Molecular simulation of curved vapour-liquid interfaces

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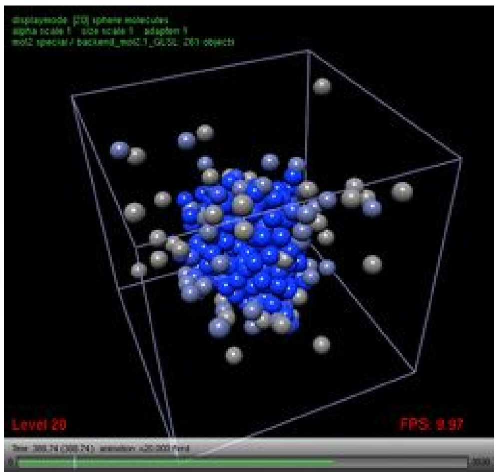
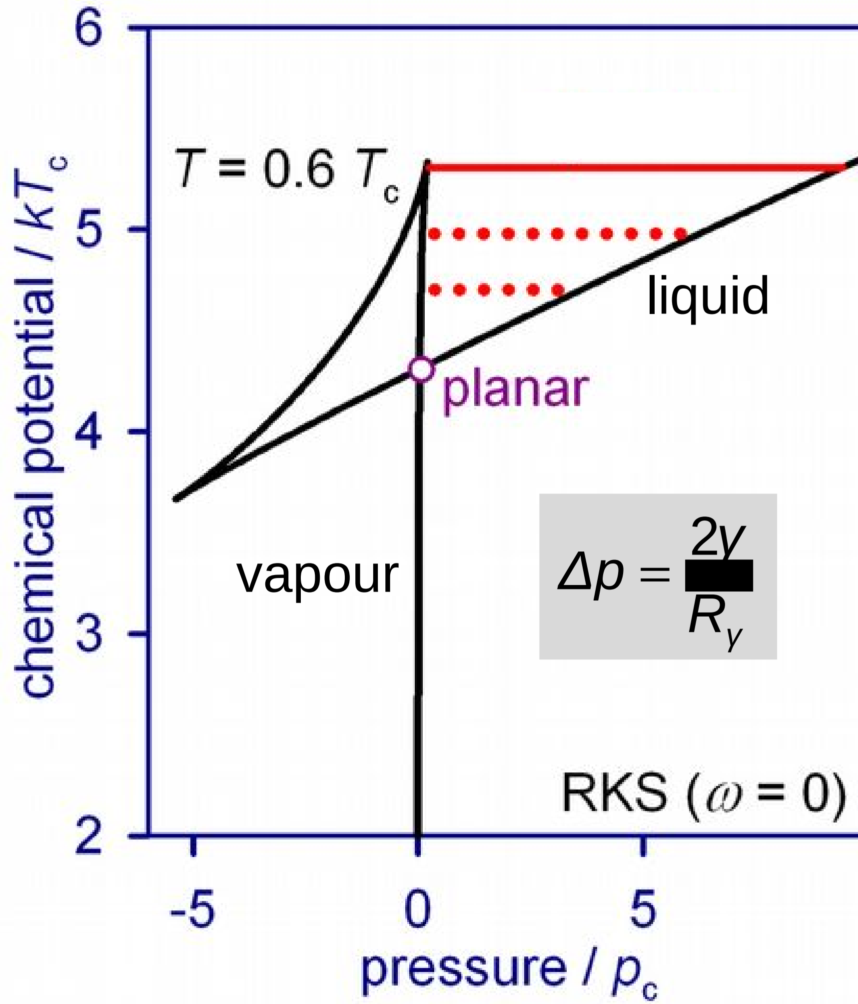
Dispersed fluid phases in equilibrium

