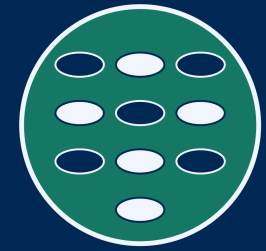




Norges miljø- og
biovitenskapelige
universitet

Materialteori og -informatikk

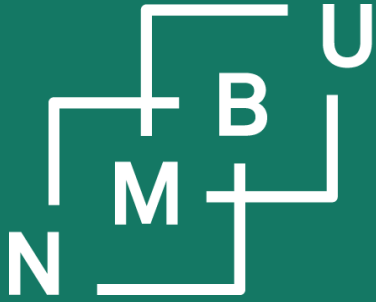


Digitalisering på Ås

Role of the frame of reference in the apparent kinetic contribution to the surface tension

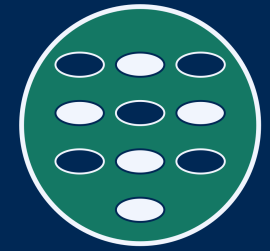
Martin Thomas Horsch
Norwegian University of Life Sciences

30th January 2025, UKRI STFC Daresbury Laboratory
CECAM Workshop on Interfacial Properties: Open Questions (IPOQ 2025)



Noregs miljø- og
biovitenskaplege
universitet

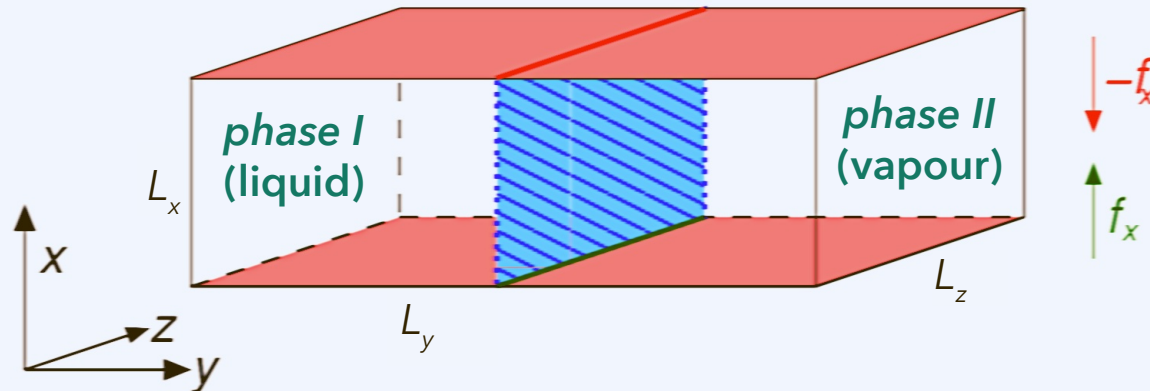
Materialteori og -informatikk



Digitalisering på Ås

1. The established view
2. *Apparent kinetic contribution*
3. *Interfacial properties: Open questions*

Surface tension: Macromechanics



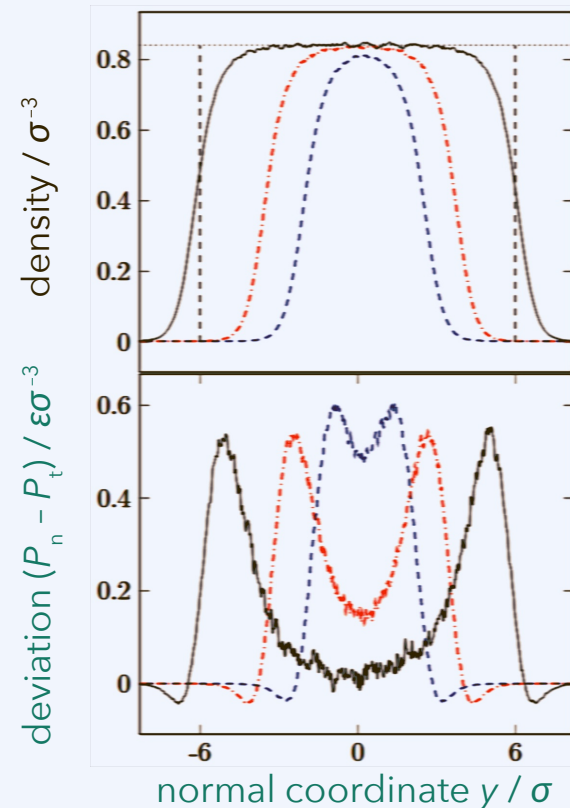
- Mechanical equilibrium \rightarrow fluid at rest, off-diagonal entries in pressure tensor are zero.
- The tangential pressure $P_t = P^{xx} = P^{zz}$ deviates from the normal pressure $P_n = P^{yy}$.
- Compared to the system boundaries perpendicular to y direction (normal direction), those in tangential direction experience an additional tangential force inward:
 - In x direction, $f_x \sim L_z$; similarly, in z direction, $f_z \sim L_x$.
 - By symmetry, the proportionality factors are equal, $f_x = -\gamma L_z$ and $f_z = -\gamma L_x$.
- For x direction, $P^{xx} - P_n = f_x / L_y L_z = -\gamma L_z / L_y L_z = -\gamma / L_y$. Therefore, $\gamma = L_y (P_n - P^{xx})$.
- The same argument applies in z direction. So we can write $\gamma = L_y (P_n - P_t)$.

