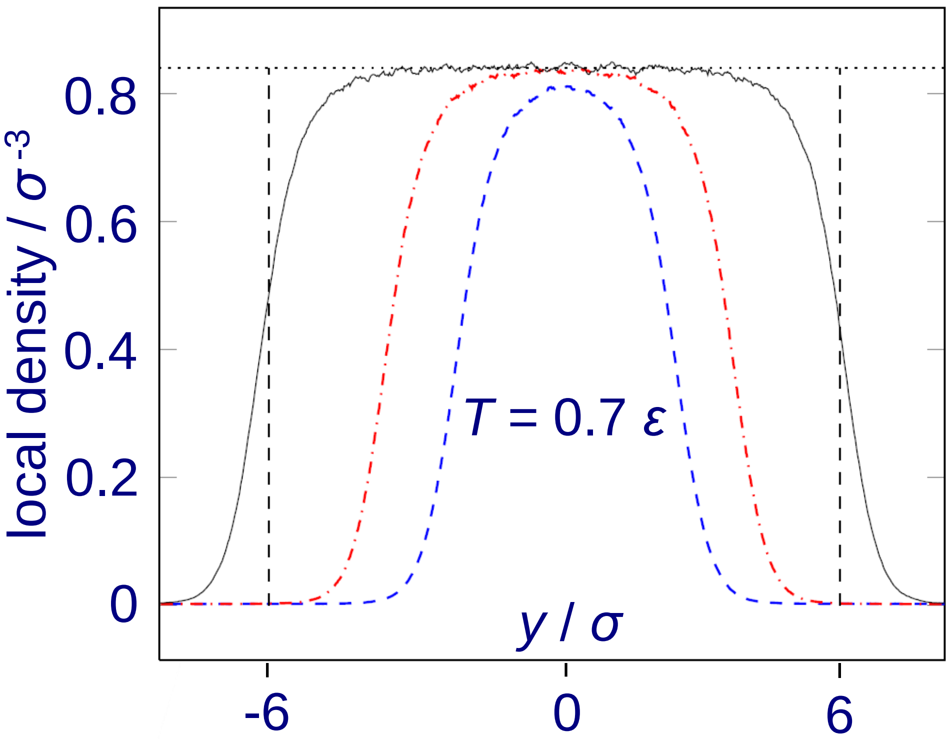
$$u_{ij}^{LRC}(r_{ij}) = 2\pi\Delta y\left(\frac{2}{5r_{ij}^{10}} - \frac{1}{r_{ij}^{4}}\right)\rho(y_k)$$