- Droplet + metastable vapour





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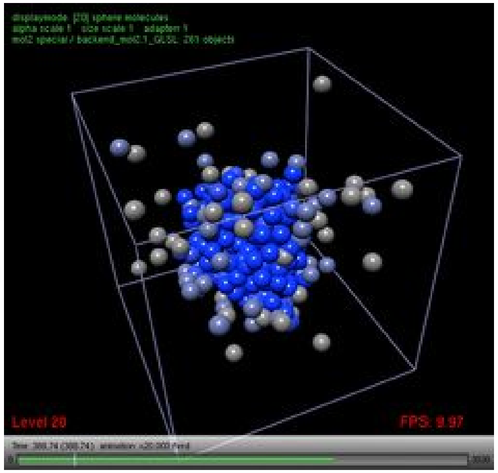
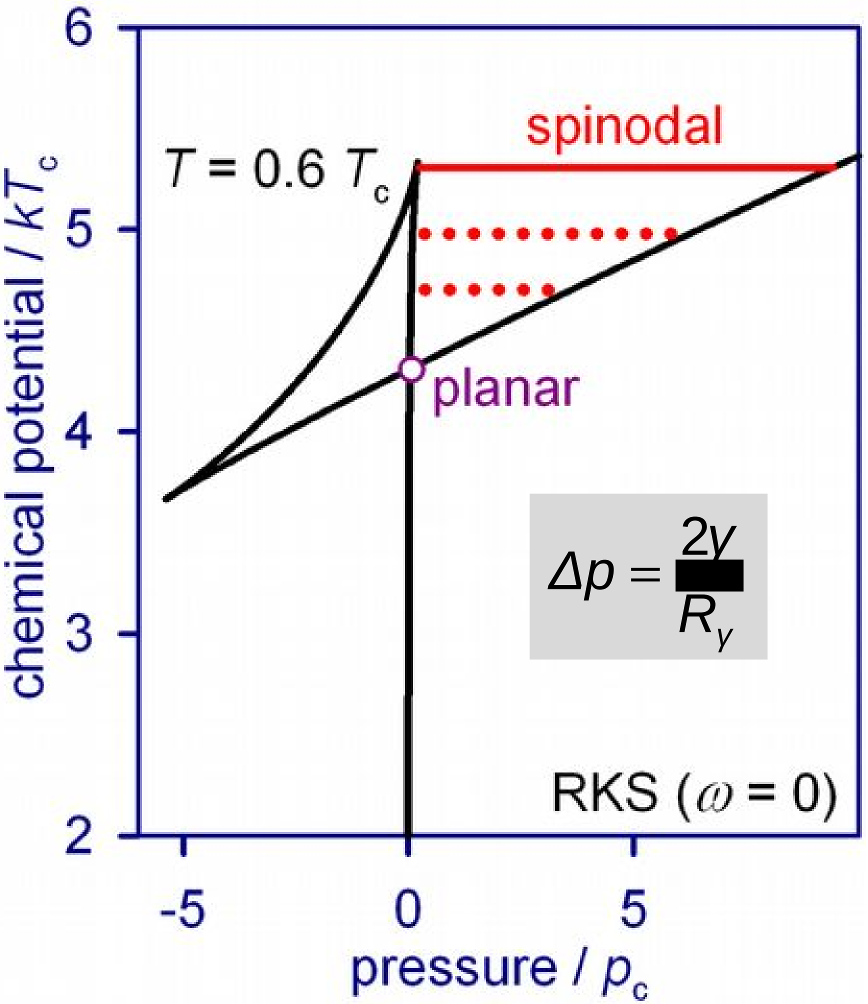
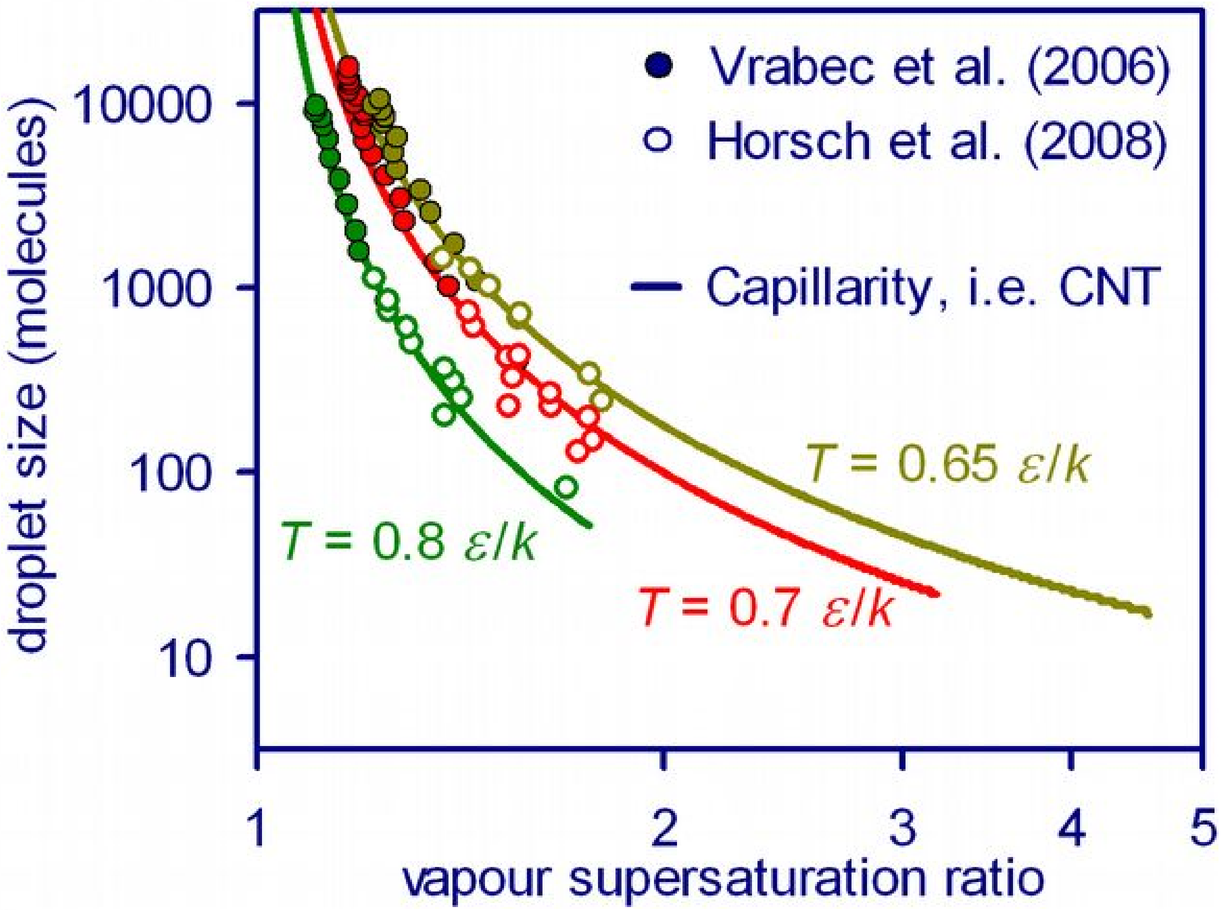




