Dependence of the surface tension on curvature

rigorously determined from the density profiles of nanodroplets

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Bundesministerium für Bildung und Forschung
memo
Computational Molecular Engineering

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ThEt DAAD Deutscher Akademischer Austausch Dienst
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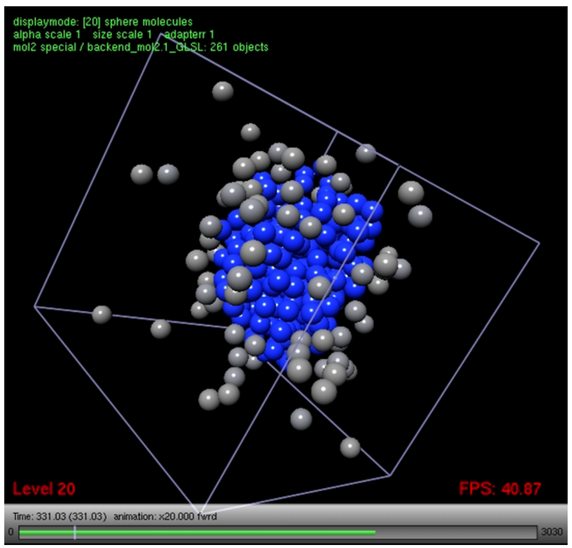
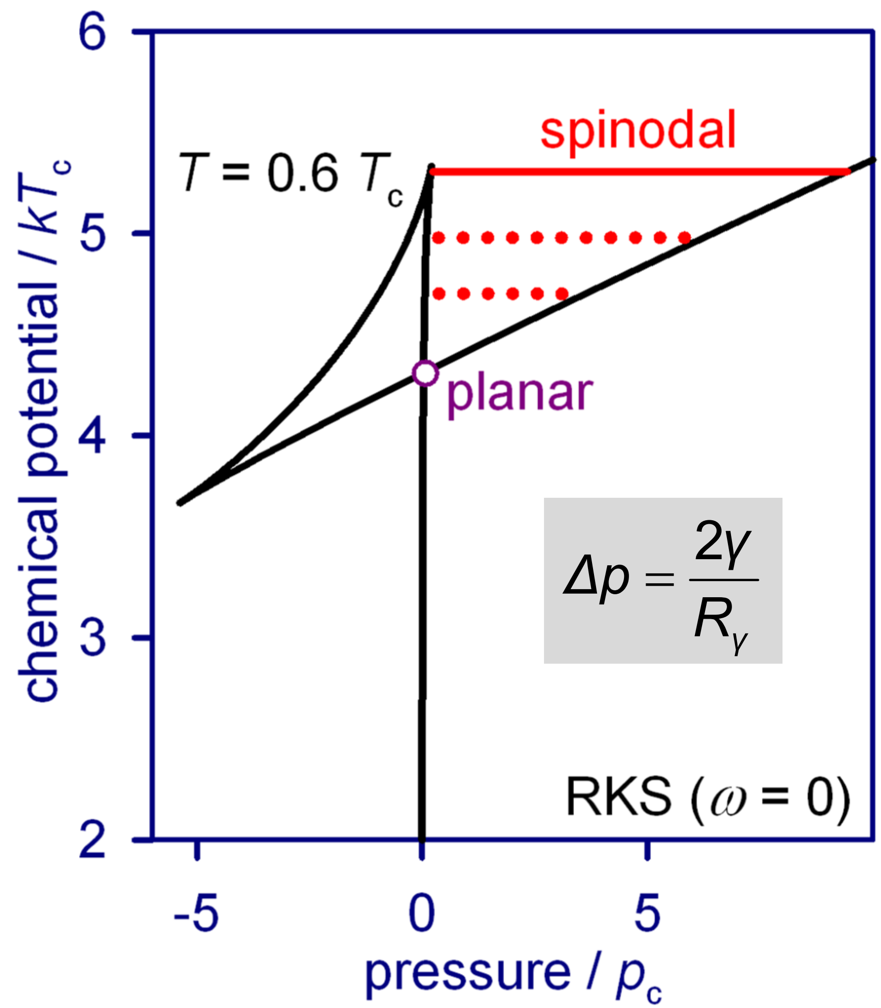
VLE at a curved interface

