A new route to evaluate the curvature dependence of the surface tension by molecular simulation

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DAAD Deutscher Akademischer Austausch Dienst
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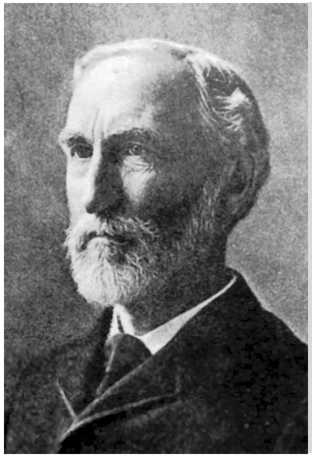
The formal dividing surface

Thermodynamic properties of an interface are determined by its **internal** 3-dimensional structure

Relations of axiomatic thermodynamics can be applied to a **formal** 2-dimensional surface.



„take some point […] and imagine a geometrical surface to pass through this point and all other points which are similarly situated […] called the **dividing surface** […] all the surfaces which can be formed in the described manner are evidently parallel" [J. W. Gibbs, On the equilibrium of heterogeneous substances (1876/77), S. 380].

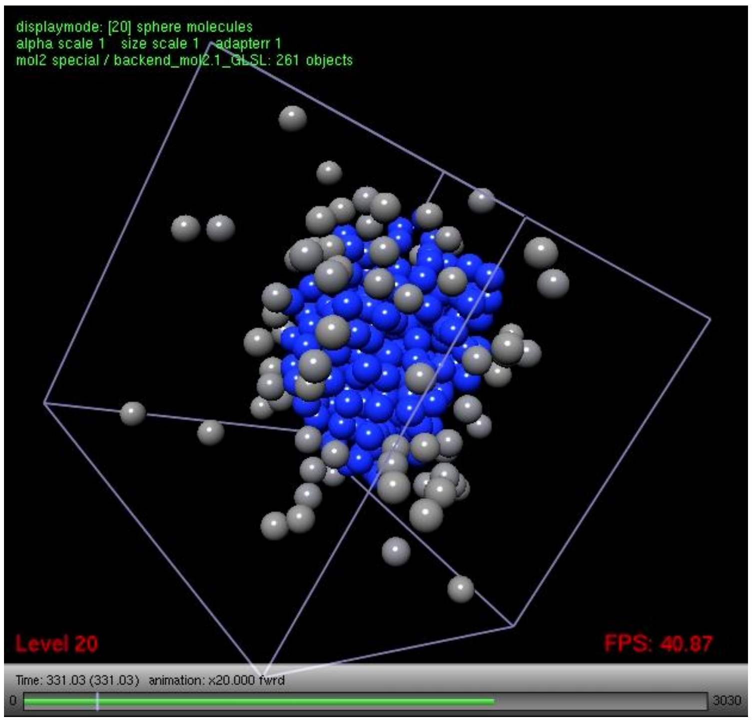
The thermodynamic laws derived by J. W. Gibbs are valid in general.

Concrete values for interfacial properties, however, depend on the way the **internal structure** of a phase boundary is projected to two dimensions, i.e. on the **choice of a dividing surface**.

Thermodynamic equilibrium condition

The Laplace equation:

Surface tension = *differential* free energy per surface area



$$dF = \gamma\ dA + dF' + dF''$$
$$= \gamma\ dA - \Delta p\ dV' - \left(S\ dT - \Delta\mu\ dN'\right)$$

Relation between *dV'* and *dA*:

$$R_\mathrm{L}\ dA = 2\ dV'$$

Mechanical equilibrium:

$$\Delta p\ dV' = \gamma\ dA$$
$$\Delta p = \frac{2\gamma}{R_\mathrm{L}}$$

The Laplace radius R_L of the surface of tension couples *dV'* and *dA*.