Spinodal limit: For the external phase, metastability breaks down.

Equilibrium vapour pressure of a droplet

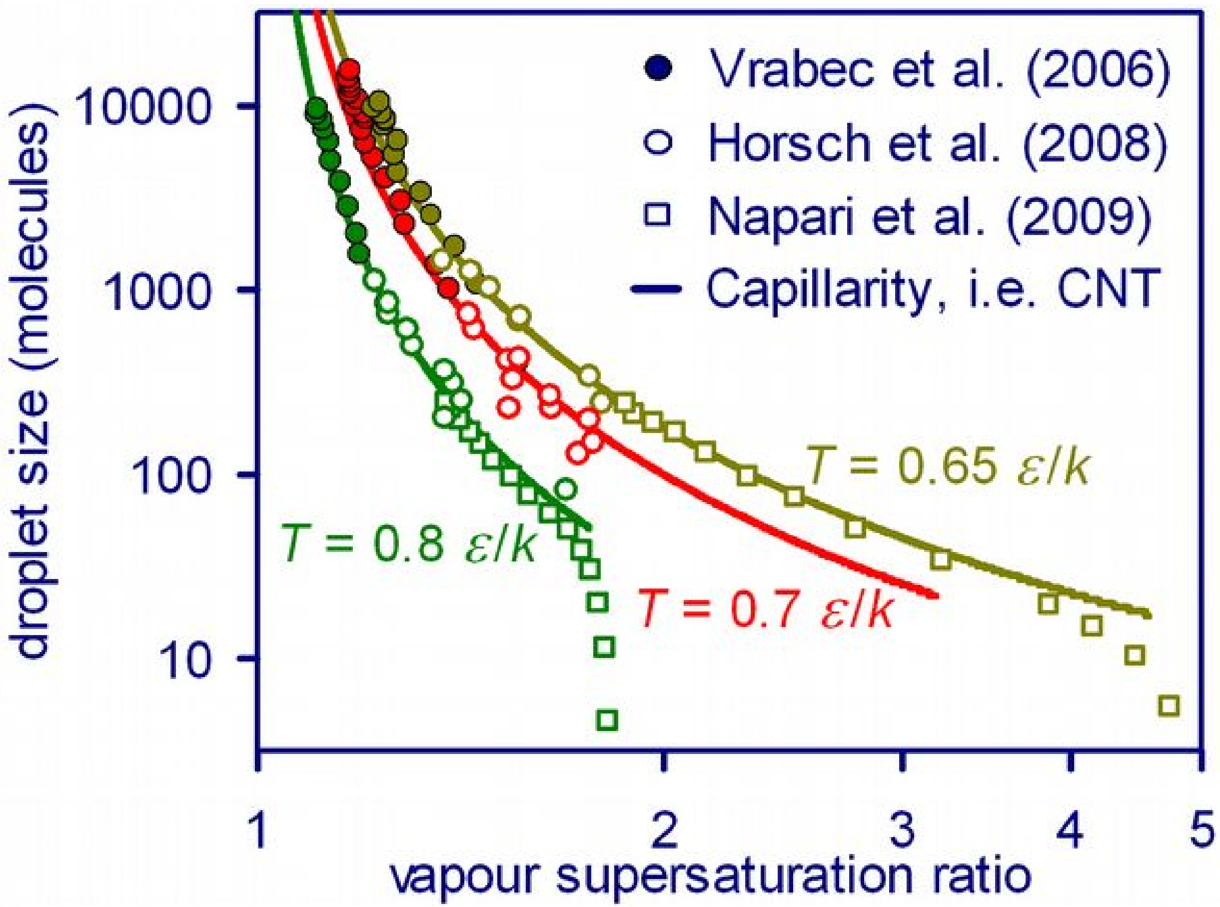
Canonical MD simulation of LJTS droplets