- Droplet + metastable vapour

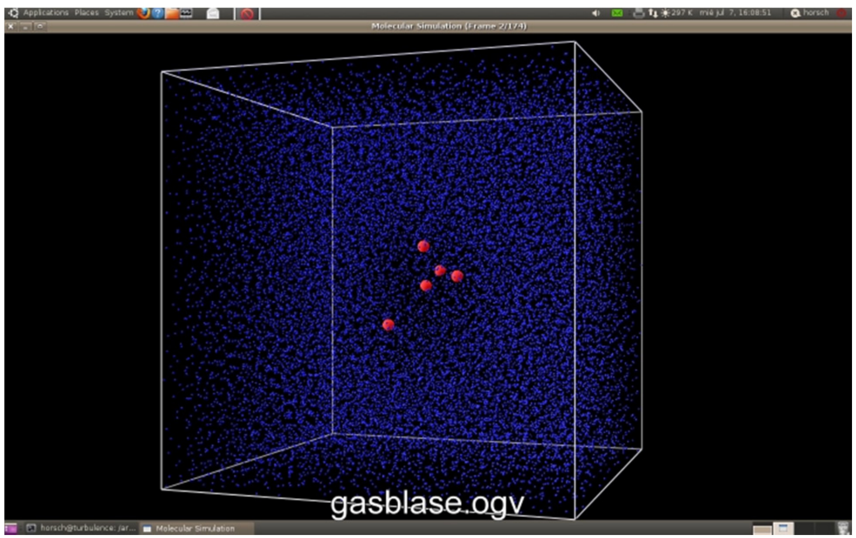


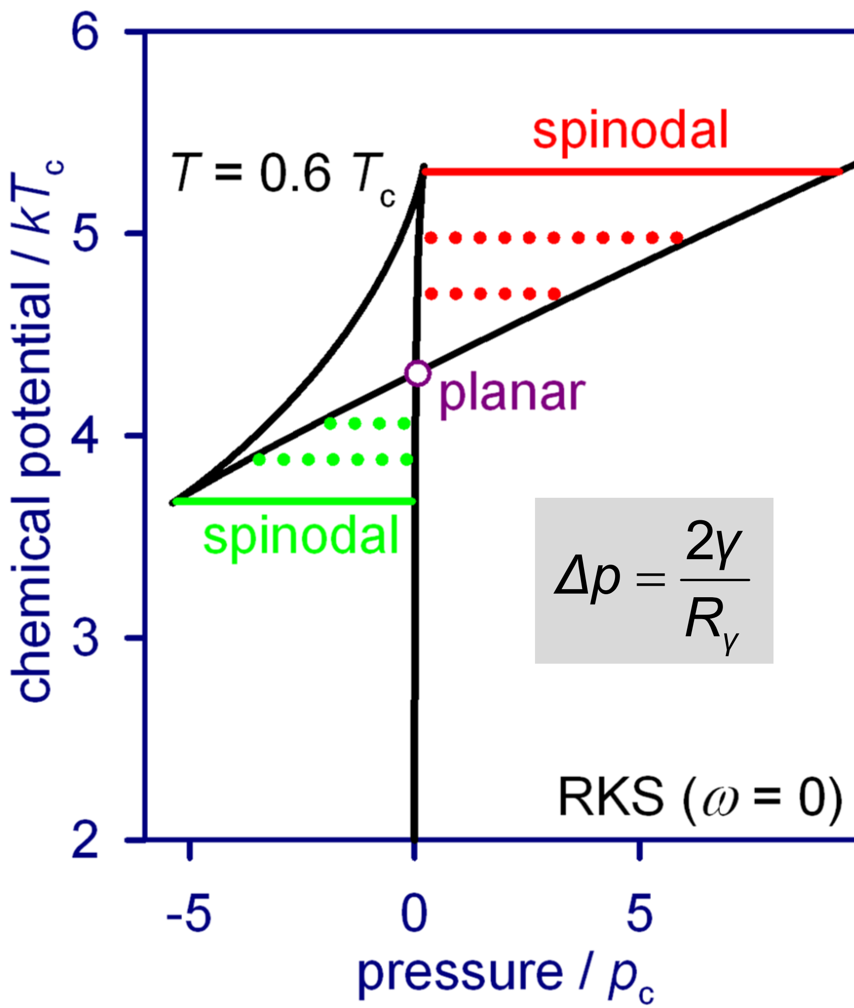
Spinodal limit: For the external phase, metastability breaks down.