From macro- to micromechanics

Using localized **pressure profiles** based on **continuum mechanics**:

$$\gamma = \int_y dy (P_n(y) - P_t(y))$$

vapour-liquid surface
tension from integral over
deviation between P_n and P_t →



LJ fluid

$T = 0.7 \epsilon$

from S. Werth
et al., *Phys. A*
392: 2359,
2013.

Compare the expression using the pressure P_n and P_t for the whole system:

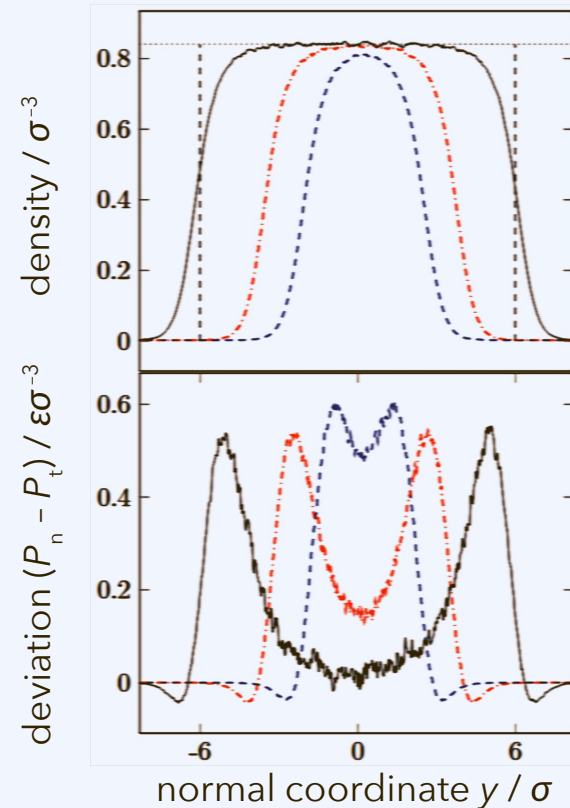
- For x direction, $P^{xx} - P_n = f_x / L_y L_z = -\gamma L_z / L_y L_z = -\gamma / L_y$. Therefore, $\gamma = L_y (P_n - P^{xx})$.
- The same argument applies in z direction. So we can write $\gamma = L_y (P_n - P_t)$.

Grounding in statistical mechanics

Using localized **pressure profiles** based on **continuum mechanics**:

$$\gamma = \int_y dy (P_n(y) - P_t(y))$$

In a **particle-based system**, localized (continuum) pressures are **not uniquely defined**. But their volume integral is uniquely defined, and therefore γ is as well - in the case of a planar interface.



LJ fluid

$T = 0.7 \epsilon$

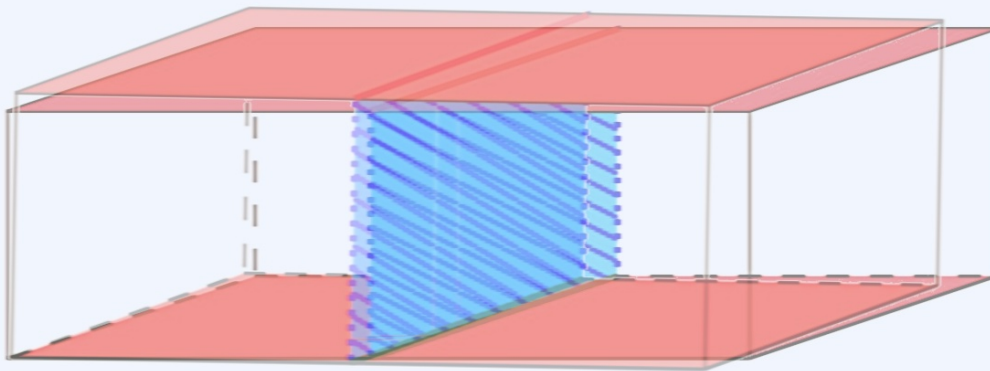
from S. Werth
et al., *Phys. A*
392: 2359,
2013.

Pressure obtained as $P_n = \rho T + V^{-1} \langle \Pi_n \rangle$ and $P_t = \rho T + V^{-1} \langle \Pi_t \rangle$.

- Therein, Π is the virial, $\Pi_n = \Pi^{yy} = \sum_{\{i,j\}} r_{ij,y} f_{ij,y}$ and $\Pi_t = \Pi^{xx} = \sum_{\{i,j\}} r_{ij,x} f_{ij,x}$.
- Since $V = aL_y$, where a is the surface area, $\gamma = a^{-1} (\langle \Pi_n \rangle - \langle \Pi_t \rangle)$. **Note that ρT cancels out!**
- While the virial for the whole system is uniquely defined, the local profiles are not.