Virial route to the surface tension

Mechanical approach:

Bakker-Buff equation

$$\gamma = R_\mathrm{L}^{-2} \int_\mathrm{in}^\mathrm{out} dz\, z^2 \left[p_\mathrm{N}(z) - p_\mathrm{T}(z) \right]$$

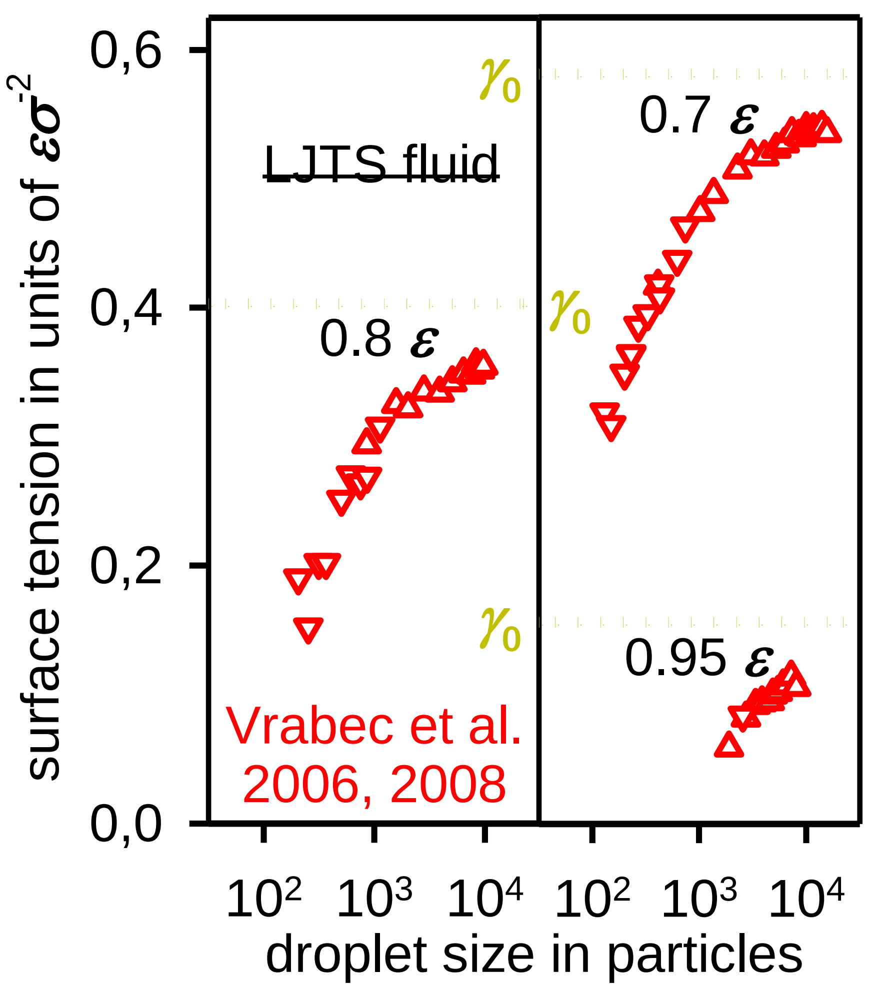
$$(2\gamma)^3 = -\Delta p^2 \int_\mathrm{in}^\mathrm{out} dp_\mathrm{N}(z)\, z^3$$

Irving-Kirkwood pressure tensor

$$p_\mathrm{N}(z) = \sum_{\{i,j\} \in \mathbf{S}(z)} \frac{f_{ij} \left| \mathbf{s} \cdot \mathbf{r}_{ij} \right|}{4\pi z^3 r_{ij}} + kT \rho(z)$$

The normal pressure $p_\mathrm{N}(z)$ decays near the Laplace radius R_L.

Very significant decrease of γ.



Variational route to the surface tension

Test area method:

Canonical partition function yields

$$\Delta F = -T \ln \left\langle \exp\left(-\frac{\Delta U}{T}\right) \right\rangle$$

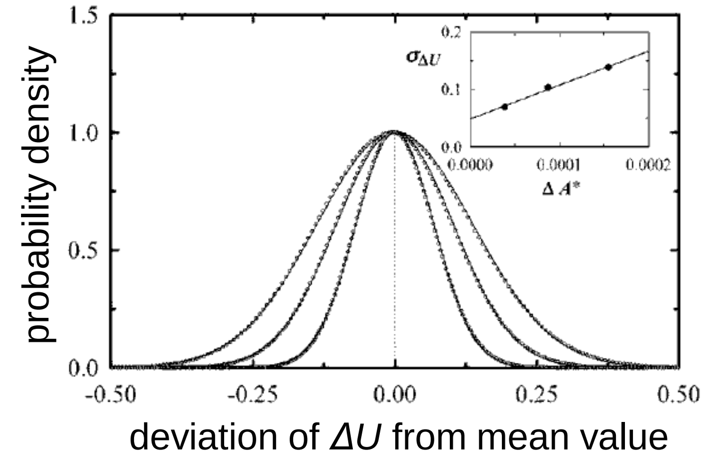
$$= f\left(\langle \Delta U \rangle, \langle \Delta U^2 \rangle, \langle \Delta U^3 \rangle\right) + \mathrm{O}\left(\langle \Delta U^4 \rangle\right)$$