VLE at a curved interface

- Droplet + metastable vapour
- Bubble + metastable liquid

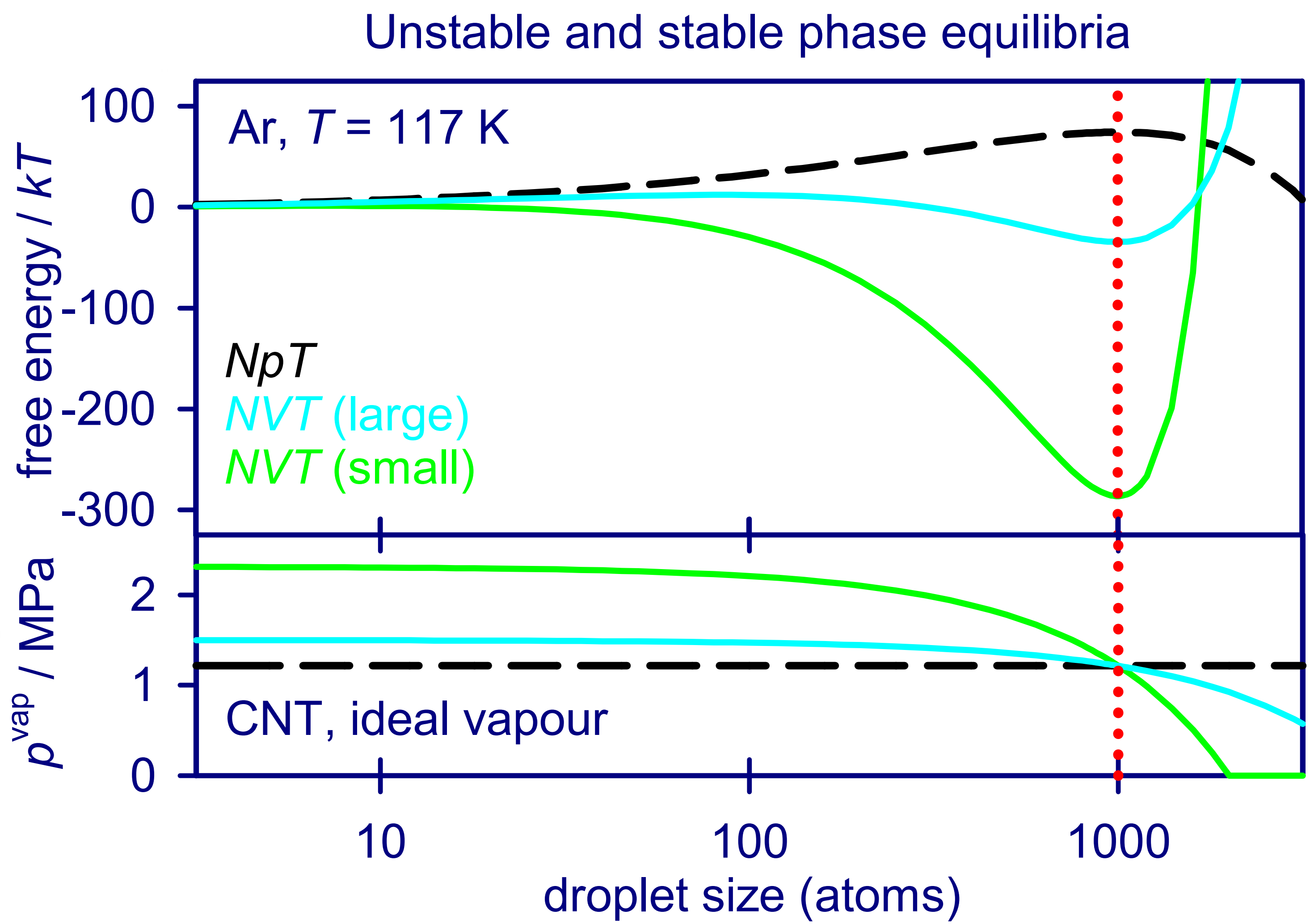




Spinodal limit: For the external phase, metastability breaks down.

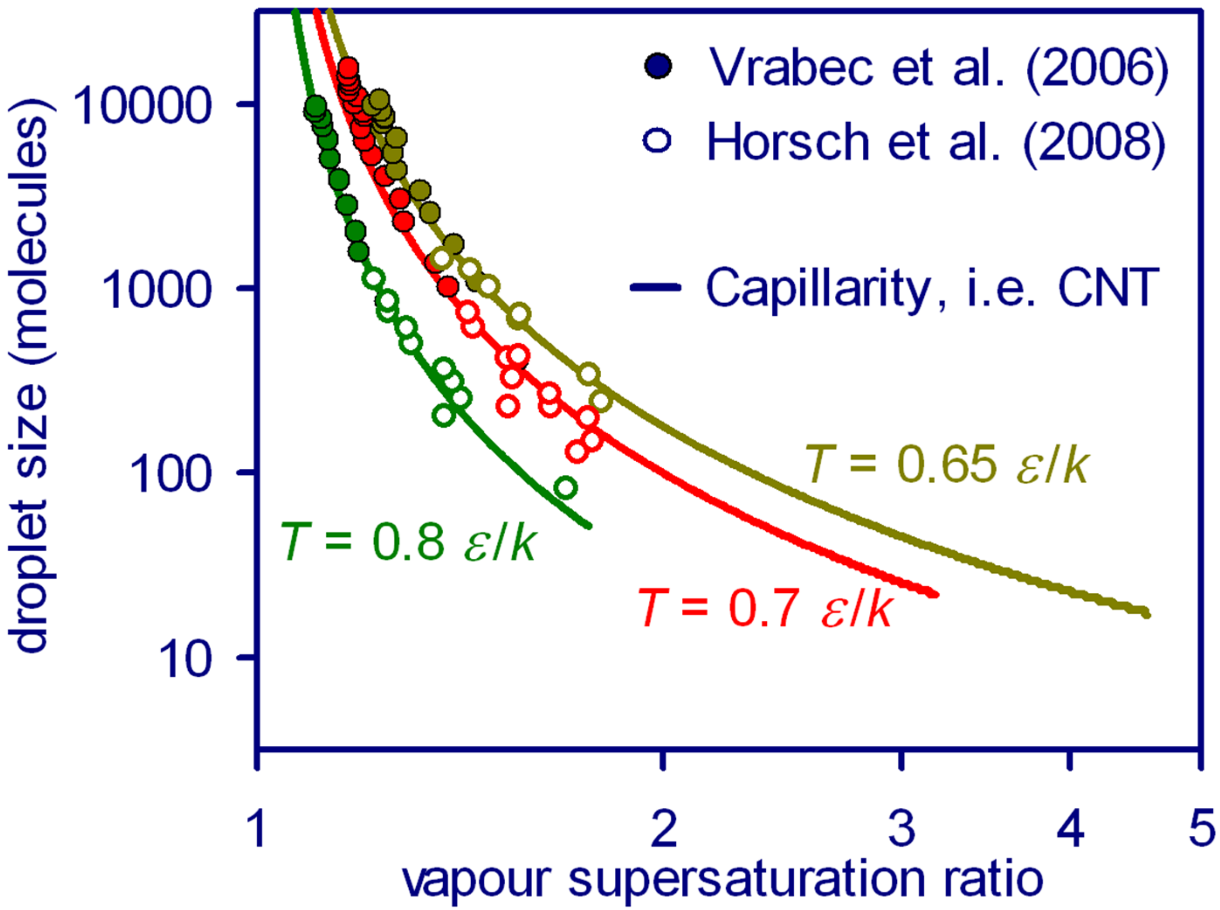
Planar limit: The curvature changes its sign and the radius R_γ diverges.