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

Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets



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

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

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

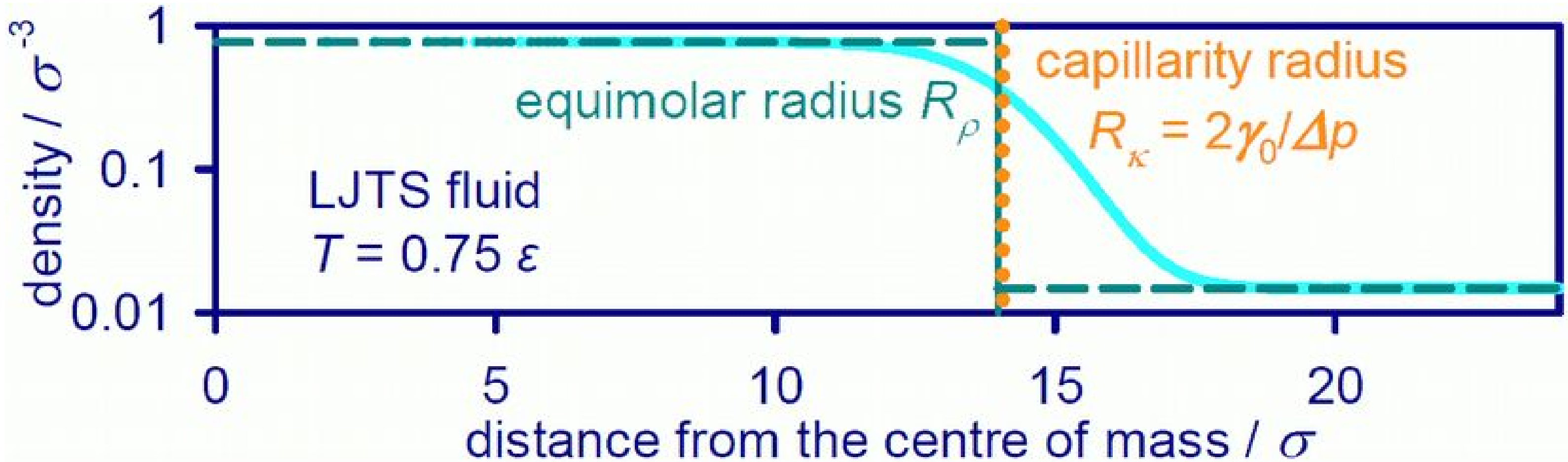
as conjectured by Tolman (1949) …

Analysis of radial density profiles

The approach of Gibbs and Tolman is based on **formal radii** of the droplet.

- Equimolar radius R_ρ (obtained from the density profile)
- Laplace radius $R_\gamma = 2\gamma/\Delta p$ (defined by the surface tension γ)
- Capillarity radius $R_\kappa = 2\gamma_0/\Delta p$ (defined by the planar surface tension γ_0)

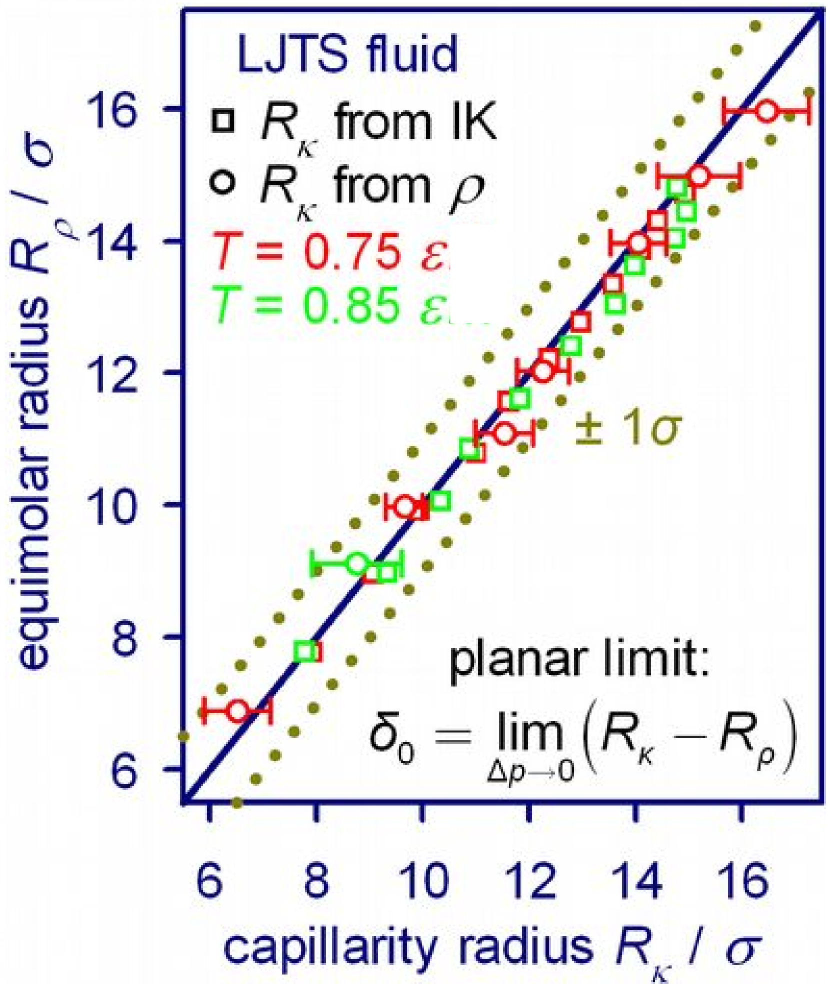
The capillarity radius can be obtained reliably from molecular simulation.