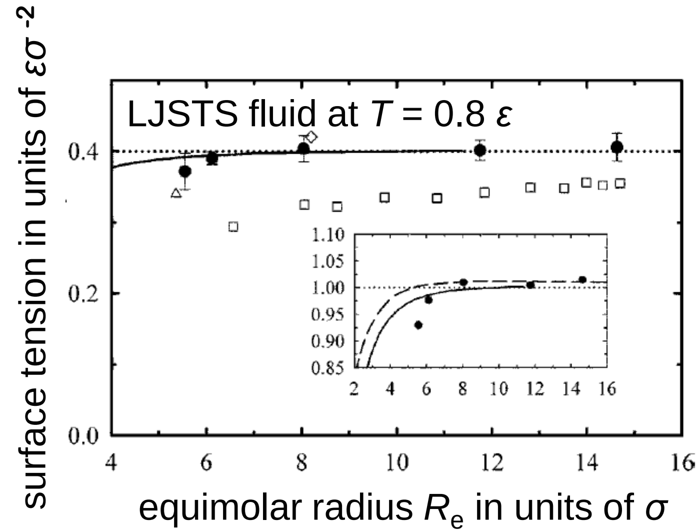
For infinitesimal deformations,

$\gamma = \Delta F / \Delta A$ with $A = 4\pi R_\mathrm{e}^2 + \mathrm{O}(R_\mathrm{e})$.

Non-linear terms represent the contribution due to fluctuations.

Small influence of curvature on γ.





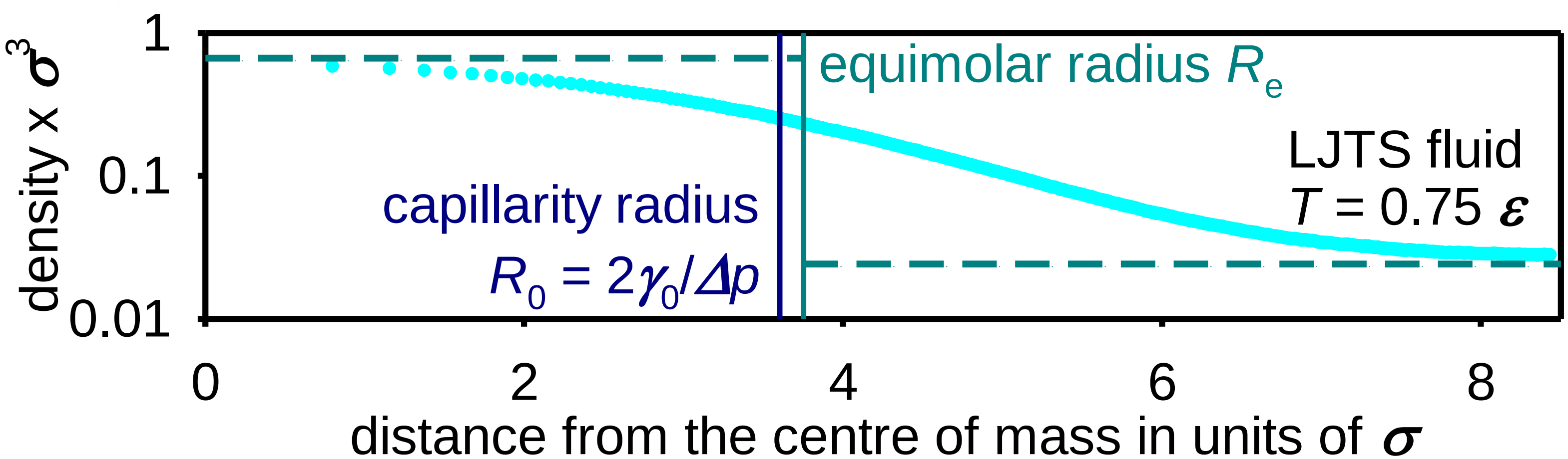
(Source: Sampayo et al., 2010)