Stability in the canonical ensemble



Equilibrium vapour pressure over a droplet

Canonical MD simulation of LJTS droplets



Down to 100 mole-cules: Agreement with CNT ($\gamma = \gamma_0$).

Equilibrium vapour pressure over a droplet

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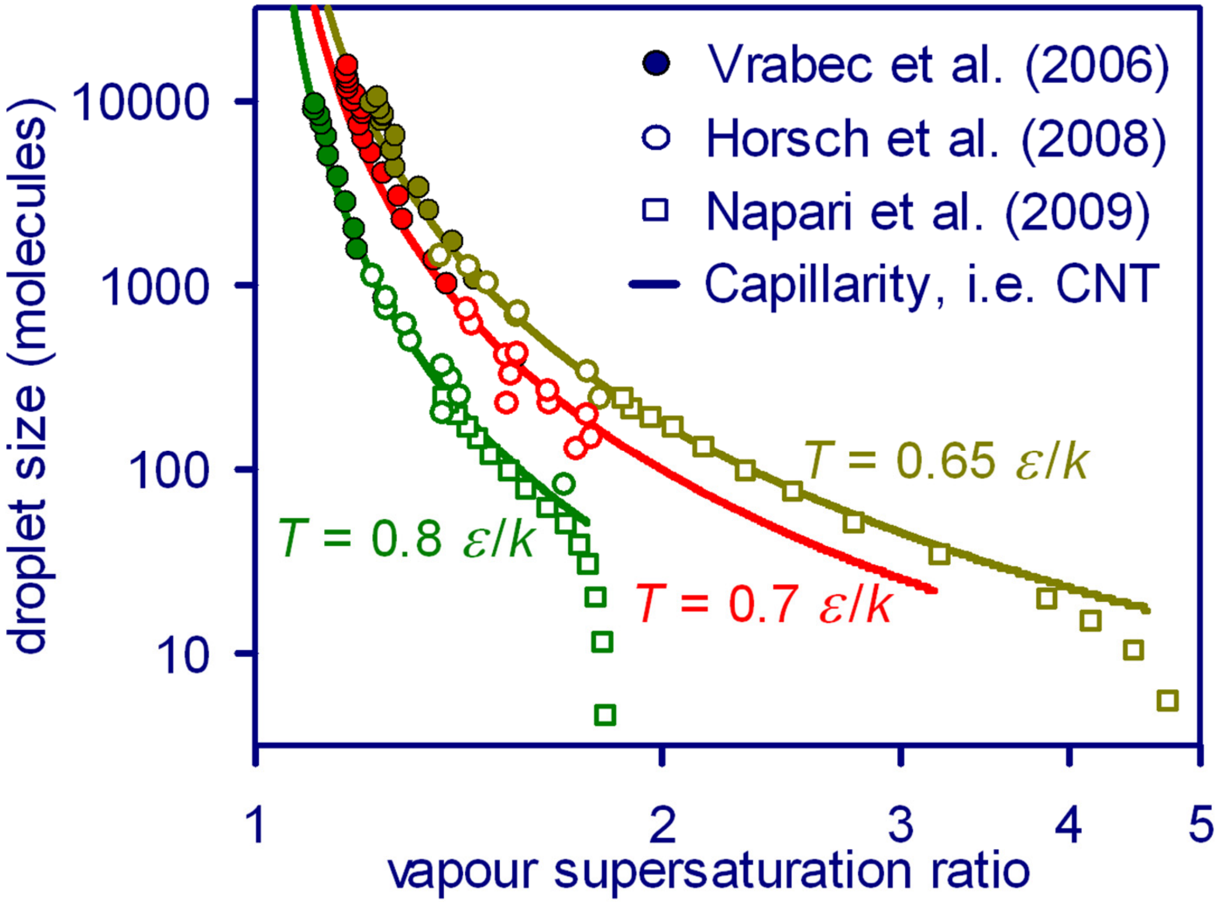


Down to 100 molecules: Agreement with CNT ($\gamma = \gamma_0$).