Here, curvature is expressed by $\gamma/R_\gamma = \Delta p/2$, droplet size by $R_\kappa = 2\gamma_0/\Delta p$.

Extrapolation to the planar limit

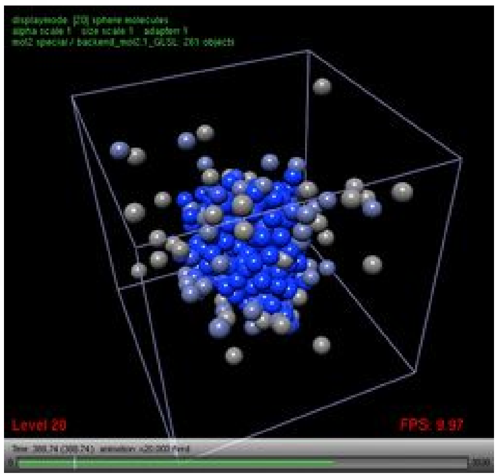
Radial parity plot

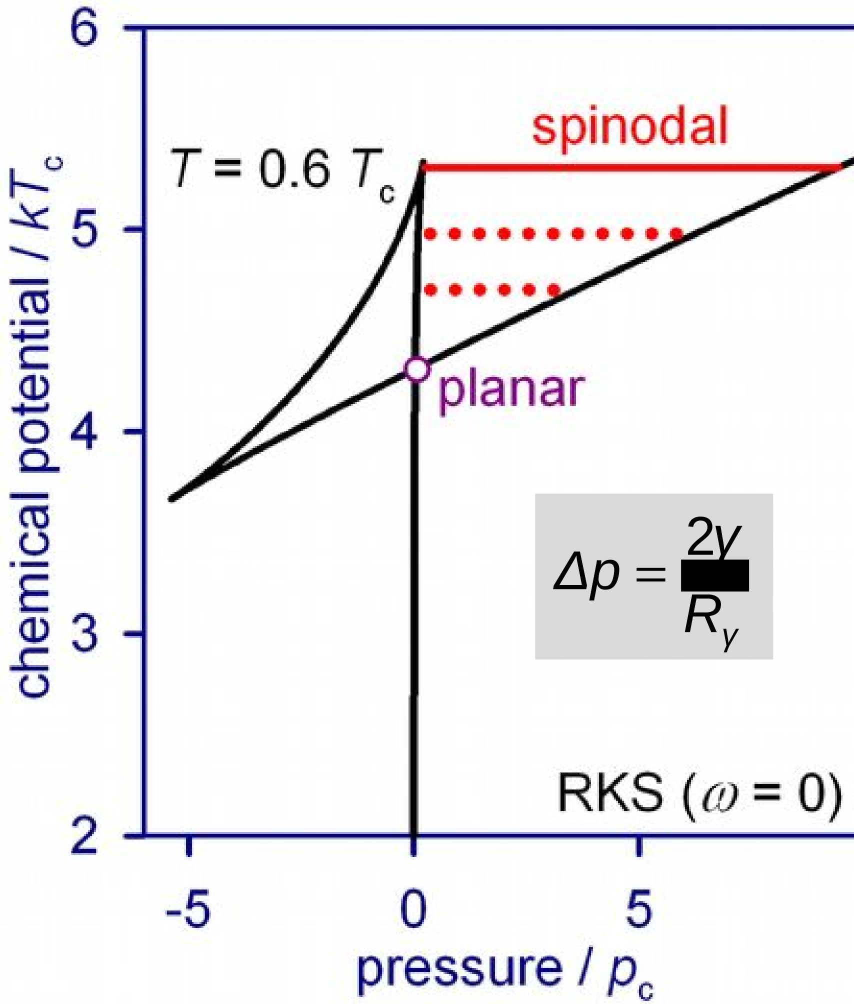


- The magnitude of the excess equimolar radius is consistently found to be smaller than σ / 2.
- This suggests that the curvature dependence of γ is weak: The deviation from the planar surface tension is smaller than 10 % for radii larger than 5 σ.