Lennard-Jones fluid

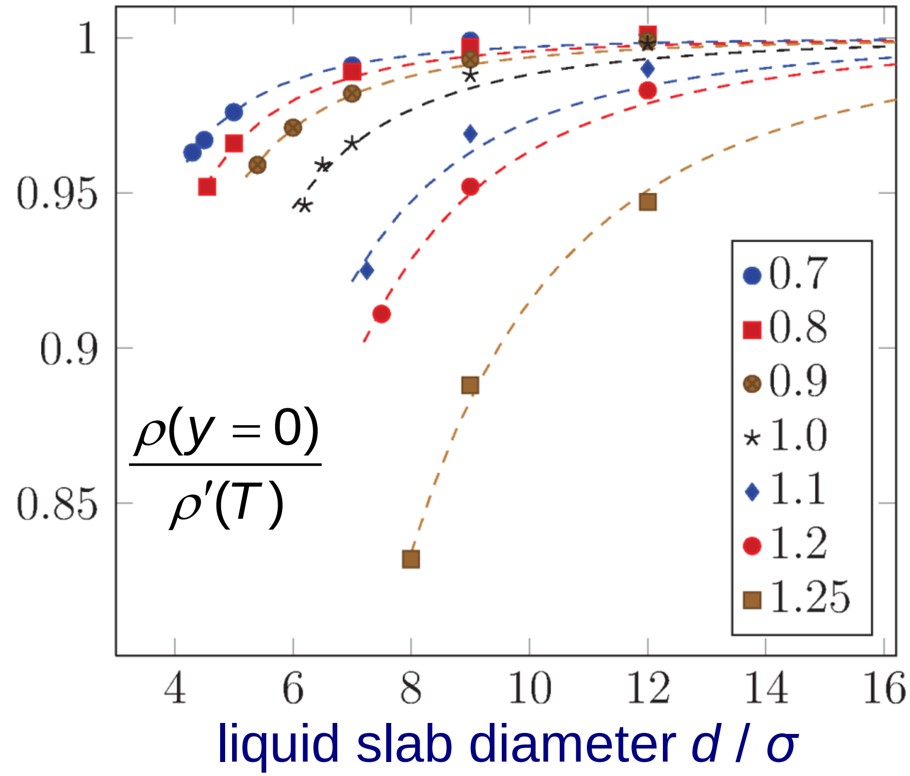


$$\gamma_0(T) = 2.94\frac{\varepsilon}{\sigma^2}\left(1 - \frac{T}{T_c}\right)^{1.23}$$

Size dependence of liquid slab properties

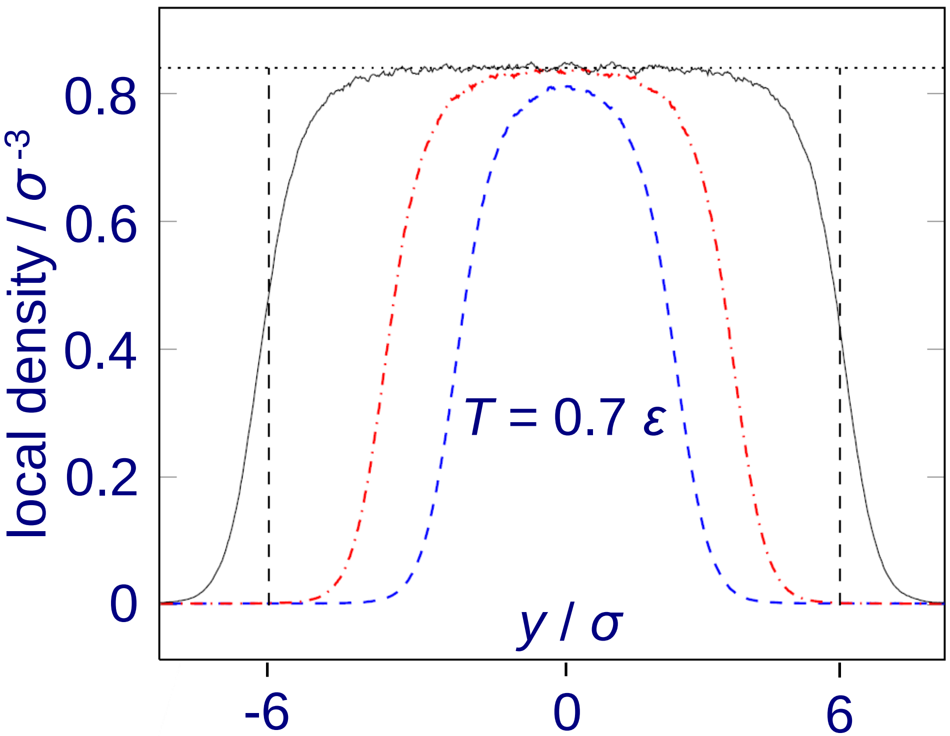


By simulating small liquid slabs, curvature-independent size effects can be considered.



As expected, the density in the centre of nanoscopic liquid slabs deviates significantly from that of the bulk liquid at saturation.

