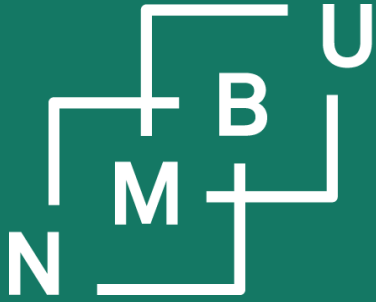# Virial and test transformation methods for the spherical surface tension: Statistical mechanical consistency and thermodynamic validity
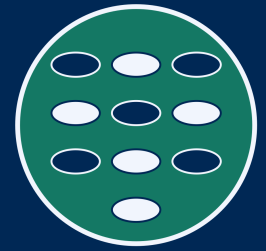
Martin Thomas Horsch
Norwegian University of Life Sciences

28th January 2025, UKRI STFC Daresbury Laboratory
CECAM Workshop on Interfacial Properties: Open Questions (IPOQ 2025)

Fakultet for realfag og teknologi   Forskergruppe materialteori og -informatikk

Gibbs' interfacial thermodynamics

Two-phase system: Total differential for the Helmholtz free energy

$$dF = \boldsymbol{\mu}\, \mathbf{dN} - p'dV' - p''dV'' - S\, dT + \gamma\, da.$$
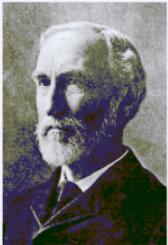
„take some point […] and **imagine a geometrical surface** to pass through this point and all other points which are similarly situated […] called the dividing surface".[1]

[1]J. W. Gibbs, *Transact. CT Acad. Arts Sci.* 3, 343 – 524, **1878**.

Thermodynamic **excess quantities** are ascribed to this dividing surface:

$$X^{\text{System}} = X^{I} + X^{II} + X^{E}.$$

The **dividing surface can be chosen freely**, and the interfacial excess properties (among others) depend on the **notion of the dividing surface**, for which we will use a subscript v.
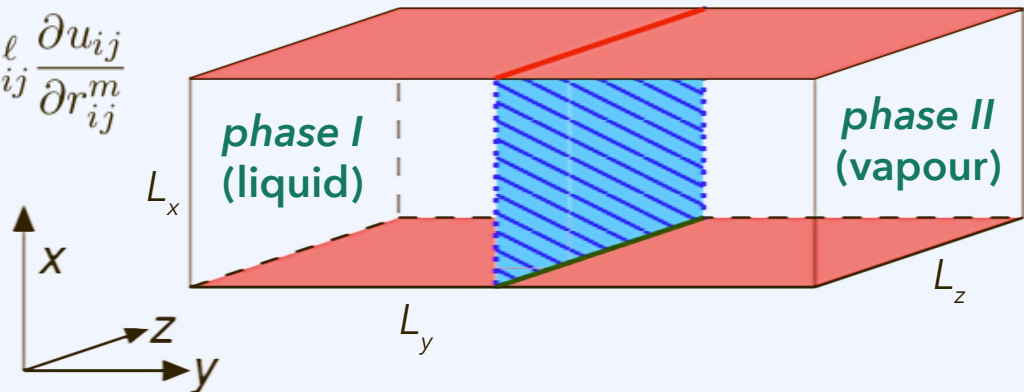
Notation: $\boldsymbol{\mu}$ and $\mathbf{N}$ are vectors (multiple components in the case of a mixture).

Molecular-level observable: The virial

$$\Pi^{\ell m} = \sum_{\{i,j\}} r_{ij}^{\ell} f_{ij}^{m} = - \sum_{\{i,j\}} r_{ij}^{\ell} \frac{\partial u_{ij}}{\partial r_{ij}^{m}}$$

phase I
(liquid)

phase II
(vapour)

L_x

L_y

L_z

Pressure tensor:

$$\mathbf{P} = \mathbf{1}\rho T + \frac{\langle \mathbf{\Pi} \rangle}{V}$$

Planar surface tension:

$$\gamma = (P_{\mathrm{n}} - P_{\mathrm{t}}) L_y$$

$$= \int_0^{L_y} [P_{\mathrm{n}}(y) - P_{\mathrm{t}}(y)]\, dy$$

planar dividing surface

liquid

vapour

molecule j

tangential

normal

molecule i

y

Non-uniqueness in the spherical case

Bakker-Buff equation: $\gamma = R^{-2} \int_0^\infty \left(P_\mathrm{n}(r) - P_\mathrm{t}(r) \right) r^2 dr$

The results from this are **not** uniquely defined!