Dispersed fluid phases in equilibrium

- Droplet + metastable vapour

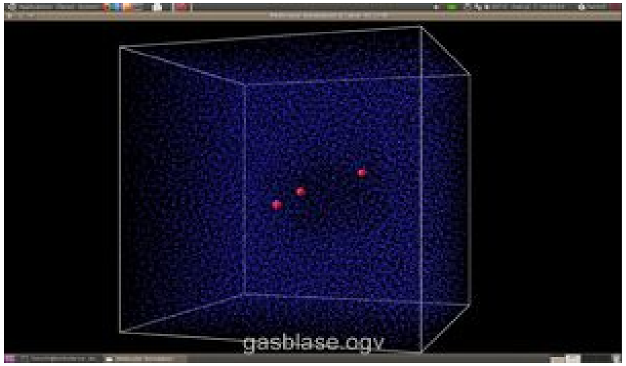


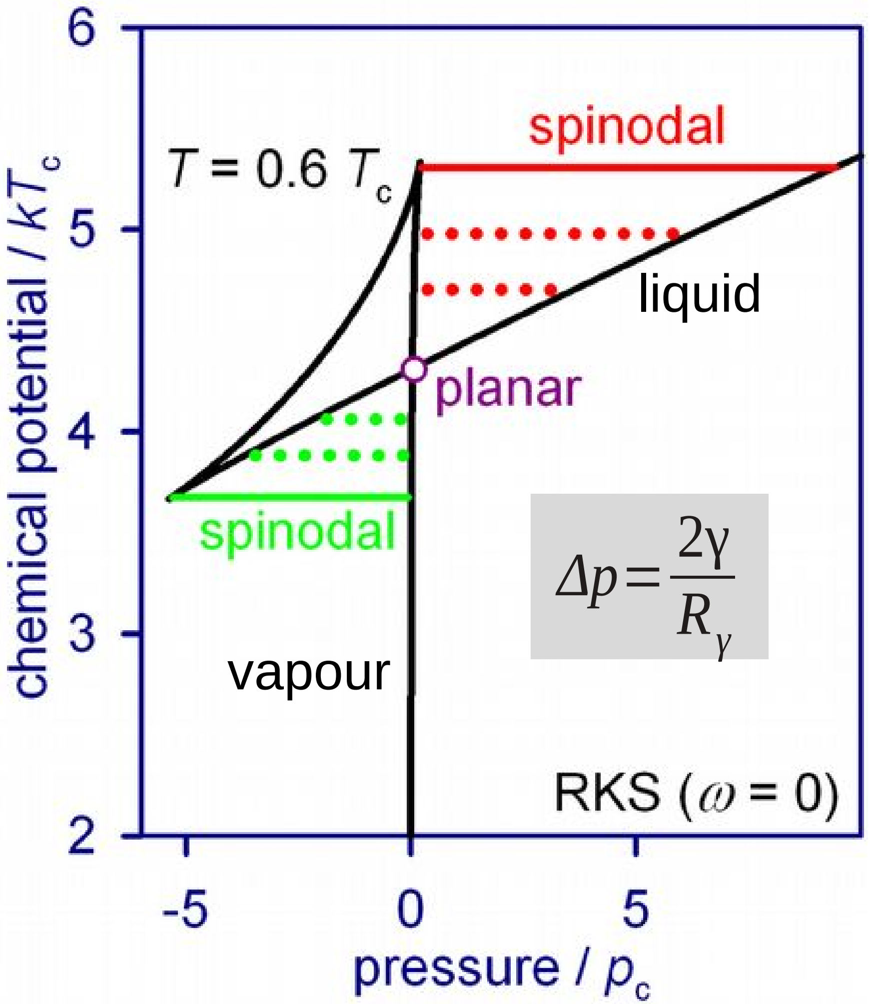


Spinodal limit: For the external phase, metastability breaks down.