Size dependence of liquid slab properties



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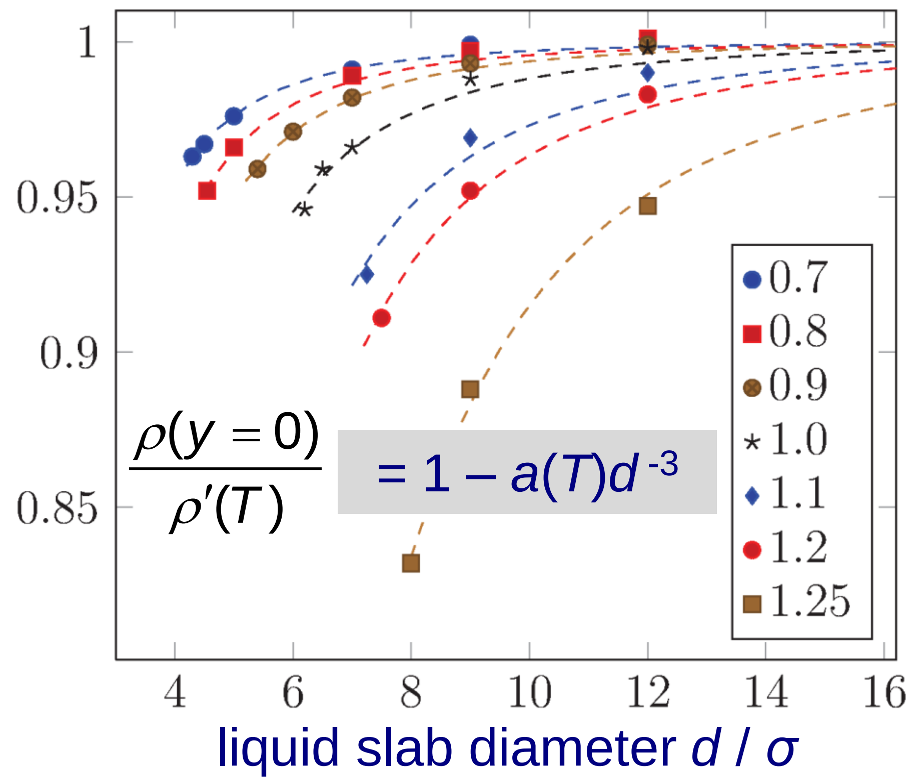
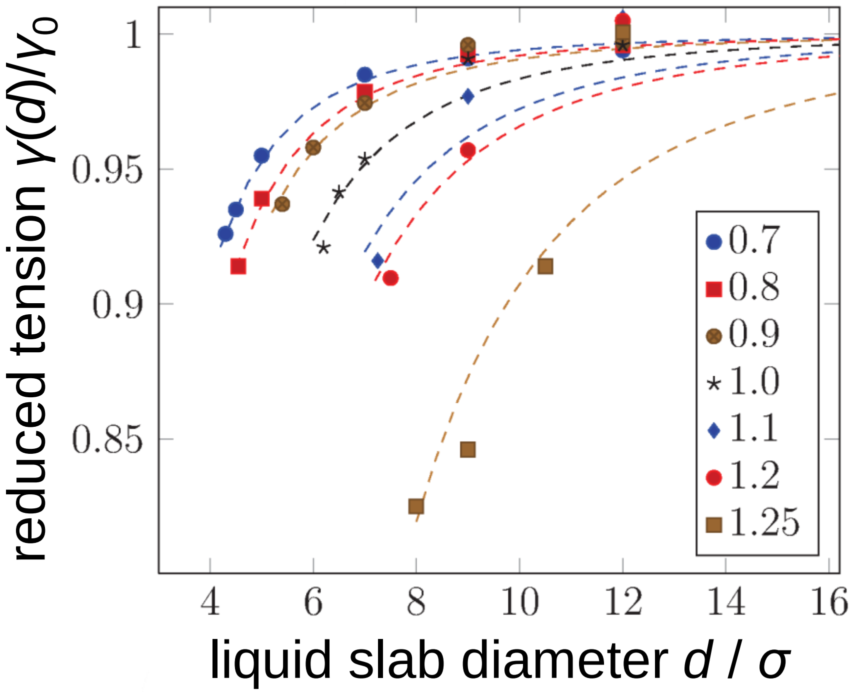


$$\frac{\rho(y=0)}{\rho'(T)} = 1 - a(T)d^{-3}$$

Curvature-independent size effect on γ

Surface tension for thin slabs:

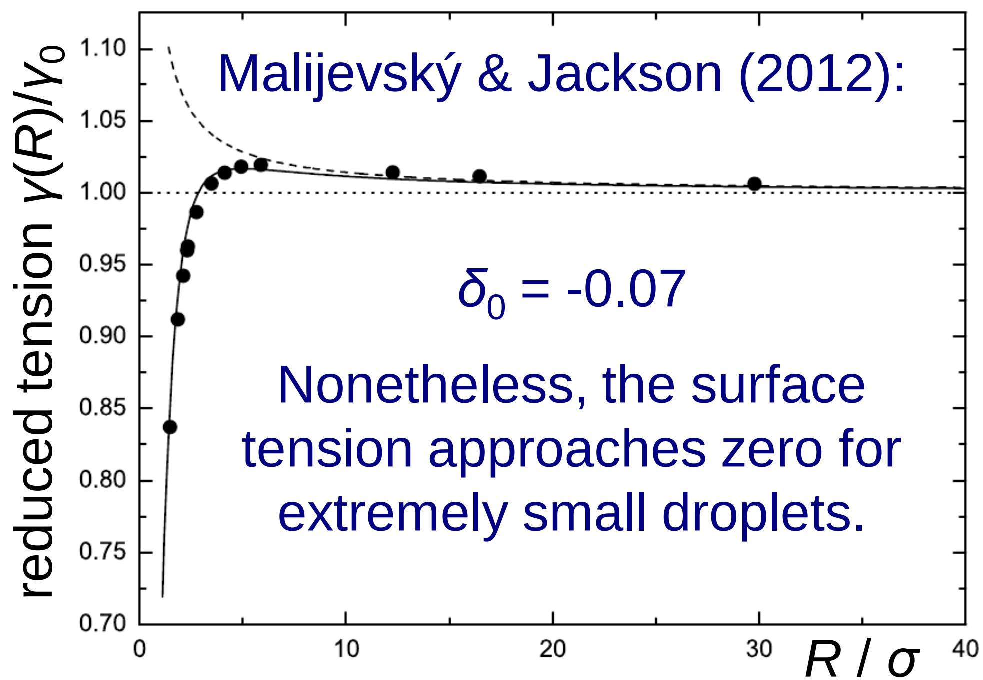


Relation with $\gamma(R)$ for droplets?

δ_0 is small and probably negative:

Ghoufi, Malfreyt (2011): δ_0 = -0.3 or -0.008

Tröster *et al.* (2012): $-0.27 < \delta_0 < +0.19$



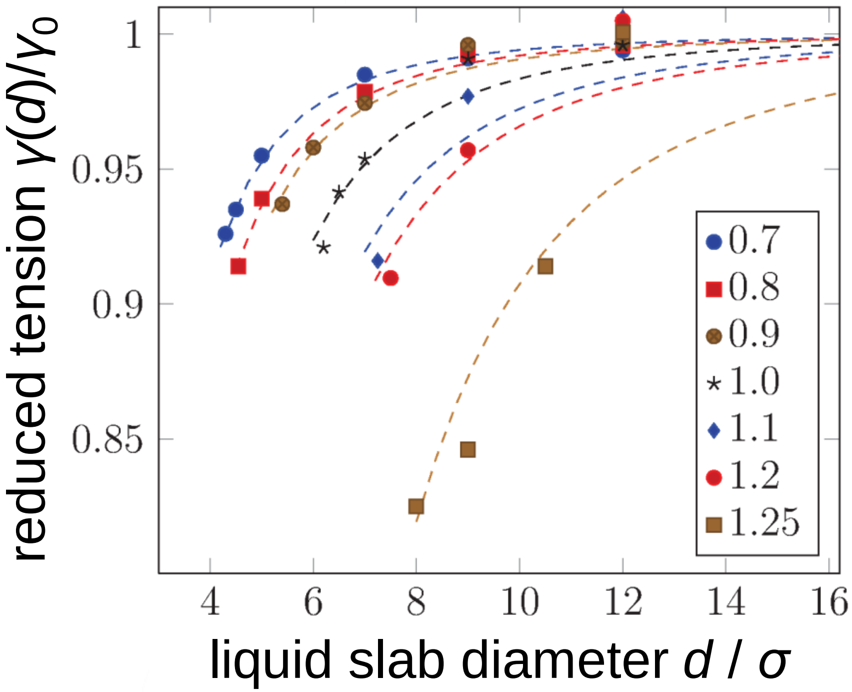
Malijevský & Jackson (2012):