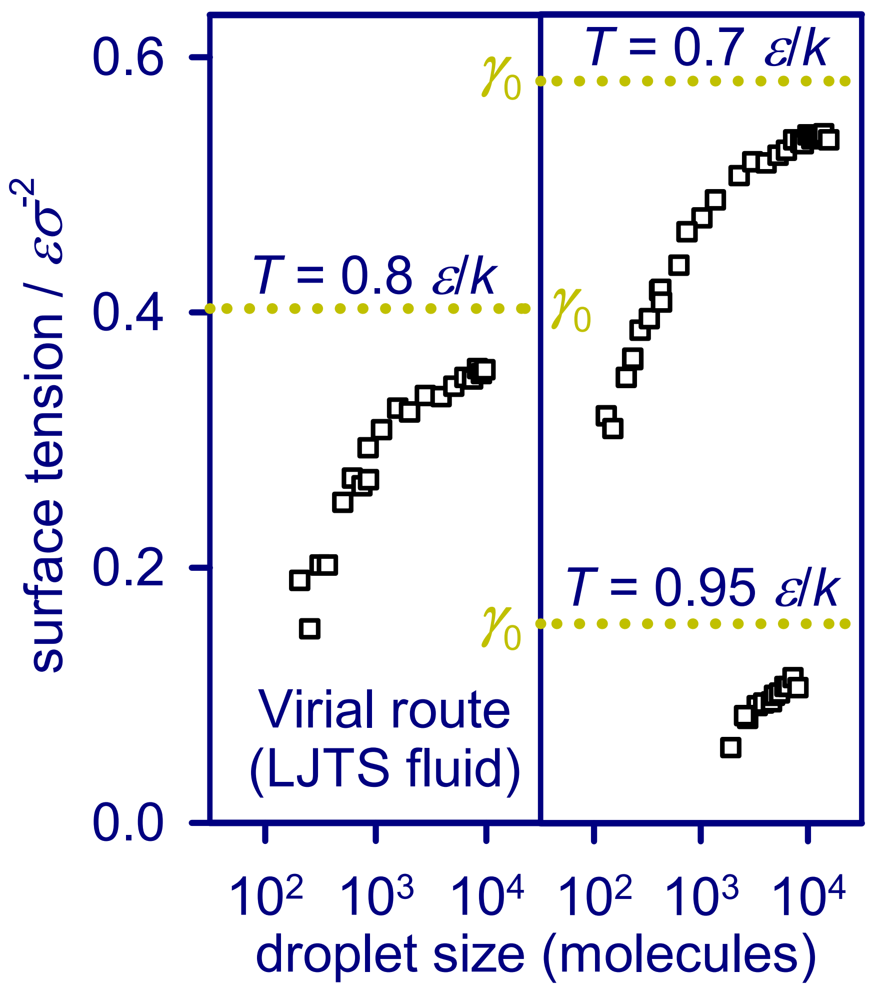
At the spinodal, the results suggest that $R_\gamma = 2\gamma / \Delta p \to 0$. This implies

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

as conjectured by Tolman (1949) …

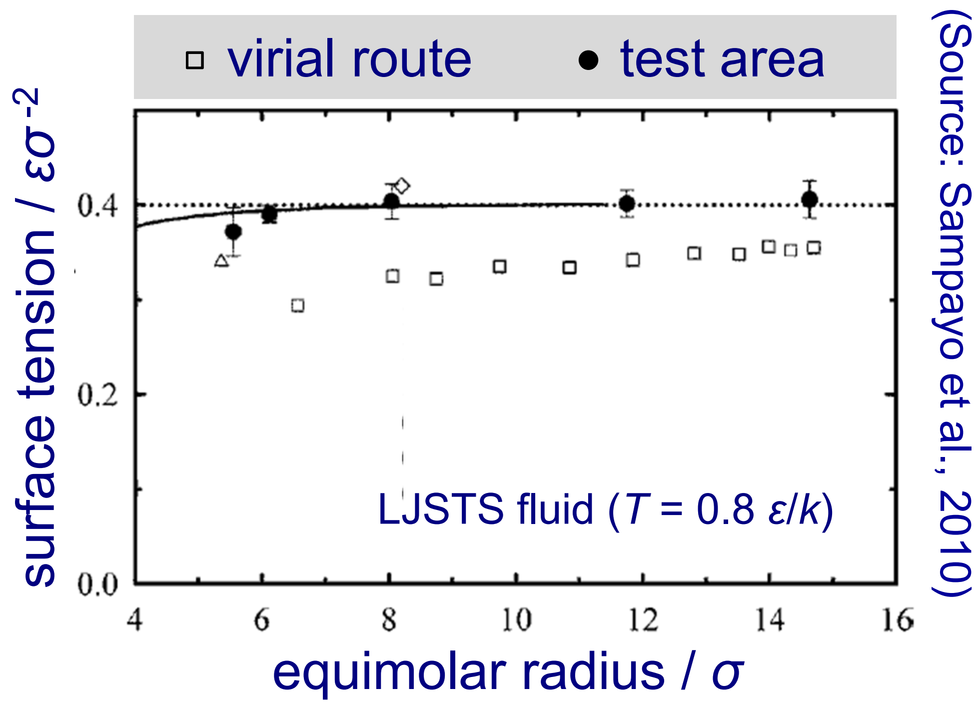
Surface tension from molecular simulation

Integral over the pressure tensor



Test area method:

Small deformations of the volume



Mutually contradicting simulation results!