Grounding in statistical mechanics

One way of obtaining a statistical mechanical expression for the surface tension is through a hypothetical **infinitesimal test transformation**:



canonical ensemble

- \mathbf{N} , V and T constant
- V' and V'' (liq, vap) constant
- Surface area a changes

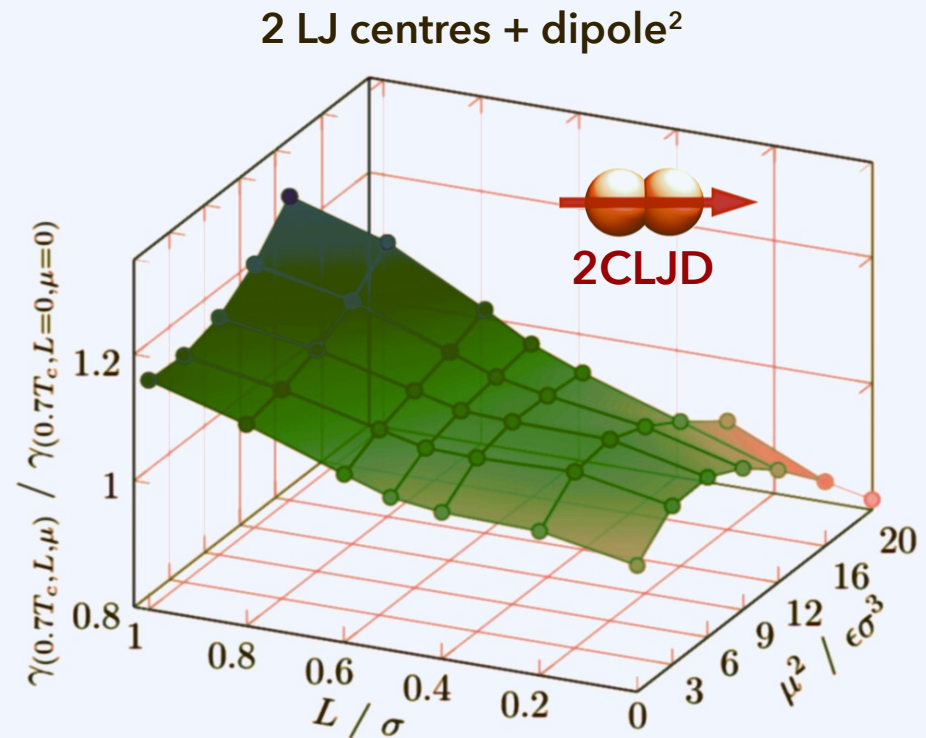
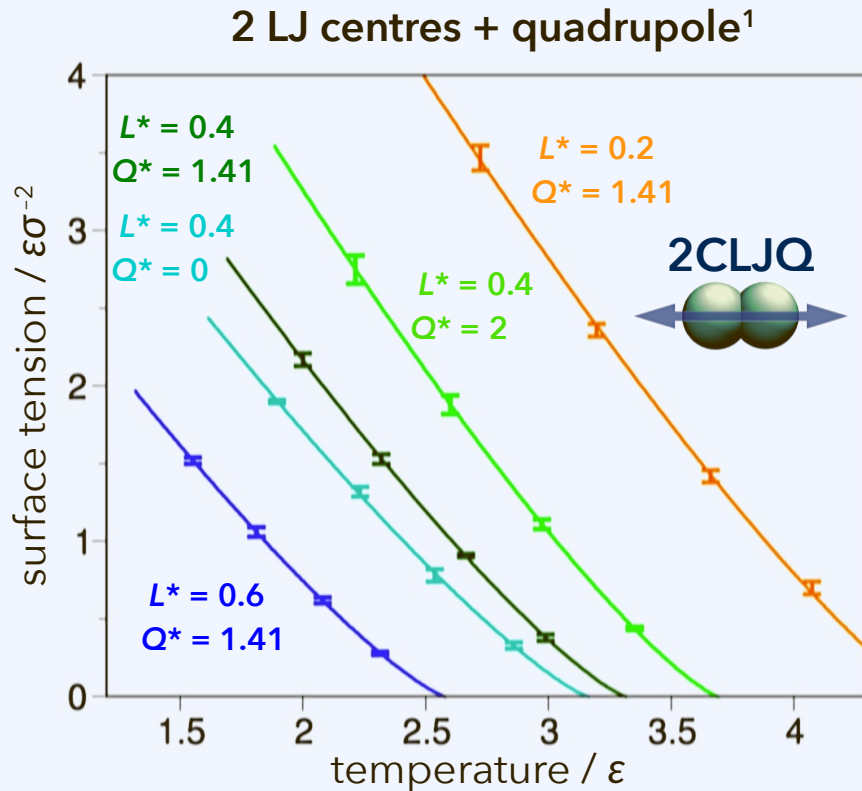
$$\gamma = \left(\frac{\partial F}{\partial a} \right)_{\mathbf{N}, V', V'', T}$$

For a system of point masses, this leads to the **same result as the argument from mechanics**, $\gamma = a^{-1} (\langle \Pi_n \rangle - \langle \Pi_t \rangle)$; there is no contribution from ρT .

Pressure obtained as $P_n = \rho T + V^{-1} \langle \Pi_n \rangle$ and $P_t = \rho T + V^{-1} \langle \Pi_t \rangle$.