Gas bubbles in equilibrium

- Droplet + metastable vapour
- Bubble + metastable liquid



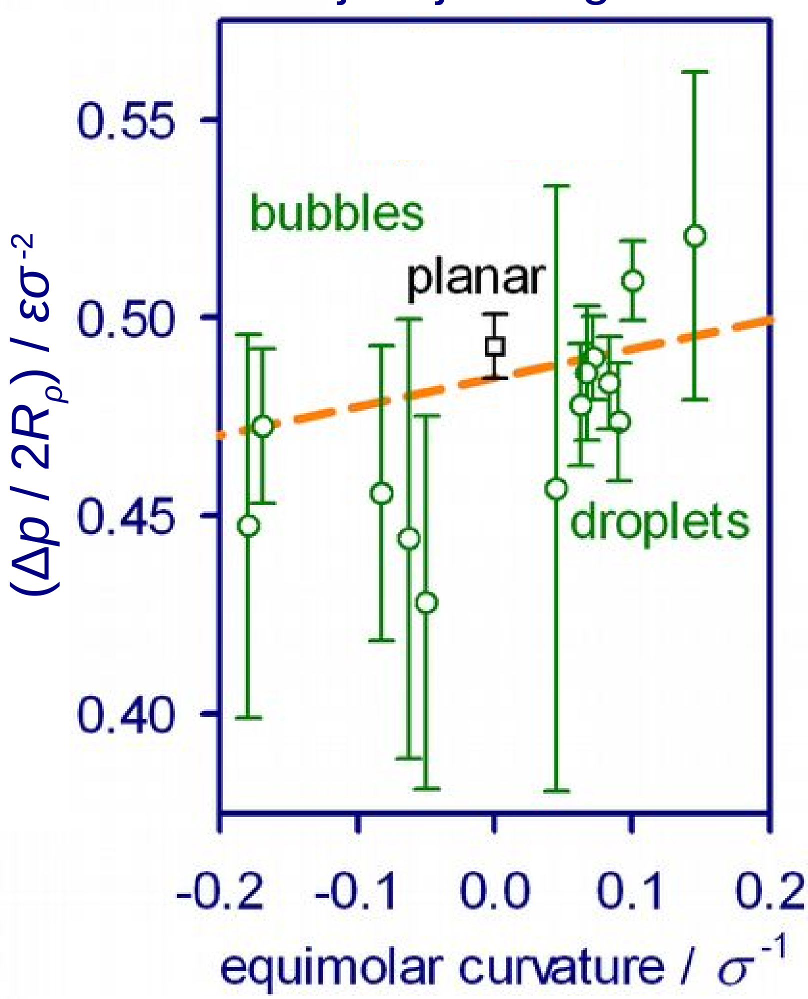


Spinodal limit: For the external phase, metastability breaks down.

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

Interpolation to the planar limit

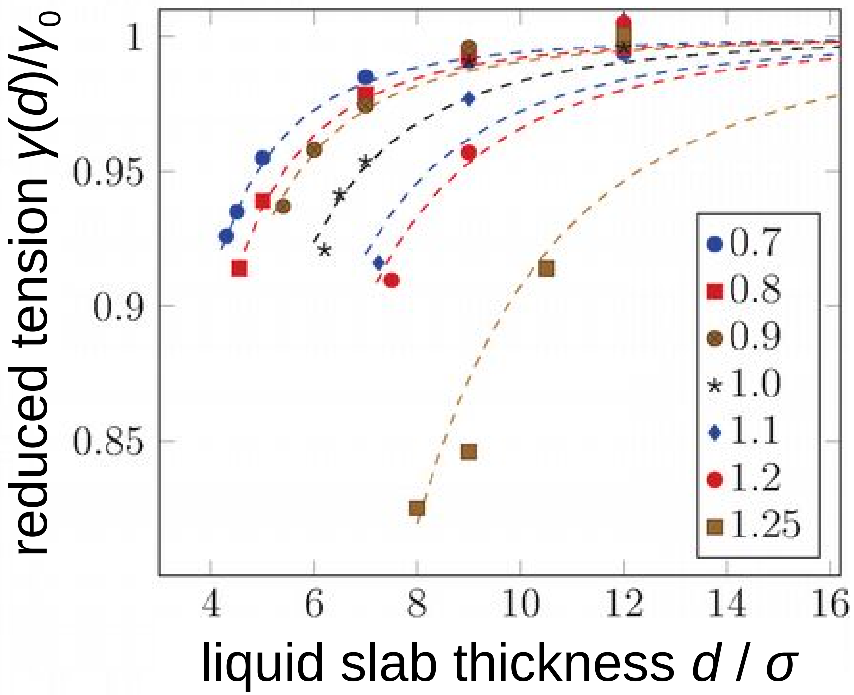
Nijmeijer diagram

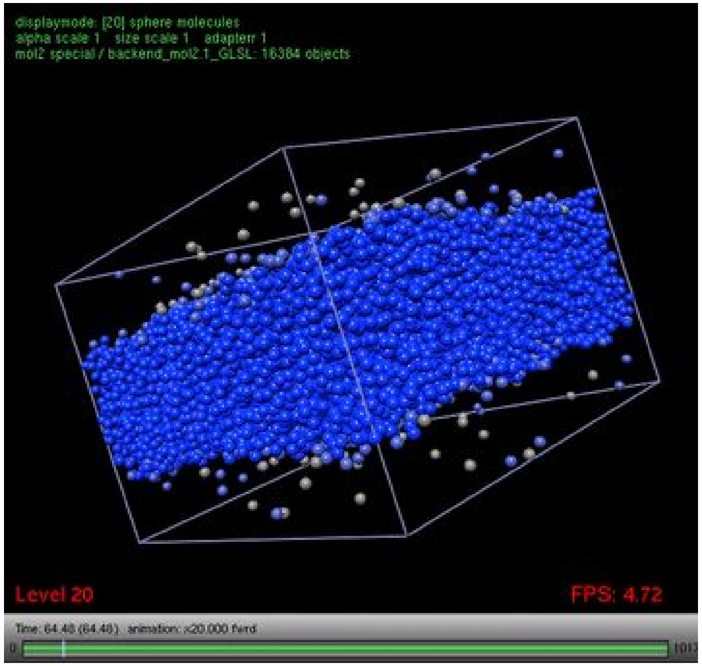


- Convention: Negative curvature (bubbles), positive curvature (droplets).
- Properties of the planar interface, such as its Tolman length, can be obtained by interpolation to zero curvature.
- A positive slope of $\Delta p/2R_\rho$ over $1/R_\rho$ in the Nijmeijer diagram corresponds to a *negative* δ, on the order of -0.1 σ here, conforming that δ *is small*.
- However, $R \rightarrow 0$ for droplets in the spinodal limit for the surrounding vapour (Napari et al.) implies $\gamma \rightarrow 0$.