spherical dividing surface

vapour

liquid

molecule *j*

tangential

normal

molecule *i*

normal

tangential
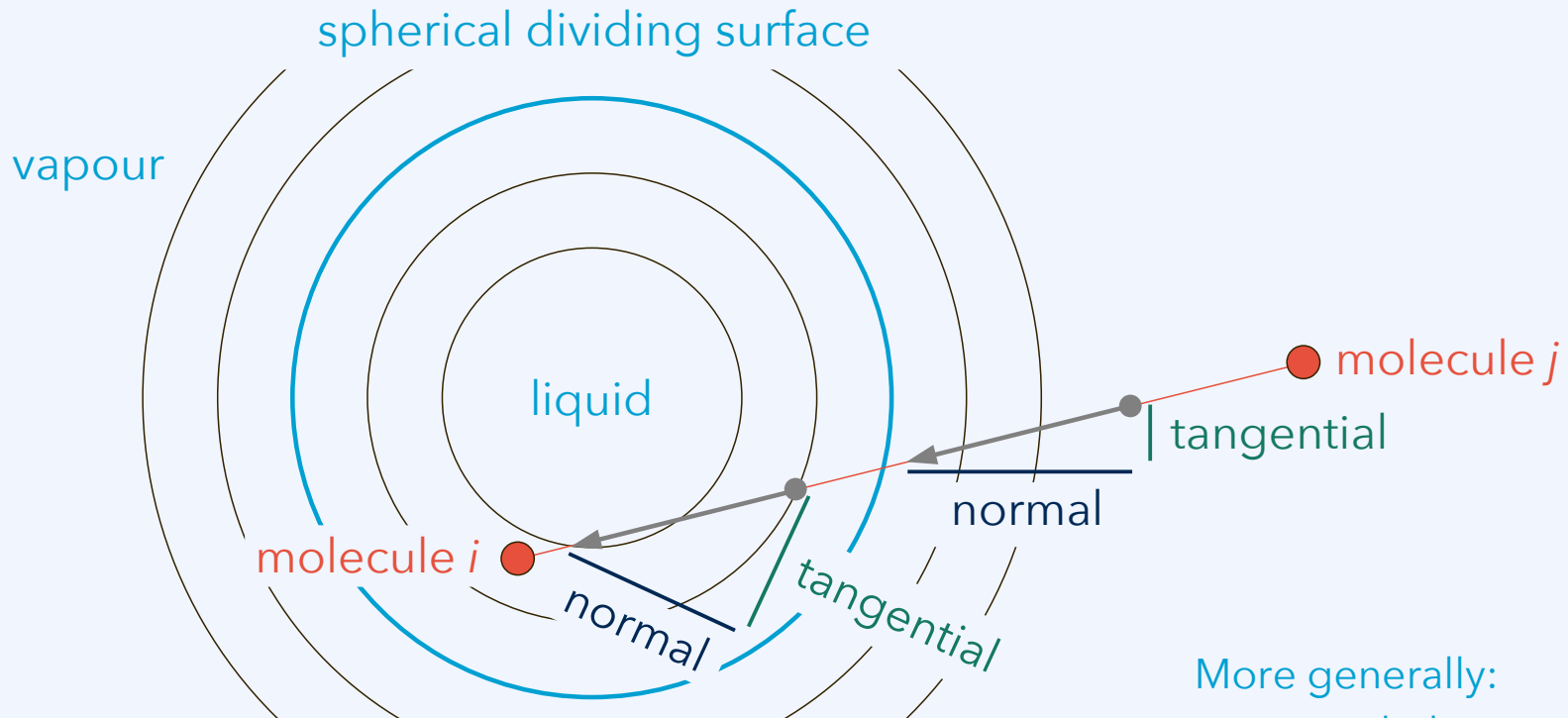
More generally:
Dispersed phase *α*
Surrounding phase *β*
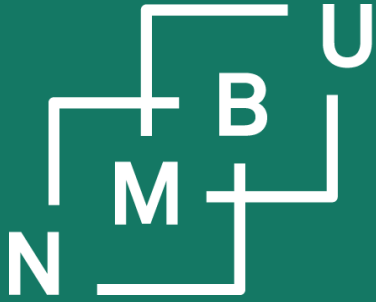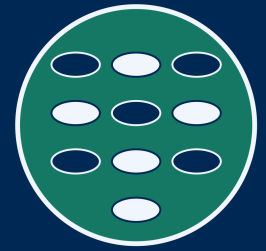
Virial & test area: Disagreement in the spherical case

Viral route over spherical profiles

Integral over pressure tensor

$T = 0.7\ \varepsilon/k$
γ_0
$T = 0.8\ \varepsilon/k$
γ_0
$T = 0.95\ \varepsilon/k$
γ_0

Virial route (LJTS fluid)

surface tension / $\varepsilon\sigma^{-2}$

droplet size (molecules)
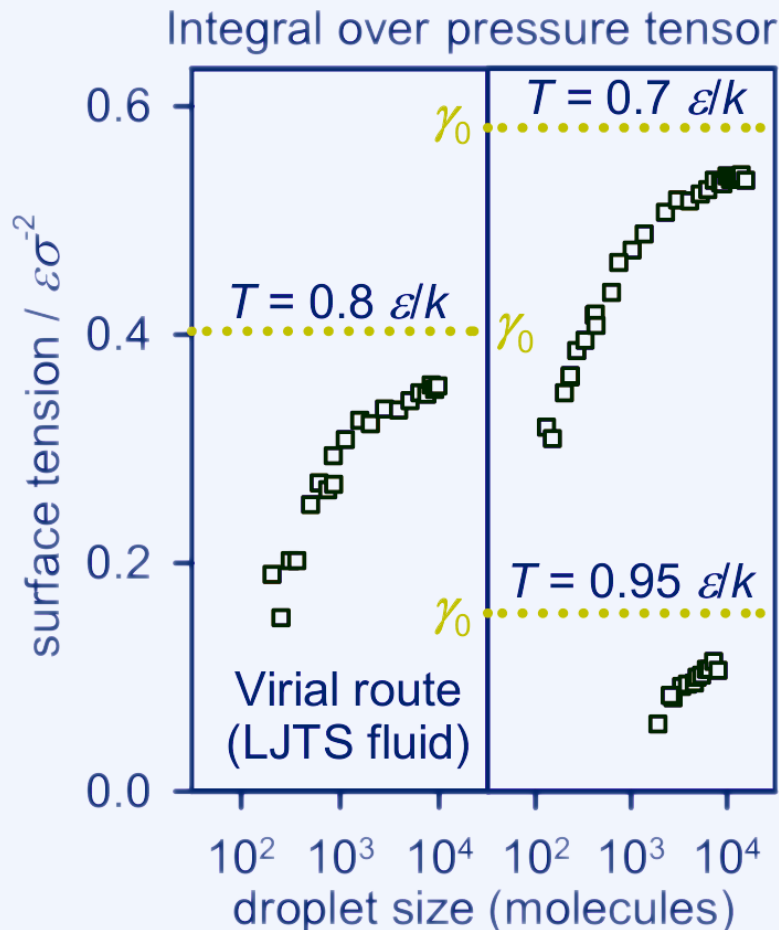
Test area – deformation of the system