- Therein, Π is the virial, $\Pi_n = \Pi^{yy} = \sum_{\{i,j\}} r_{ij,y} f_{ij,y}$ and $\Pi_t = \Pi^{xx} = \sum_{\{i,j\}} r_{ij,x} f_{ij,x}$.
- Since $V = aL_y$, where a is the surface area, $\gamma = a^{-1} (\langle \Pi_n \rangle - \langle \Pi_t \rangle)$. **Note that ρT cancels out!**
- While the virial for the whole system is uniquely defined, the local profiles are not.

Rigid multisite models: Surface tension



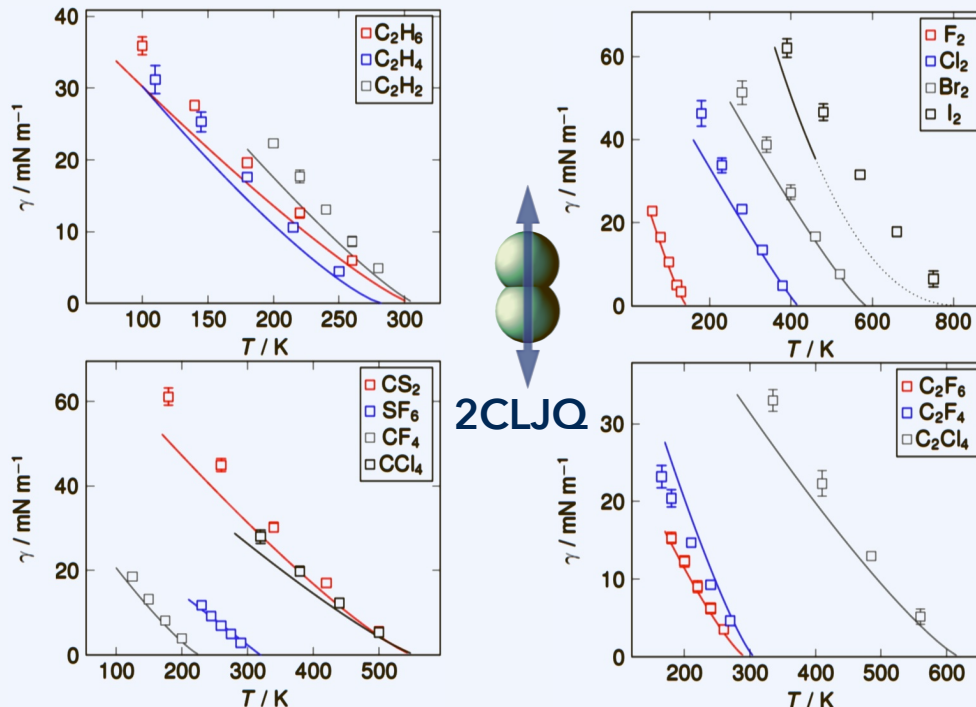
- Systematic exploration of the physically relevant part of the model parameter space
- Correlation of the 2LJQ and 2LJD surface tension by critical-scaling expressions

¹S. Werth *et al.*, *Chem. Eng. Sci.* **121**: 110–117, doi:10.1016/j.ces.2014.08.035, **2015**.

²S. Werth, M. Horsch, H. Hasse, *J. Chem. Phys.* **144**: 054702, doi:10.1063/1.4940966, **2016**.

Accuracy of surface tension from molecular models

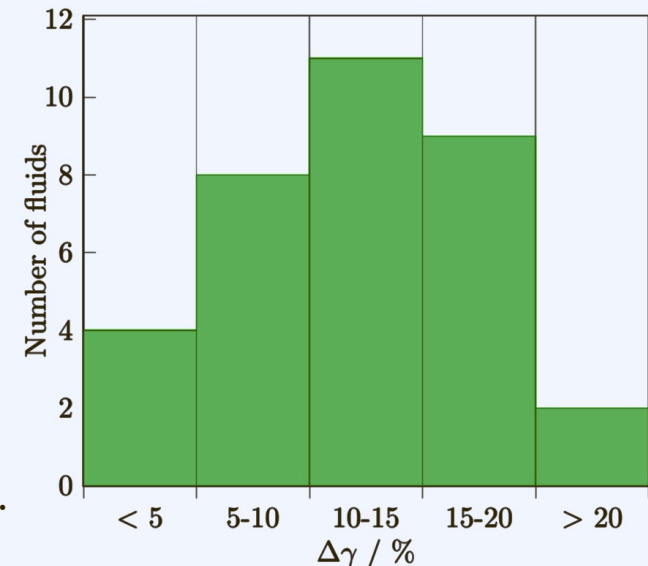
2 LJ centres + quadrupole¹



Models (squares) overestimate surface tension from experiment (lines: correlations from DIPPR).

Deviation between surface tension of the models and correlated experimental data:

2 LJ centres + dipole²



¹S. Werth *et al.*, *Chem. Eng. Sci.* **121**: 110-117, doi:10.1016/j.ces.2014.08.035, **2015**.

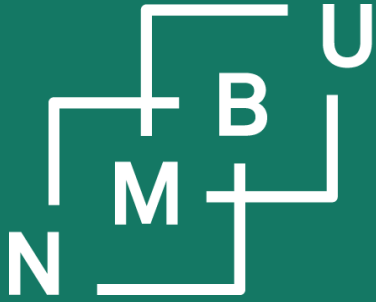
²S. Werth, M. Horsch, H. Hasse, *J. Chem. Phys.* **144**: 054702, doi:10.1063/1.4940966, **2016**.