δ_0 = -0.07

Nonetheless, the surface tension approaches zero for extremely small droplets.

Curvature-independent size effect on γ

Surface tension for thin slabs:



Correlation: $\frac{\gamma(d,\ T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$

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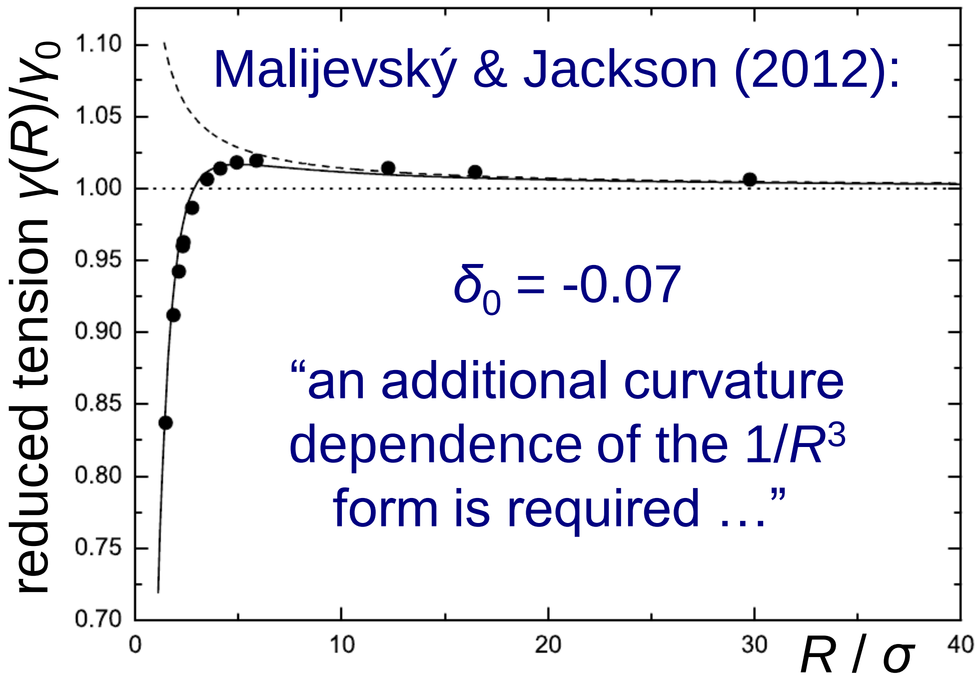

Conclusion

- Mechanical (virial) and thermodynamic (test area and grand canonical) routes lead to contradicting results for the curvature dependence of γ.
- Without knowledge of the surface tension, it is impossible to determine the Laplace radius R_γ. In terms of the capillarity radius R_κ and the pressure difference Δp (or μ), Tolman's approach can still be applied.
- Results for the excess equimolar radius confirm the thermodynamic routes to the surface tension: In the planar limit, the Tolman length is small (and negative, according to the most recent literature).
- However, for extremely small liquid phases, the surface tension decreases due to a curvature-independent effect.