Analysis of spherical density profiles

The approach of R. C. Tolman (1949) is based on the quantities:

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

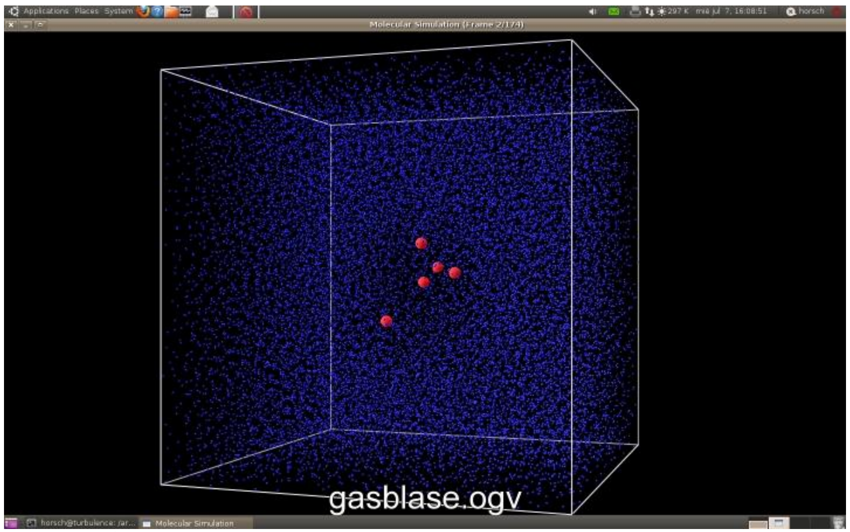
Without previous knowledge of $\gamma(R_L)$, this set of variables is inconvenient.



Novel approach: Use Δp instead of $1/R_L$, use $R_0 = 2\gamma_0/\Delta p$ instead of R_L.

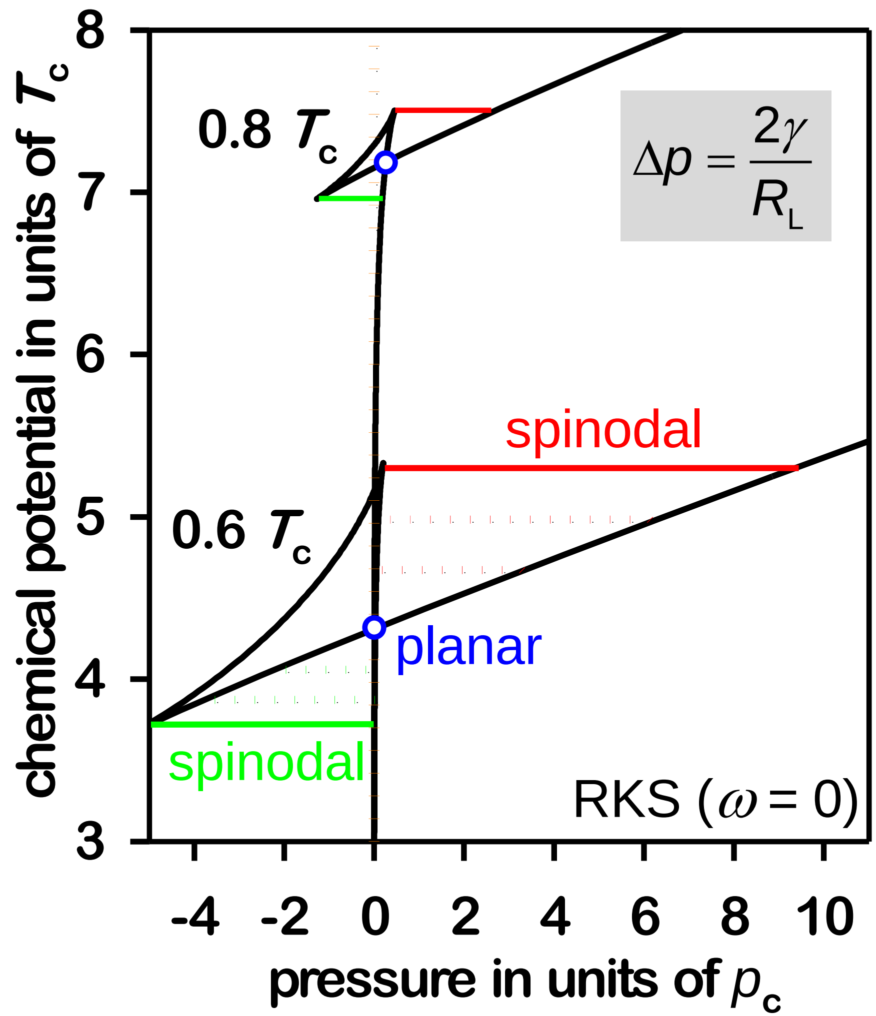
VLE at curved interfaces: Limiting cases