Accuracy of surface tension from molecular models

Models' overestimation of γ by different model classes on average:

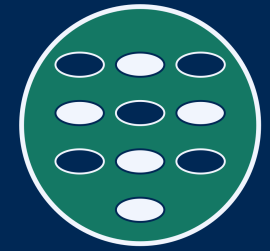
<p>Dipolar: 2CLJD</p> <p>Carbon monoxide (CO) R11 (CFCl₃) R12 (CF₂Cl₂) R13 (CF₃Cl) R13B1 (CBrF₃) R22 (CHF₂Cl) R23 (CHF₃) R41 (CH₃F) R123 (CHCl₂-CF₃) R124 (CHFCl-CF₃) R125 (CHF₂-CF₃) R134a (CH₂F-CF₃) R141b (CH₃-CFCl₂) R142b (CH₃-CF₂Cl) R143a (CH₃-CF₃) R152a (CH₃-CHF₂) R40 (CH₂Cl) R40B1 (CH₃Br) Methyl iodide (CH₃I) R30B1 (CH₂BrCl) R20 (CHCl₃) R20B3 (CHBr₃) R21 (CHFCl₂) R32 (CH₂F₂) R30 (CH₂Cl₂)</p>	<p>12 %</p>	<p>Dipolar: 2CLJD (contd.)</p> <p>R30B2 (CH₂Br₂) Methylene iodide (CH₂I₂) R12B2 (CBr₂F₂) R12B1 (CBrClF₂) R10B1 (CBrCl₃) R161 (CH₂F-CH₃) R150a (CHCl₂-CH₃) R140 (CHCl₂-CH₂Cl) R140a (CCl₃-CH₃) R130a (CH₂Cl-CCl₃) R160B1 (CH₂Br-CH₃) R150B2 (CHBr₂-CH₃) R131b (CH₂F-CCl₃) R123B1 (CHClBr-CF₃) R112a (CCl₂-CF₂Cl) R1141 (CHF=CH₂) R1132a (CF₂=CH₂) R1140 (CHCl=CH₂) R1122 (CHCl=CF₂) R1113 (CFCl=CF₂) R1113B1 (CFBr=CF₂)</p> <p>Quadrupolar: 2CLJQ</p> <p>Fluorine (F₂) Chlorine (Cl₂) Bromine (Br₂) Iodine (I₂) Nitrogen (N₂) Oxygen (O₂) Carbon dioxide (CO₂)</p>	<p>20 %</p>	<p>Quadrupolar: 2CLJQ (contd.)</p> <p>Carbon disulfide (CS₂) Ethane (C₂H₆) Ethylene (C₂H₄) Acetylene (C₂H₂) R116 (C₂F₆) R1114 (C₂F₄) R1110 (C₂Cl₄) Propadiene (CH₂=C=CH₂) Propyne (CH₃-C≡CH) Propylene (CH₃-CH=CH₂) R846 (SF₆) R14 (CF₄) R10 (CCl₄) R113 (CFCl₂-CF₂Cl) R114 (CF₂Cl-CF₂Cl) R115 (CF₃-CF₂Cl) R134 (CHF₂-CHF₂) R150B2 (CH₂Br-CH₂Br) R114B2 (CBrF₂-CBrF₂) R1120 (CHCl=CCl₂)</p> <p>Multi-site models</p> <p>Isobutane (C₄H₁₀) Cyclohexane (C₆H₁₂) Methanol (CH₃OH) Ethanol (C₂H₅OH) Formaldehyde (CH₂=O) Dimethylether (CH₃-O-CH₃) Acetone (C₃H₆O)</p>	<p>22 %</p>	<p>Multi-site models (contd.)</p> <p>Ammonia (NH₃) Methylamine (NH₂-CH₃) Dimethylamine (CH₃-NH-CH₃) R227ea (CF₃-CHF-CF₃) Sulfur dioxide (SO₂) Ethylene oxide (C₂H₄O) Dimethylsulfide (CH₃-S-CH₃) Hydrogen cyanide (HCN) Acetonitrile (NC₂H₃) Thiophene (SC₄H₄) Nitromethane (NO₂CH₃) Phosgene (COCl₂) Benzene (C₆H₆) Toluene (C₇H₈) Chlorobenzene (C₆H₅Cl) Dichlorobenzene (C₆H₄Cl₂) Cyclohexanol (C₆H₁₁OH) Cyclohexanone (C₆H₁₀O) Cyanogen (C₂N₂) Cyanogen chloride (CClN) Formic acid (CH₂O₂) Ethylene glycol (C₂H₆O₂) Water (H₂O) Hydrazine (N₂H₄) Methylhydrazine (CH₃N₂) Dimethylhydrazine (C₂H₈N₂) Perfluorobutane (C₄F₁₀) Ethyl acetate (C₄H₈O₂) Hexamethyldisiloxane (C₆H₁₂OSi₂) Octamethylcyclotetrasiloxane (C₈H₂₄O₄Si₄)</p>
---	--------------------	--	--------------------	--	--------------------	--

1. If the employed method was wrong, all this work (and more) must be redone!
2. If the models' actual surface tension is greater, the models are even worse!