□ virial route   ● test area

surface tension / $\varepsilon\sigma^{-2}$

equimolar radius / σ

$(T = 0.8\ \varepsilon/k)$
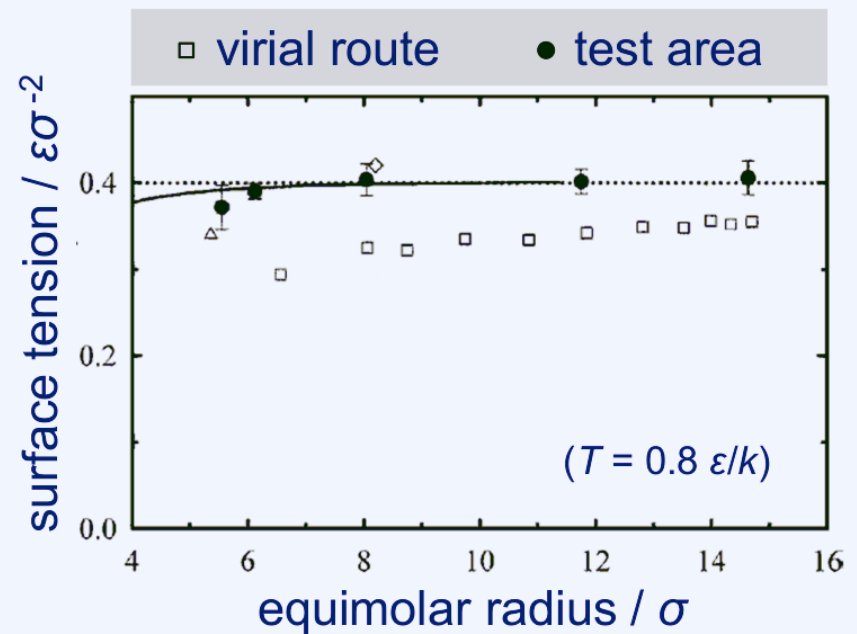
Results obtained from the two methods are clearly not in agreement with each other.

Left: Vrabec *et al.*, 2006, Horsch *et al.*, 2008.
Right: Sampayo *et al.*, 2010.

Test area method for spherical geometries[1, 2]

N, *V*, and *T*

same **N**, *V*, and *T*

dispersed
phase *α*

surrounding phase *β*

Test transformation:

$$\mathbf{q}_i \ \mapsto \ \mathbf{\Lambda}\mathbf{q}_i \ = \ \begin{pmatrix} \sqrt{1+\chi} & 0 & 0 \\ 0 & \sqrt{1+\chi} & 0 \\ 0 & 0 & 1/[1+\chi] \end{pmatrix} \mathbf{q}_i$$

Sample ΔF from potential energy change:

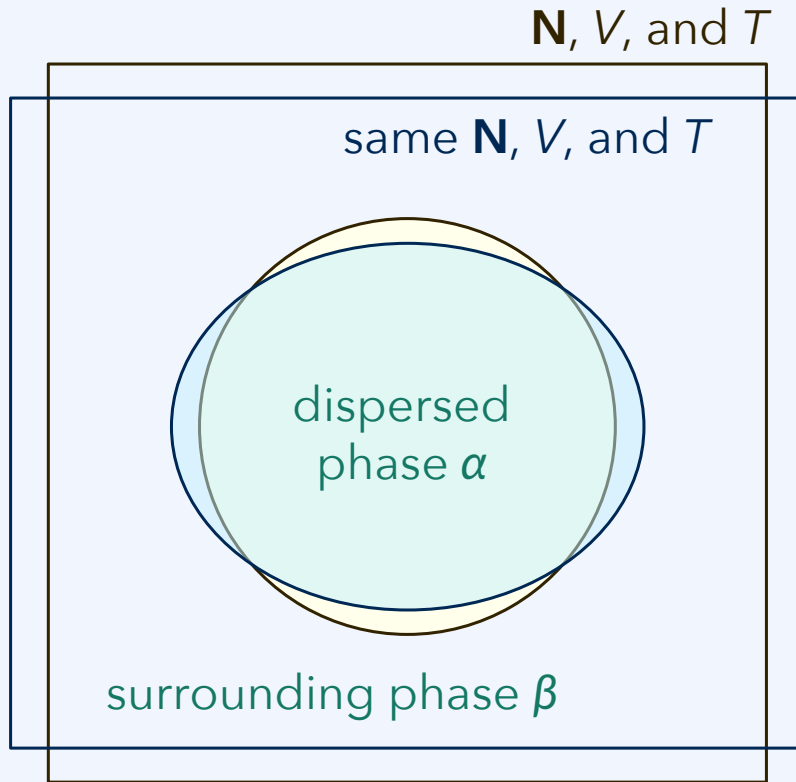$$\Delta F \ = \ \boxed{\langle \Delta U \rangle} - \boxed{\frac{1}{2T}\left(\langle \Delta U^2 \rangle - \langle \Delta U \rangle^2 \right)} + \mathcal{O}(\chi^3),$$