- Droplet + metastable vapour
- Bubble + metastable liquid

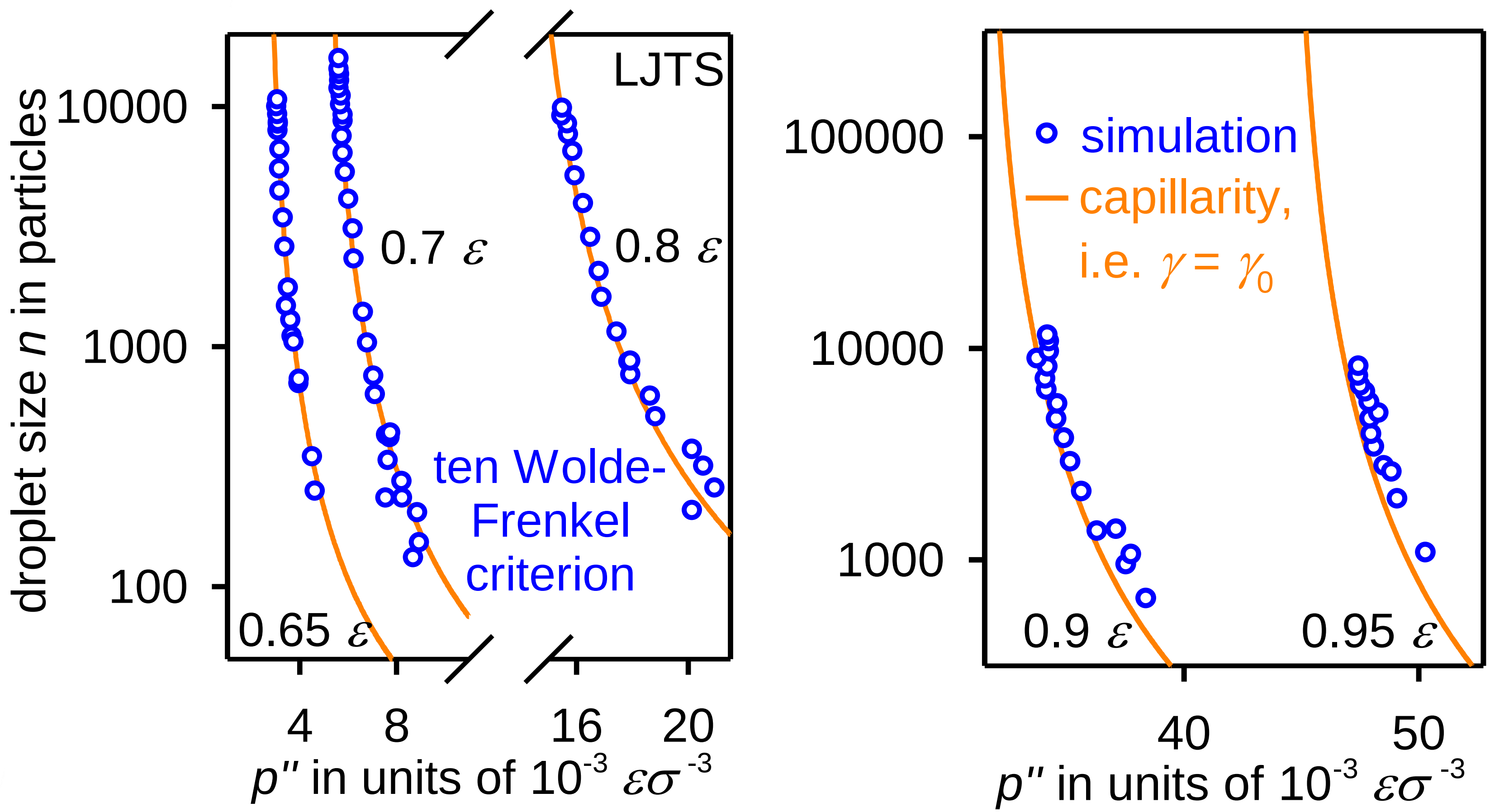


Planar limit: The curvature changes its sign and the radius R_L diverges.