Noregs miljø- og
biovitenskaplege
universitet

Materialteori og -informatikk

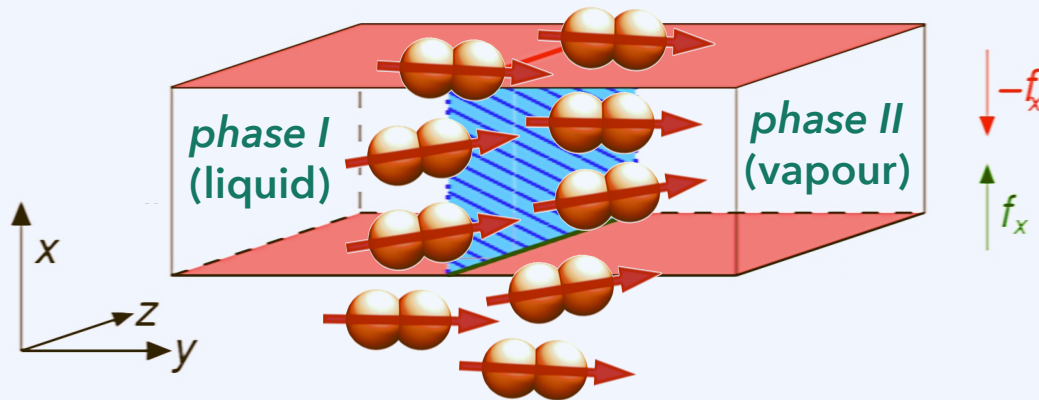


Digitalisering på Ås

1. The established view
2. Apparent kinetic contribution
3. *Interfacial properties: Open questions*

The apparent kinetic contribution¹

At interfaces, there can be a **preferred orientation**:



Assume, e.g., most molecules are arranged normal to the interface, where the models are rigid. The **rotation** then contributes much more to **motion in tangential direction** than normal direction.

$$p_{ab} = \frac{2}{V} \left(\frac{1}{2} \sum_i m_i v_i^a v_i^b - \Xi_{ab} \right)$$

micromechanical pressure following Segal *et al.*²

If, as they claim, this is the right definition:

- all our simulations were wrong
- models might become worse

Segal *et al.*^{1,2} distinguish:

surface tension γ^{Ξ} computed using the **virial tensor only** (which, they claim, is inaccurate)

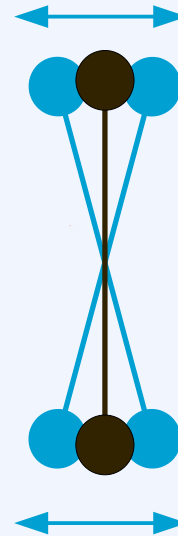
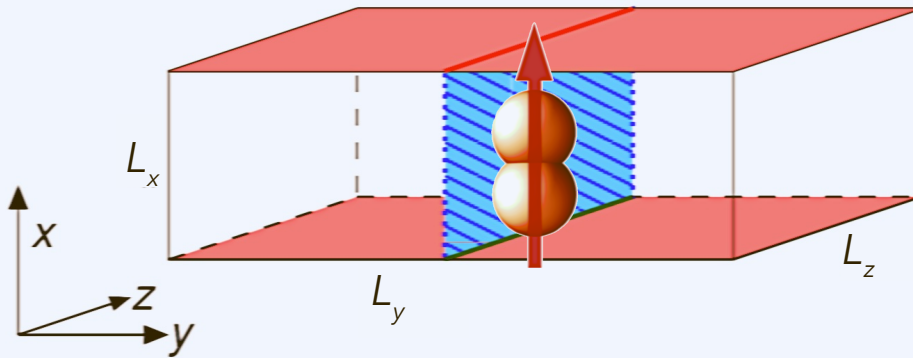
surface tension γ^p computed using the **micromechanical pressure tensor**

¹M. Segal, B. Fábián, P. Jedlovsky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcl.7b01024, **2017**.

²M. Segal, G. Horvai, P. Jedlovsky, *J. Mol. Liq.* **262**: 58–62, doi:10.1016/j.molliq.2018.04.004, **2018**.

The argument from intuition

Case 1: Tangential orientation preferred.

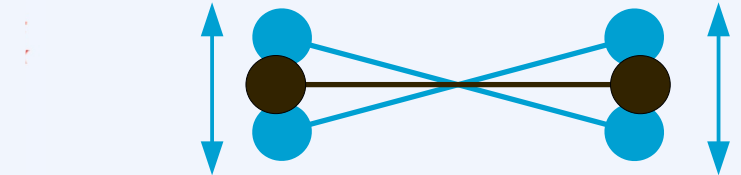
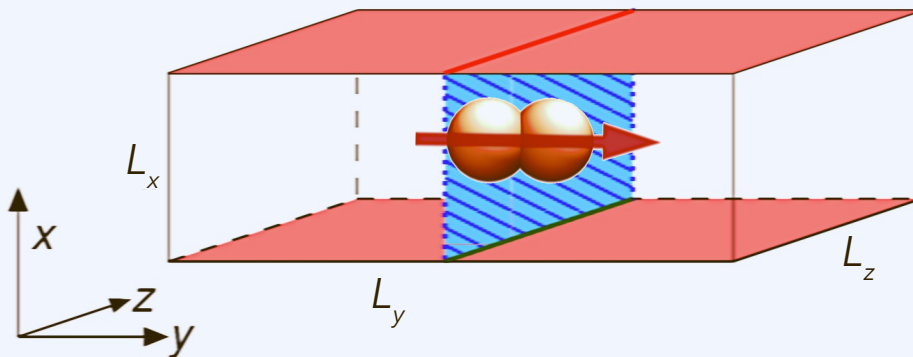


Rotation contributes most to *normal motion* of sites.