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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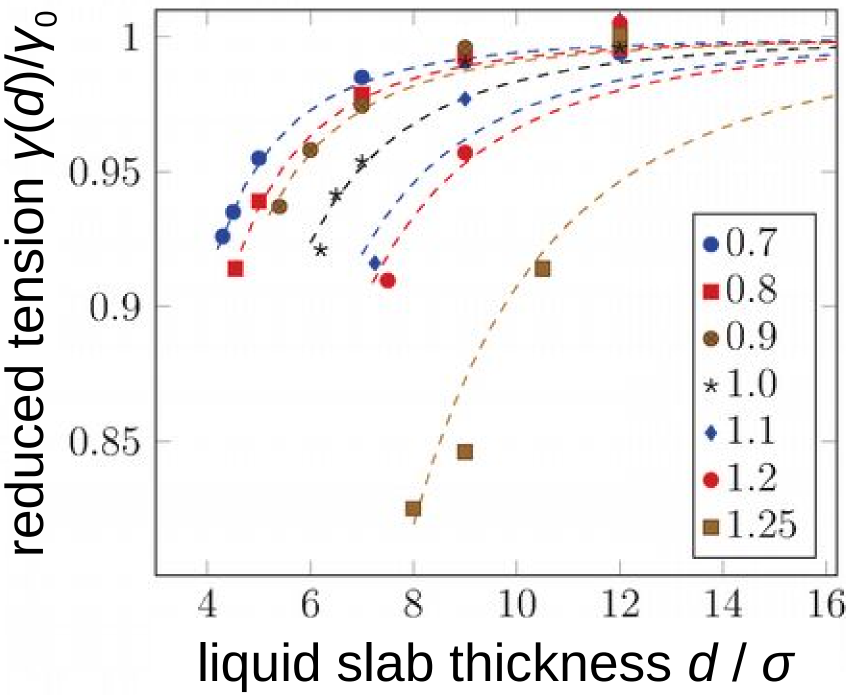
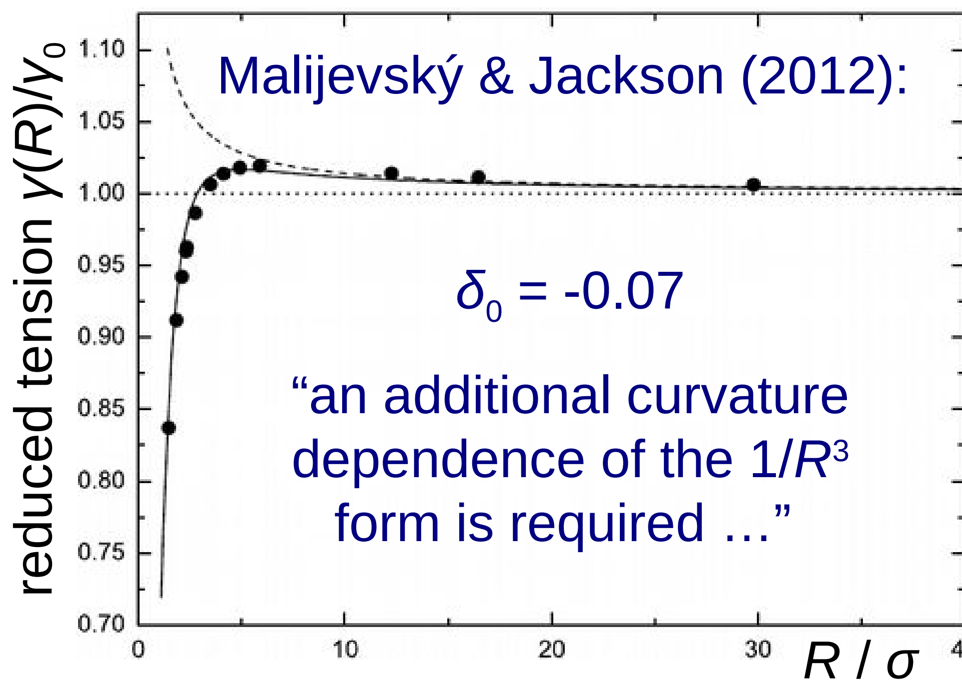


Correlation: [redacted] $= 1 -$ [redacted]

Relation with *γ*(*R*) for droplets?

δ_0 is small and probably negative



Malijevský & Jackson (2012):

$\delta_0 = -0.07$

"an additional curvature dependence of the $1/R^3$ form is required …"

Conclusion

- In agreement with the Laplace equation, the vapour pressure of droplets is **supersatured** due to **curvature**.

- The magnitude of this effect agrees well with the **capillarity approximation** down to droplets containing 100 molecules. Very high supersaturations, however, correspond to extremely small droplets, implying a decrease in the surface tension.

- An approach based on effective radii which can be rigorously determined by simulation proves the **Tolman length** to be small, explaining the good agreement with the capillarity approximation.

- For a dispersed liquid phase that occupies an extremely small volume, the surface tension is reduced due to a **curvature-independent effect** which is present in planar slabs as well as spherical droplets.