The Tolman length

… characterizes the curvature dependence of the surface tension according to the Tolman equation

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

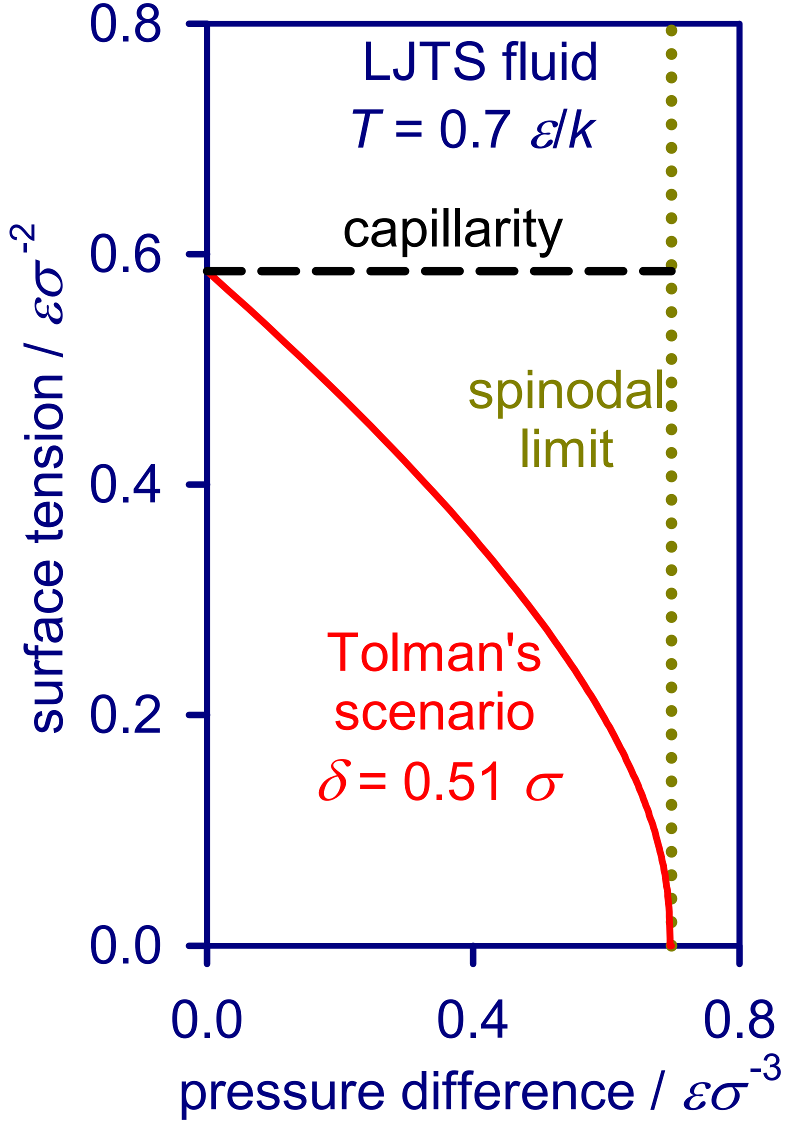
in terms of γ and $1/R_\gamma$. It is defined by the deviation

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

between the equimolar radius R_ρ with

$$\int_0^{R_\rho} (\rho_0 - \rho_R) R^2 dR = \int_{R_\rho}^{\infty} (\rho_R - \rho_\infty) R^2 dR,$$

and the Laplace radius R_γ.