Kinetic energy and micro-mechanical pressure in tangential direction are lowest.

This works *with surface tension*, so that γ is increased.

Case 2: Normal orientation preferred.



Rotation contributes most to *tangential motion* of sites.

This works *against surface tension*, so that γ is reduced.

The argument¹ according to Lbadaoui-Darvas et al.²

The argument is presented by M. Lbadaoui-Darvas et al.² as follows:

*“Although the virial route has the advantage that it only requires molecular coordinates [...] while for the pressure route velocities are also needed, the underlying assumption is not always true [...]. Namely, the **equipartition theorem states that the average of the total energy of the particles (i.e., the sum of their potential and kinetic energies) rather than the kinetic energy itself is distributed evenly along all spatial directions.**”*

$$p_{\alpha\beta} = \frac{1}{V} \left(\sum_i m_i v_i^\alpha v_i^\beta + \left\langle \sum_{ij} f_{ij}^\alpha \int_{C_{ij}} \delta(\mathbf{r} - \mathbf{s}) ds^\beta \right\rangle \right) \quad (3)$$

Sega et al.¹ distinguish:

surface tension $\gamma^{\bar{}}$ which, using the

statistical-mechanical pressure, is $L_y(P_n - P_t)$

surface tension γ^p which, using the

micromechanical pressure, is $L_y(P_n - P_t)$

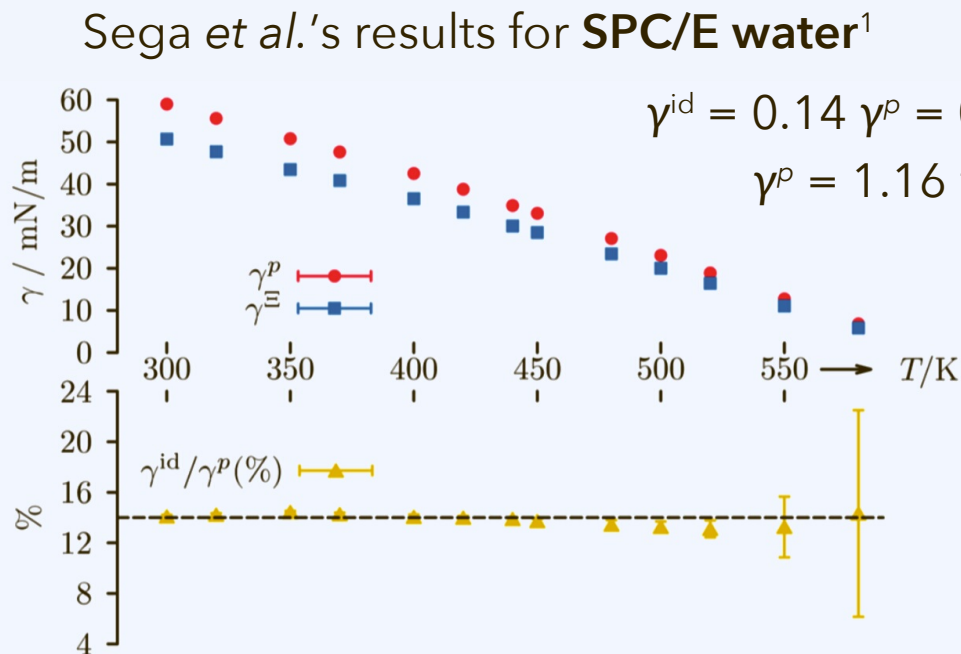
pressure tensor following
Lbadaoui-Darvas et al.²

(just another notation for
the **micromechanical**
pressure tensor observable)

¹M. Sega, B. Fábíán, P. Jedlovsky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcl.7b01024, **2017**.

²M. Lbadaoui-Darvas et al., *J. Phys. Chem. B* **126(4)**: 751–765, doi:10.1021/acs.jp.1c08553, **2022**. 13

Magnitude of the apparent kinetic contribution¹



For SPC/E water, Sega *et al.*¹ obtain a surface tension γ^{p} that is increased by 16% over γ^{E} .

vapour-liquid surface tension from integral over deviation between P_n and P_t

Figure 3. Upper panel: surface tension γ^{p} and virial contribution γ^{E} as a function of temperature. Lower panel: ratio $\gamma^{\text{id}}/\gamma^{\text{p}} = 1 - \gamma^{\text{E}}/\gamma^{\text{p}}$. Error bars are always smaller than the symbols in the upper panel and are for all temperatures of the order of 0.1–0.2 mN/m.

¹M. Sega, B. Fábián, P. Jedlovszky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcllett.7b01024, **2017**.