ΔF_1 ΔF_2

average ΔU variance of ΔU
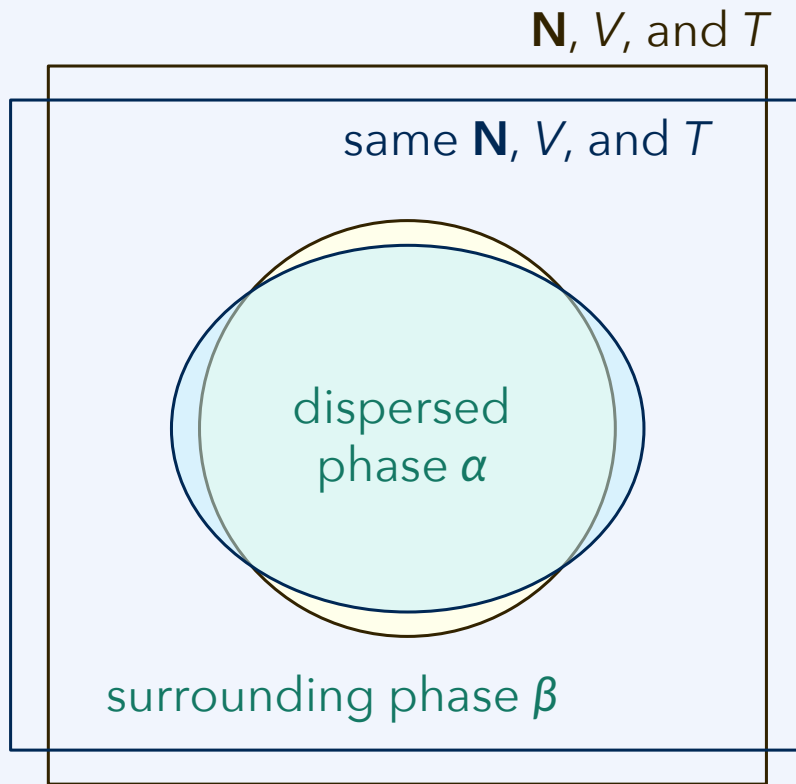
Surface change Δa is proportional to the
square distortion (different from planar case):

$$\Delta a = \frac{8\pi}{5} R^2 \chi^2 + \mathcal{O}(\chi^3)$$

[1]J. G. Sampayo, A. Malijevský, *et al.*, *J. Chem. Phys.* **132**: 141101, doi:10.1063/1.3376612, **2010**.
[2]G. V. Lau, I. J. Ford, *et al.*, *J. Chem. Phys.* **142**: 114701, doi:10.1063/1.4913371, **2015**.

Test area method for spherical geometries[1, 2]

N, *V*, and *T*

same **N**, *V*, and *T*

dispersed
phase *α*

surrounding phase *β*

Sampayo *et al.*,[1] LJTS, *T* = 0.8 *ε*

$\Delta F / \Delta a$

$\gamma^* = 0.3716$

ΔF_1

ΔF_3

$\Delta F_2 / \Delta a$

ΔF_2

Δa

$\sigma_{\Delta U}$

$\mathcal{P}(\Delta U)$

$\Delta U - \langle \Delta U \rangle$

In the planar case, the contribution from ΔF_2 is negligible. Not so for spheres.
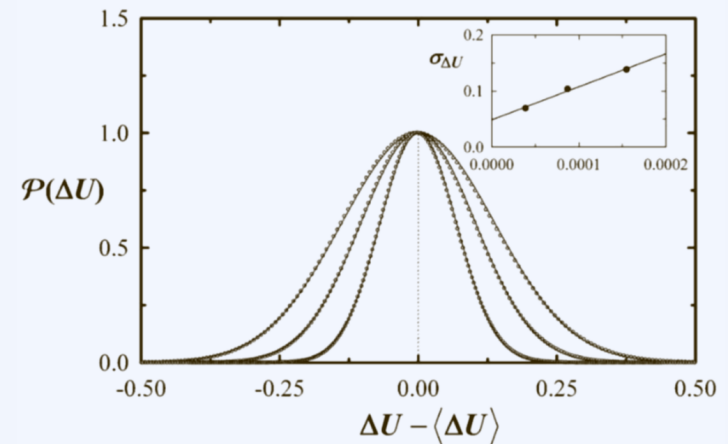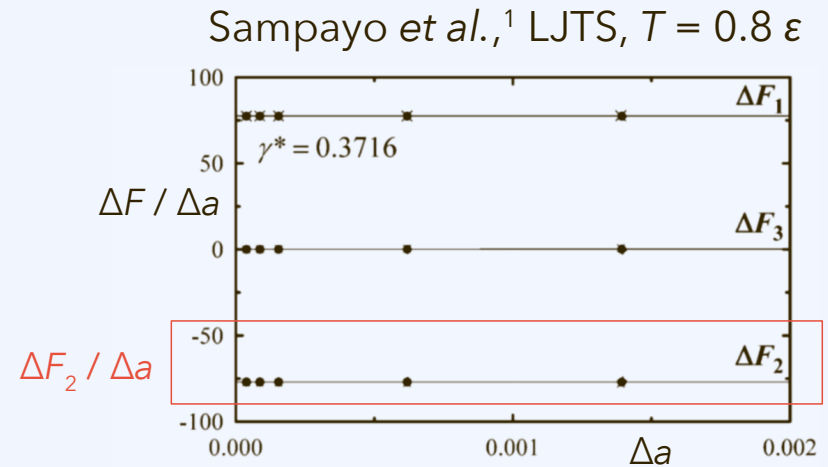
[1] J. G. Sampayo, A. Malijevský, *et al.*, *J. Chem. Phys.* **132**: 141101, doi:10.1063/1.3376612, **2010**.
[2] G. V. Lau, I. J. Ford, *et al.*, *J. Chem. Phys.* **142**: 114701, doi:10.1063/1.4913371, **2015**.

Virial route in agreement with the test area method

From the planar case, we know: Taking the limit $\chi \to 0$ for the test area method results in the virial route expression. The two are then in agreement by design.

We can do the same for the spherical case, from expressions by Lau *et al.*:[1]

$$\Delta U(\mathbf{q}) = \alpha(\mathbf{q})\chi + \beta(\mathbf{q})\chi^2 + \mathcal{O}(\chi^3)$$

this is the sampled quantity

This expansion results in:[1]

note that the leading contribution is quadratic in χ

$$\Delta F_1 = \langle \Delta U \rangle = \langle \beta \rangle \chi^2 + \mathcal{O}(\chi^3)$$

$$\Delta F_2 = -\frac{\text{Var}\,\Delta U}{2T} = -\frac{\langle \alpha^2 \rangle}{2T}\chi^2 + \mathcal{O}(\chi^3)$$

$$\left(\frac{\partial F}{\partial[\chi^2]}\right)_{\mathbf{N},V,T} = \langle \beta \rangle - \frac{\langle \alpha^2 \rangle}{2T}$$

The surface tension is obtained as:[1]

$$\gamma = \left(\frac{\partial F}{\partial[\chi^2]}\frac{\partial[\chi^2]}{\partial a}\right)_{\mathbf{N},V,T} = \frac{5\left\langle \beta - \alpha^2/2T \right\rangle}{8\pi R^2}$$

[1]G. V. Lau, I. J. Ford, *et al.*, *J. Chem. Phys.* **142**: 114701, doi:10.1063/1.4913371, **2015**.