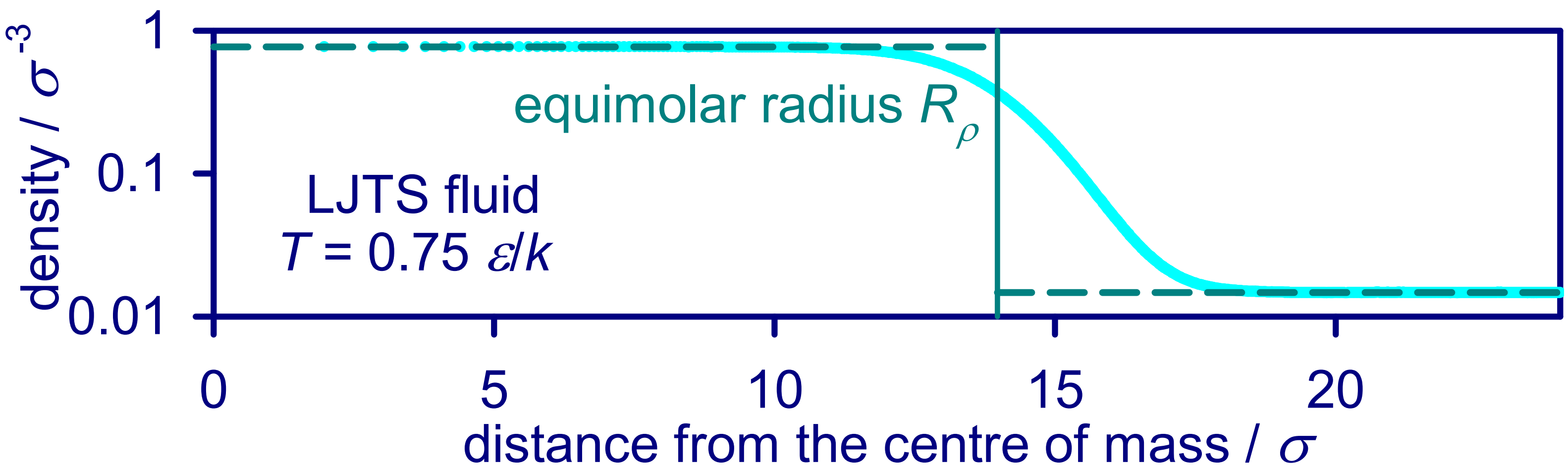


Analysis of spherical density profiles

The Tolman approach is based on the quantities:

- Equimolar radius R_ρ (from the density profile)
- Laplace radius $R_\gamma = 2\gamma/\Delta p$ of the surface of tension (determined via γ)
- Surface tension γ as a function of $1/R_\gamma$ (which requires γ …)

Without previous knowledge of $\gamma(R_\gamma)$, this set of variables is inconvenient.



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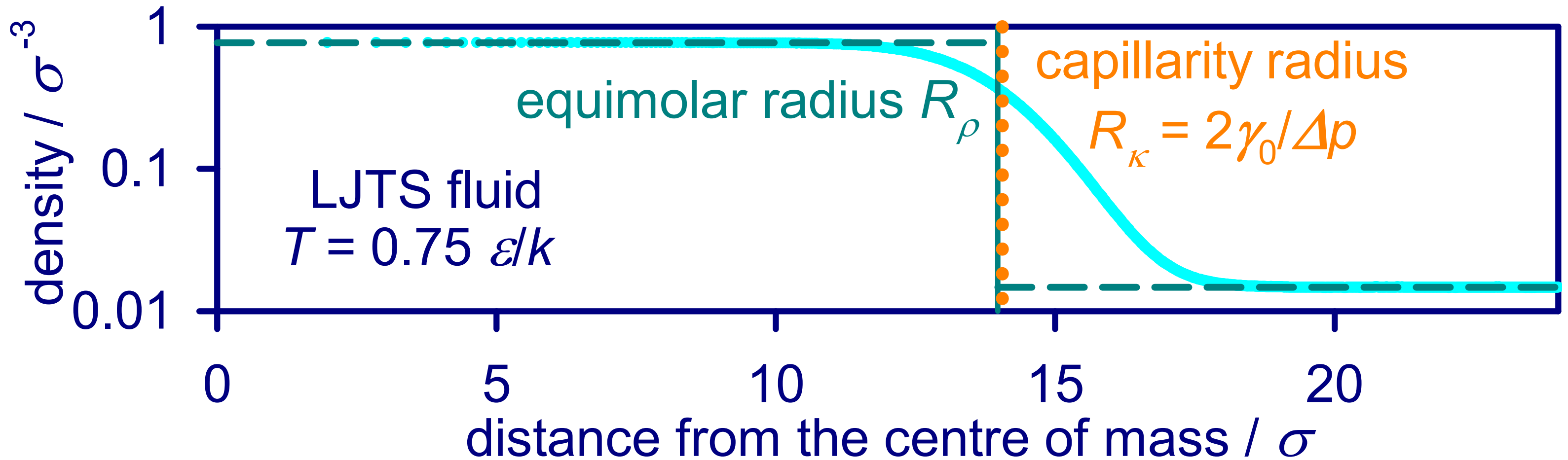


Novel approach: Use Δp instead of $1/R_\gamma$, use $R_\kappa = 2\gamma_0/\Delta p$ instead of R_γ.

The excess equimolar radius

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

Tolman length:

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

Tolman equation:

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

First-order expansion:

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

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:

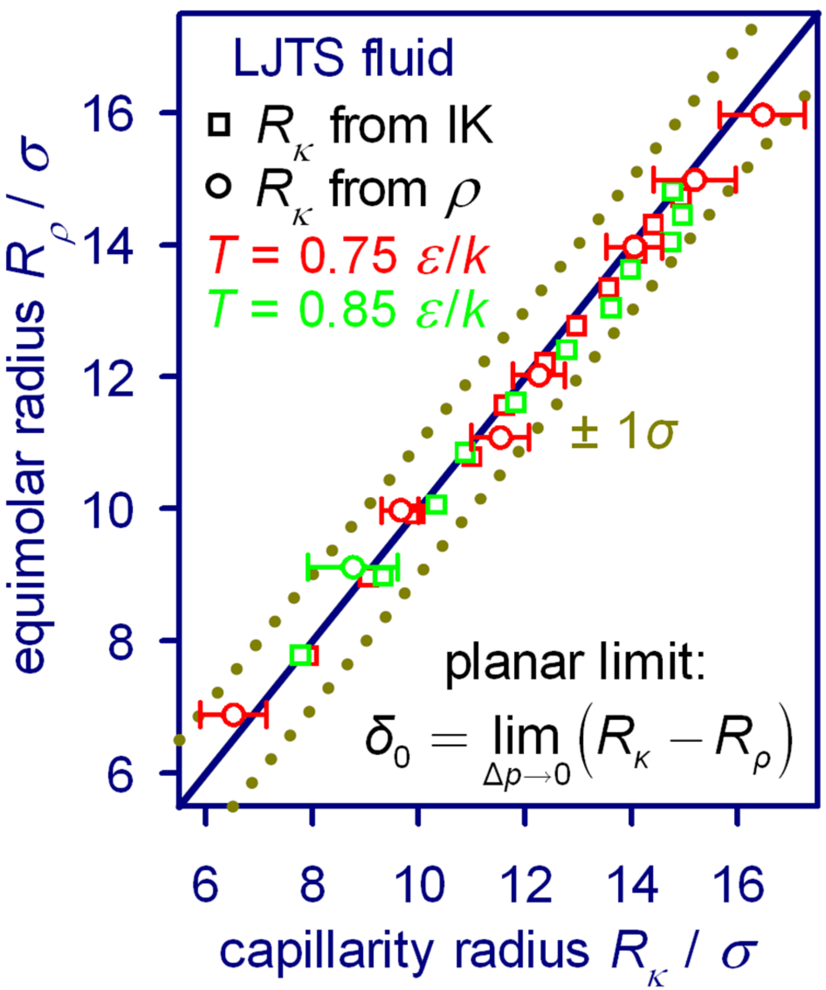
$$\gamma = \gamma_0 + 2\eta_0 \frac{\gamma}{R_\gamma} + O\left(\frac{\gamma^2}{R_\gamma^2}\right)$$

How do these notations relate to each other?

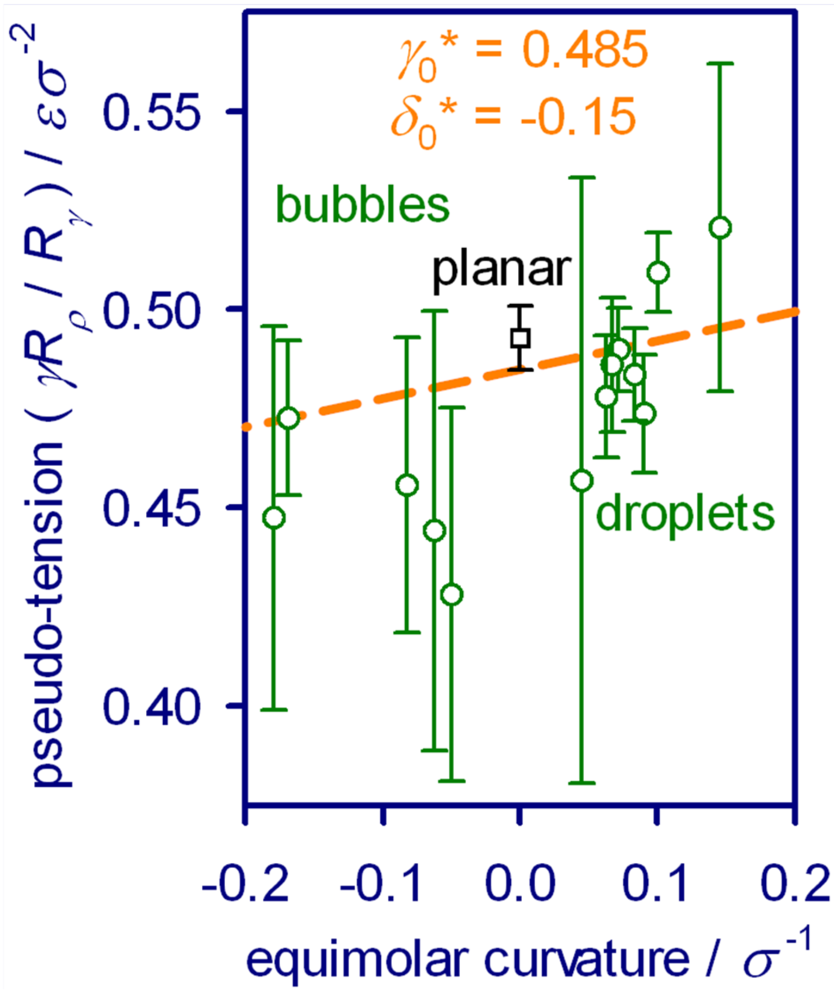
$$\eta_0 = \lim_{\Delta p \to 0}\left(R_\rho - \frac{\gamma_0}{\gamma R_\gamma^{-1}}\right) = -\lim_{\Delta p \to 0}\left(Q - \frac{\gamma}{\gamma R_\gamma^{-1}}\right) = -\delta_0$$

Extrapolation to the planar limit

Radial parity plot



Nijmeijer diagram



Conclusion

- The virial (Irving-Kirkwood) and test area approaches 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 (instead of R_γ) and the pressure difference Δp (instead of $1/R_\gamma$), Tolman's approach can still be applied.
- For the LJTS fluid, the planar limit of the Tolman length δ is smaller in magnitude than 1 σ.
- This result is consistent with "Tolman's scenario" ($R \to 0$ and $\gamma \to 0$) for the spinodal limit, if δ is assumed to be curvature independent.