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

St. Petersburg, 25th June 11

M. T. Horsch,1,2,3 S. K. Miroshnichenko,2 J. Vrabec,2 A. K. Shchekin,4 E. A. Müller,3 G. Jackson,3 and H. Hasse1

1 TU Kaiserslautern  2 Universität Paderborn  3 Imperial College  4 St. Petersburg State Univ.

DAAD  Deutscher Akademischer Austausch Dienst  German Academic Exchange Service
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**.
The Laplace equation:

Surface tension = \textit{differential} free energy per surface area

\[ dF = \gamma \, dA + dF' + dF'' \]
\[ = \gamma \, dA - \Delta p \, dV' - (S \, dT - \Delta \mu \, dN') \]

Relation between \( dV' \) and \( dA \):

\[ R_L \, dA = 2 \, dV' \]

Mechanical equilibrium:

\[ \Delta p \, dV' = \gamma \, dA \]
\[ \Delta p = \frac{2 \gamma}{R_L} \]

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

\[ \gamma = R_L^{-2} \int_{\text{in}}^{\text{out}} dz \, z^2 \left[ \rho_N(z) - \rho_T(z) \right] \]

\[ (2\gamma)^3 = -\Delta p^2 \int_{\text{in}}^{\text{out}} dp_N(z) \, z^3 \]

Irving-Kirkwood pressure tensor

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

The normal pressure \( \rho_N(z) \) decays near the Laplace radius \( R_L \).

Very significant decrease of \( \gamma \).
Variational route to the surface tension

Test area method:
Canonical partition function yields

\[ \Delta F = -T \ln\left\{ \exp\left( -\frac{\Delta U}{T} \right) \right\} \]

\[ = f\left( \langle \Delta U \rangle, \langle \Delta U^2 \rangle, \langle \Delta U^3 \rangle \right) + O\left( \langle \Delta U^4 \rangle \right) \]

For infinitesimal deformations,

\[ \gamma = \Delta F/\Delta A \quad \text{with} \quad A = 4\pi R_e^2 + O\left( R_e \right). \]

Non-linear terms represent the contribution due to fluctuations.
Small influence of curvature on \( \gamma \).
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 $\gamma$)
- Surface tension $\gamma$ as a function of $1/R_L$ (which requires $\gamma$ …)

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

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

25th June 11
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 \( n > 1000 \).
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

\[ \Delta p \text{ in units of } \varepsilon \sigma^{-3} \]

- \[ \delta = R_e - R_L \]
- \[ \eta = R_e - R_0 \]

\[ \text{deviation in units of } \sigma \]

\[ \text{radius in units of } \sigma \]

\[ \text{surface tension in units of } \frac{\varepsilon}{\sigma^2} \]

\[ T = 0.7 \varepsilon \]

Tolman scenario
\[ \delta = 0.51 \sigma \]
\[ (\delta = 1.2 \Delta p) \]

capillarity
spinodal limit

LJTS
Conclusion

• The virial (Irving-Kirkwood) and variational (test area) approaches lead to contradictory results for the curvature dependence of $\gamma$.

• 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 $\Delta p$ (instead of $1/R_L$), Tolman’s approach can still be applied.

• For the LJTS fluid, the planar limits of the Tolman length $\delta$ and the excess equimolar radius $\eta$ are smaller in magnitude than $\zeta$.

• This result is consistent with “Tolman’s scenario” ($R \to 0$ and $\gamma \to 0$) for the spinodal limit, if $\delta$ does not depend on higher powers of $\Delta p$. 