Virial route in agreement with the test area method

We need to find the corresponding statistical mechanical observables.

For this, we introduce the *k*-th order virial tensor:

$$\Pi_k^{\ell_1\cdots\ell_{2k}}(\mathbf{q}) = \frac{(-1)^k}{k!} \sum_{\{i,j\}} r_{ij}^{\ell_1} \cdots r_{ij}^{\ell_k} \frac{\partial^k u_{ij}}{\partial r_{ij}^{\ell_{k+1}} \cdots \partial r_{ij}^{\ell_{2k}}}$$

$$\Pi_k(\mathbf{q}) = \Pi_k^{x\cdots x}(\mathbf{q}) + \Pi_k^{y\cdots y}(\mathbf{q}) + \Pi_k^{z\cdots z}(\mathbf{q})$$

The *k*-th order virial contains the *k*-th derivative of the pair potential.

Result: In a molecular simulation, the following would need to be sampled.

$$\langle \alpha^2 \rangle = \frac{1}{2} \langle \Pi_1^2 \rangle - \frac{3}{2} \sum_{\{\ell,m\}} \langle \Pi_1^{\ell\ell} \Pi_1^{mm} \rangle$$

$$\langle \beta \rangle = -\frac{1}{2} \langle \Pi_1 \rangle + \frac{1}{2} \langle \Pi_2 \rangle - \frac{1}{2} \sum_{\{\ell,m\}} \langle \Pi_2^{\ell m\ell m} \rangle$$

We need the **second-order virial tensor** Π_2, and hence, the second derivative of $u_{ij}(r_{ij})$.

The pre-existing virial-route methods are wrong because they lack this contribution.
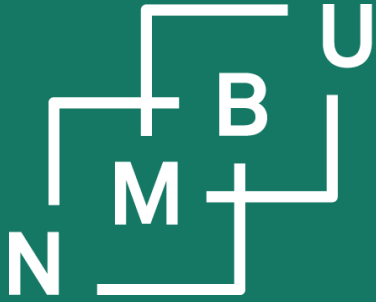
Materialteori og -informatikk
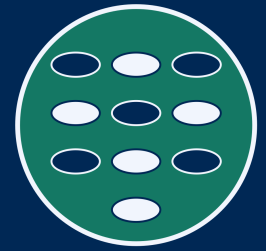
Digitalisering på Ås

Definitions of the surface tension

Excess free energy of an interface with the area *f*

macroscale

surface free energy

surface area

scale influenced by nano-effects

nanoscale

surface free energy

surface area

γ

σ

γ may depend on the surface area
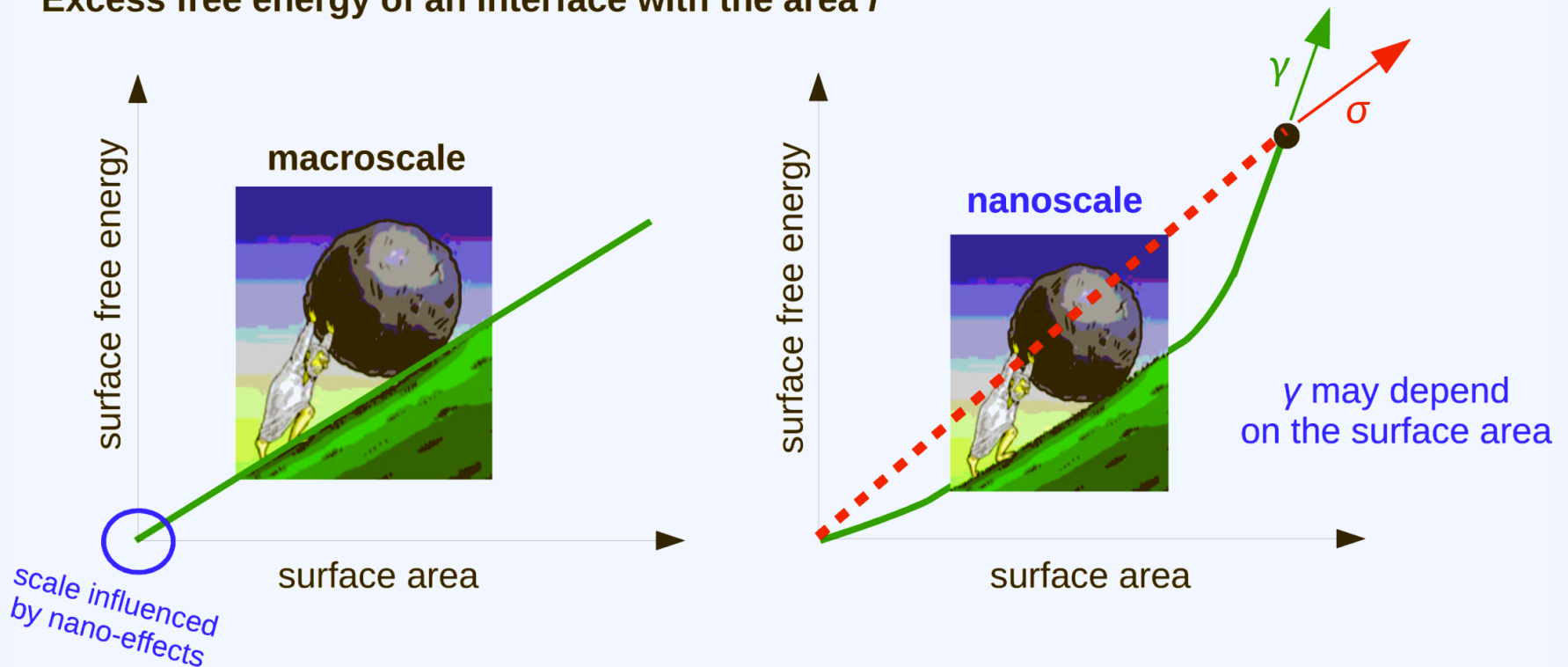
Let us denote surface tensions defined as derivatives of a thermodynamic potential by γ, and surface tensions defined as absolute excesses by σ.