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



Droplet size in equilibrium



Simulation results support the capillarity approximation for n > 1 000.

The planar limit

… for the Tolman length:

$$-\delta_0 = \frac{1}{2}\lim_{\Delta p \to 0}\frac{d(\gamma/\gamma_0)}{d(1/R_L)} = \lim_{\Delta p \to 0}\frac{d\gamma}{d(\Delta p)}$$

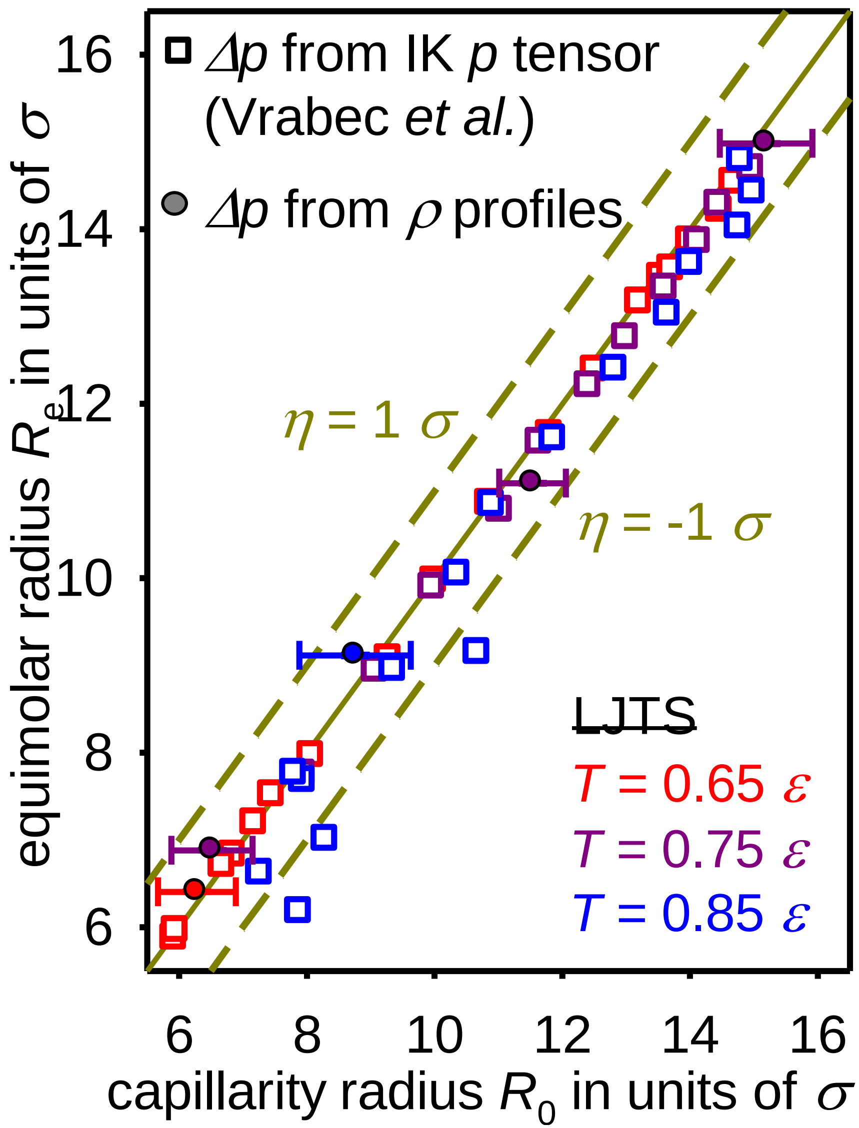
The Tolman length $\delta = R_e - R_L$ characterizes the dependence of the surface tension on curvature.