Definitions of the surface tension

Recall: The notion of the dividing surface ν is represented by subscript indices.

Absolute surface tension $\sigma_\nu = \dfrac{\Omega^{\mathrm{E}}_\nu}{a_\nu}$

   – Used to define the Laplace radius ($\nu = $ L), by $\Delta P = 2\sigma_L / R_L$
   – Choosing $\nu = $ L means minimizing the absolute surface tension.[1]

Total-differential surface tension γ_ν from

$$dF = \boldsymbol{\mu}\,\mathbf{dN} - P^\alpha\,dV^\alpha_\nu - P^\beta\,dV^\beta_\nu - S\,dT + \gamma_\nu\,da_\nu$$

   – The Laplace equation $\Delta P = 2\gamma_\nu / R_\nu$ holds for any ν. Hence, $\gamma_L = \sigma_L$.

[1]S. Kondo, *J. Phys. Soc. Jap.* **10**(5): 381–386, doi:10.1143/jpsj.10.381, **1955**.

Definitions of the surface tension

Recall: The notion of the dividing surface *v* is represented by subscript indices.

Absolute surface tension $\sigma_\nu = \dfrac{\Omega_\nu^{\mathrm{E}}}{a_\nu}$

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Total-differential surface tension γ_v from

$$dF = \boldsymbol{\mu}\,\mathbf{dN} - P^\alpha\,dV_\nu^\alpha - P^\beta\,dV_\nu^\beta - S\,dT + \gamma_\nu\,da_\nu$$

- The Laplace equation $\Delta P = 2\gamma_v / R_v$ holds for any *v*. Hence, $\gamma_L = \sigma_L$.
- Note that we may not write $F(\mathbf{N}, V^\alpha, V^\beta, T, a_v)$ or $\gamma_v = (\partial F / \partial a_v)_{\mathbf{N},\,V^\alpha,\,V^\beta,\,T}$

Partial-differential surface tension $\hat{\gamma}_\nu^{\mathbb{B}} = \left(\dfrac{\partial \Omega_\nu^{\mathrm{E}}}{\partial a_\nu}\right)_{\mathbb{B}}$ for a set of variables $\mathbb{B}$.

- Only well-defined in cases where we can write $\Omega_\nu^{\mathrm{E}}(a_\nu, \mathbb{B})$

[1]S. Kondo, *J. Phys. Soc. Jap.* **10**(5): 381–386, doi:10.1143/jpsj.10.381, **1955**.

Gibbs adsorption equation

Compare the total differential

$$d\Omega \;=\; -\mathbf{N}\,\mathbf{d\mu} - P^\alpha\,dV_\nu^\alpha - P^\beta\,dV_\nu^\beta - S\,dT + \gamma_\nu\,da_\nu$$

to the differentiated form of $\Omega = -P^\alpha V_\nu^\alpha - P^\beta V_\nu^\beta + \sigma_\nu a_\nu.$

$$d\Omega \;=\; -P^\alpha\,dV_\nu^\alpha - V_\nu^\alpha\,dP^\alpha - P^\beta\,dV_\nu^\beta - V_\nu^\beta\,dP^\beta + \sigma_\nu\,da_\nu + a_\nu\,d\sigma_\nu$$

$$d\Omega \;=\; -\mathbf{N}\,\mathbf{d\mu} - P^\alpha\,dV_\nu^\alpha - P^\beta\,dV_\nu^\beta - S\,dT + \gamma_\nu\,da_\nu$$

$$0 \;=\; \mathbf{N}\,\mathbf{d\mu} - V_\nu^\alpha\,dP^\alpha - V_\nu^\beta\,dP^\beta + S\,dT + (\sigma_\nu - \gamma_\nu)da_\nu + a_\nu\,d\sigma_\nu$$

$$0 \;=\; \mathbf{N}_\nu^\alpha\,\mathbf{d\mu} - V_\nu^\alpha\,dP^\alpha + S_\nu^\alpha\,dT$$

$$0 \;=\; \mathbf{N}_\nu^\beta\,\mathbf{d\mu} - V_\nu^\beta\,dP^\beta + S_\nu^\beta\,dT$$

Gibbs-Duhem equation

$$0 \;=\; \mathbf{N}_\nu^{\mathrm{E}}\,\mathbf{d\mu} + S_\nu^{\mathrm{E}}\,dT + (\sigma_\nu - \gamma_\nu)da_\nu + a_\nu\,d\sigma_\nu$$

$$\mathbf{\Gamma}_\nu = \mathbf{N}_\nu^{\mathrm{E}}/a_\nu \qquad \zeta_\nu = S_\nu^{\mathrm{E}}/a_\nu$$

$$\gamma_{\mathrm{L}} = \sigma_{\mathrm{L}}$$

For the Laplace surface, this becomes $d\gamma_{\mathrm{L}} \;=\; -\mathbf{\Gamma}_{\mathrm{L}}\,\mathbf{d\mu} - \zeta_{\mathrm{L}}\,dT.$

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Absolute vs. total-differential surface tension[1]

The chart plots surface tension / Laplace surface tension γ_L versus radius R_v / Laplace radius R_L.

$$\frac{\gamma_v}{\gamma_L} = \frac{R_v}{R_L}$$

total-differential surface tension γ_v

absolute surface tension σ_v

$$\frac{\sigma_v}{\sigma_L} = \frac{2}{3}\frac{R_v}{R_L} + \frac{1}{3}\left(\frac{R_v}{R_L}\right)^{-2}$$

$\gamma_L = \sigma_L$
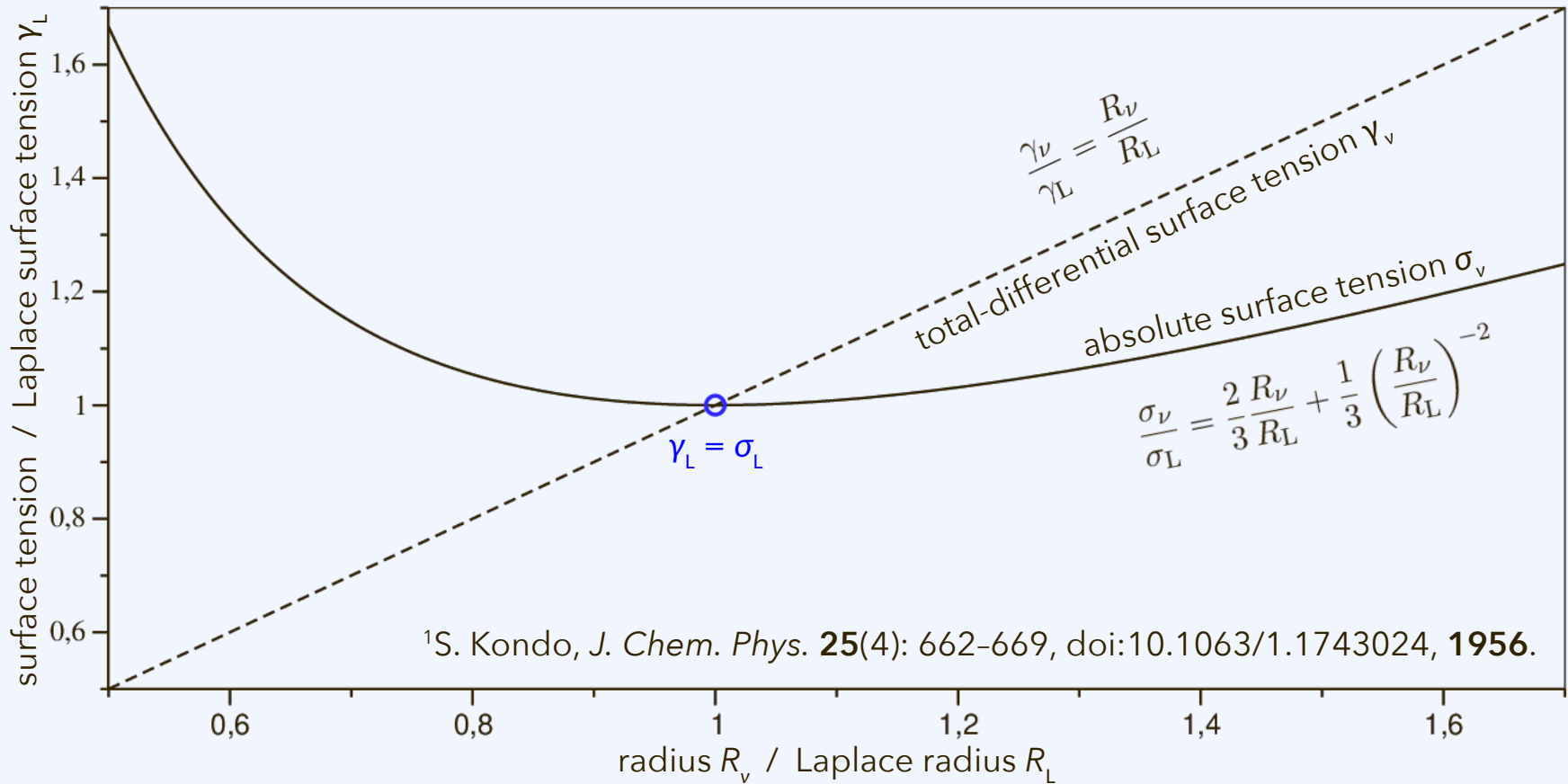
We need to find the Laplace surface tension and the Laplace radius to use the Gibbs adsorption equation, Tolman's law, and other thermodynamic identities. A simulation method must allow us to determine them … *or it is useless.*

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This all looks normal – how is it a problem?

1. **What value** are the test area and the new Π_2 method **computing**?

or this??

is it this?

$\frac{\gamma_\nu}{\gamma_L} = \frac{R_\nu}{R_L}$

total-differential surface tension γ_ν

absolute surface tension σ_ν

$\frac{\sigma_\nu}{\sigma_L} = \frac{2}{3}\frac{R_\nu}{R_L} + \frac{1}{3}\left(\frac{R_\nu}{R_L}\right)^{-2}$

some other thing ...

$\gamma_L = \sigma_L$

See also S. Kondo, *J. Chem. Phys.* **25**(4): 662–669, doi:10.1063/1.1743024, **1956**.

surface tension / Laplace surface tension γ_L
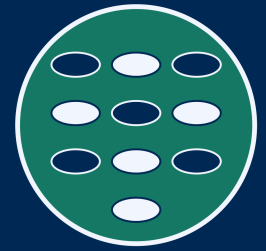
radius R_ν / Laplace radius R_L