Transformation: "R_0 rather than R_L"

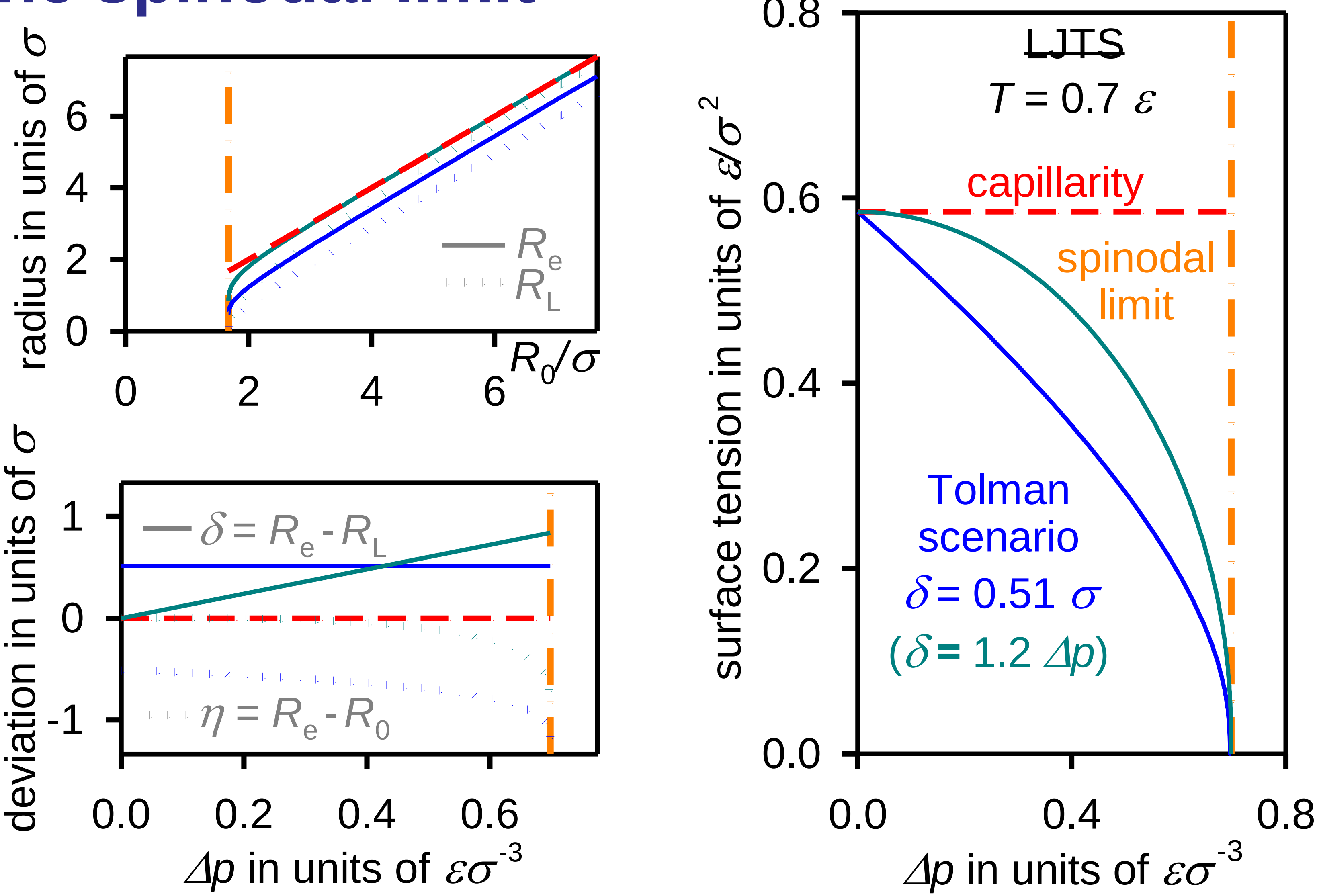
$$\delta_0 = \lim_{R_e \to \infty}(R_e - R_L) = \lim_{R_e \to \infty}(R_0 - R_e)$$

➡ Compare the radii R_0 and R_e

"excess equimolar radius" $\eta = R_e - R_0$



The spinodal limit



Conclusion

- The virial (Irving-Kirkwood) and variational (test area) approaches lead to contradictory results for the curvature dependence of γ.
- Without knowledge of the surface tension, it is impossible to determine the Laplace radius R_L of the surface of tension.
- In terms of the capillarity radius R_0 (instead of R_L) and the pressure difference Δp (instead of $1/R_\mathrm{L}$), Tolman's approach can still be applied.
- For the LJTS fluid, the planar limits of the Tolman length δ and the excess equimolar radius η are smaller in magnitude than σ.
- This result is consistent with "Tolman's scenario" ($R \to 0$ and $\gamma \to 0$) for the spinodal limit, if δ does not depend on higher powers of Δp.