R_e
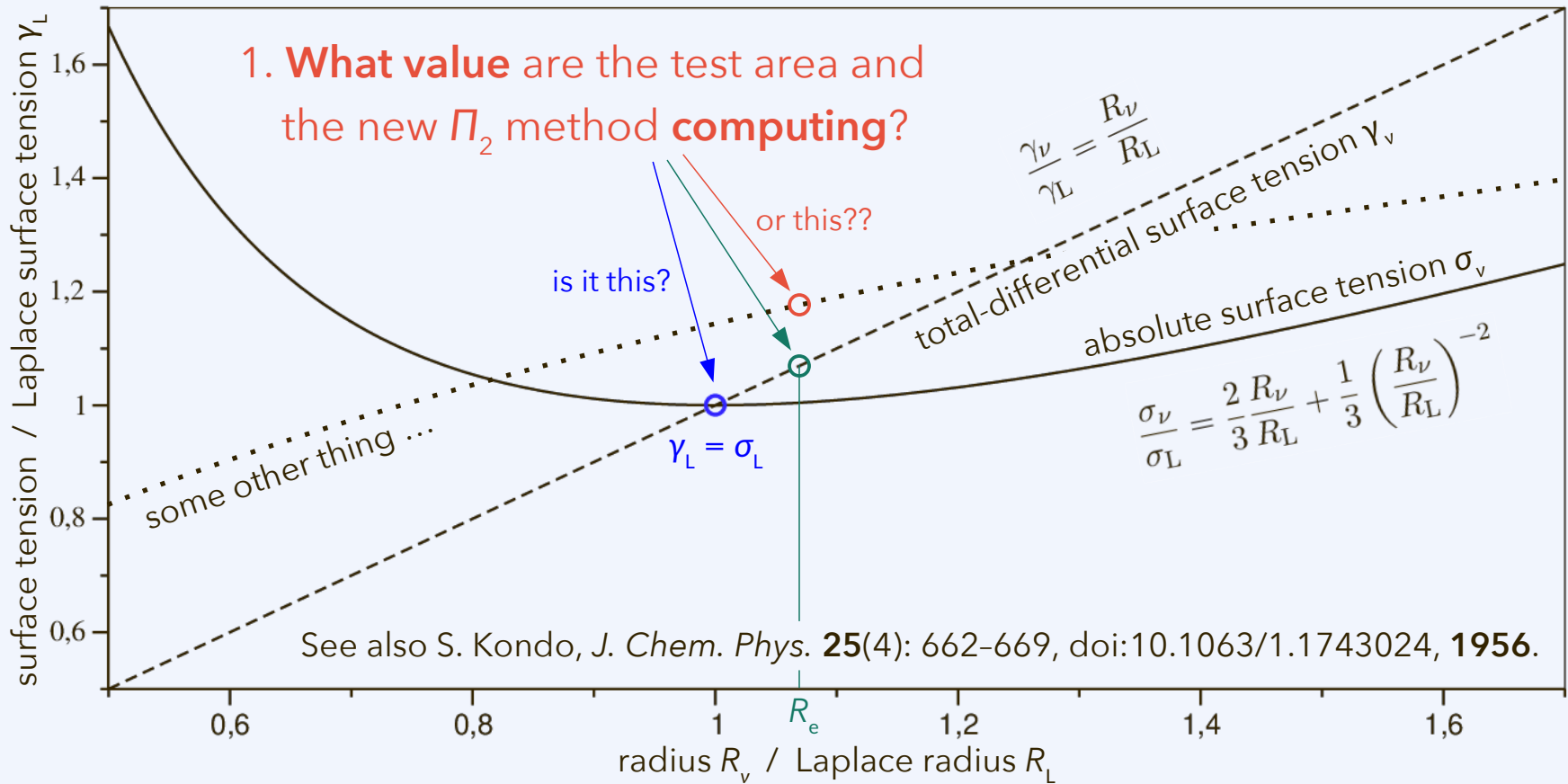
2. We are interested in the **Laplace surface tension** $\gamma_L = \sigma_L$.

3. Our methods are designed to compute a **free energy derivative**.

4. But **I could not figure out how** to express γ_L or σ_L as a free energy derivative.
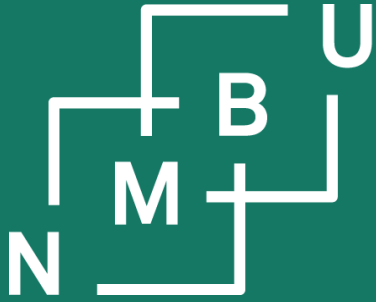
1. Background and motivation
2. Statistical mechanical perspective
3. Thermodynamic perspective
4. Interfacial properties: Open questions

Open questions

1) It looks like all approaches based on only the first-order virial are necessarily inaccurate. The proposed **second-order virial** route would no longer require the ill-defined localized virial and pressure. But it is not implemented and validated. Once implemented, we can check if it agrees with the TA method.
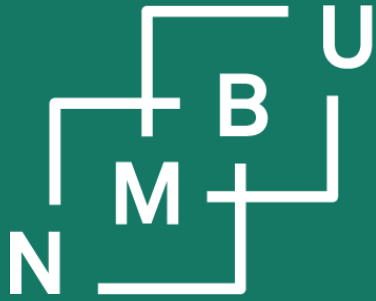
2) The TA method is empirically validated, its results make sense. It also looks like it is computing some free-energy derivative. But there is no convincing theoretical grounding for it, so far. We could attempt describing it as similar to an external field, *e.g.*, based on theory for interfaces in an electric field.

   (Suggested name: **Sampayo's demon** – the entity that establishes the distorting field.)

3) Maybe the "demon argument" is not needed, and it can still be proven that the TA method in fact computes a **partial-differential surface tension**.
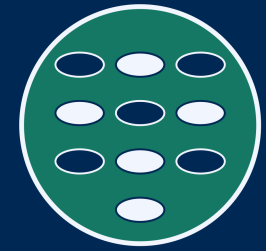
$$\hat{\gamma}_\nu^{\mathbb{B}} = \left(\frac{\partial \Omega_\nu^{\mathrm{E}}}{\partial a_\nu} \right)_{\mathbb{B}} \longleftarrow$$

Could work for $\mathbb{B} = \{\boldsymbol{\mu}, T\}$ with some $\nu \neq L$.
Then it can be proven that this is equal to γ_ν.

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