Magnitude of the apparent kinetic contribution¹

Homes *et al.*'s results for the **2CLJQ fluid**³

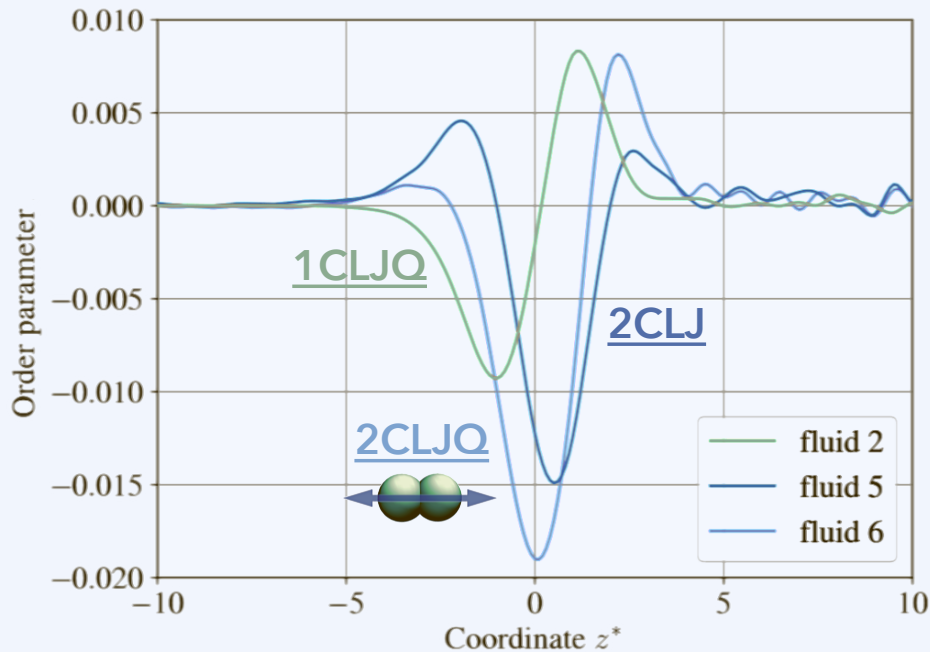


FIG. 10. Profiles of the order parameter of three fluids over the spatial coordinate z^* , where the interface is at $z^* = 0$. The shown simulations were conducted with a reduced bulk liquid temperature $T_{liq}/T_c = 0.7$ and a hydrodynamic velocity $v_z^* = 0.1$.

order parameter^{2,3}

$$\langle 3 \cos^2 \theta - 1 \rangle / 2$$

(evaporation, not equilibrium)

For SPC/E water, Sega *et al.*¹ obtain a surface tension γ^p that is increased by 16% over $\gamma^{\bar{}}$.

Orientation profiles for Stockmayer and 2CLJD done by Mecke *et al.*² long ago.

Results from Homes *et al.*³ on 2CLJ and 2CLJQ.

¹M. Sega, B. Fábián, P. Jedlovsky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcllett.7b01024, **2017**.

²M. Mecke, J. Fischer, J. Winkelmann, *J. Chem. Phys.* **114(13)**: 5842–5852, doi:10.1063/1.1349177, **2001**.

³S. Homes, M. Heinen, J. Vrabec, *Phys. Fluids* **35**: 052111, doi:10.1063/5.0147306, **2023**.

Pressure-tensor observables

From work preceding Segá *et al.*,¹ two different expressions were often used for the *microscopic pressure-tensor observable* in the literature:

statistical-mechanical

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

where $\mathbf{\Pi} = \sum_{\{i,j\}} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$

micromechanical

$$\mathbf{P} = V^{-1}\langle \mathbf{K} + \mathbf{\Pi} \rangle$$

where $\mathbf{\Pi} = \sum_{\{i,j\}} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$ and $\mathbf{K} = \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i$

The two definitions were thought of as equivalent. The merit of the Segá *et al.*¹ paper consists in showing that, for rigid multi-site models, there is a deviation.

¹M. Segá, B. Fábíán, P. Jedlovsky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcllett.7b01024, **2017**.

Pressure-tensor observables

From work preceding Sega *et al.*,¹ two different expressions were often used for the *microscopic pressure-tensor observable* in the literature:

statistical-mechanical

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

where $\mathbf{\Pi} = \sum_{\{i,j\}} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$

micromechanical

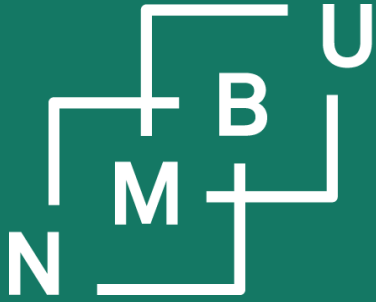
$$\mathbf{P} = V^{-1}\langle \mathbf{K} + \mathbf{\Pi} \rangle$$

where $\mathbf{\Pi} = \sum_{\{i,j\}} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$ and $\mathbf{K} = \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i$

The two definitions were thought of as equivalent. The merit of the Sega *et al.*¹ paper consists in showing that, for rigid multi-site models, there is a deviation **if the sum is evaluated over coordinates of individual interaction sites / atoms.**

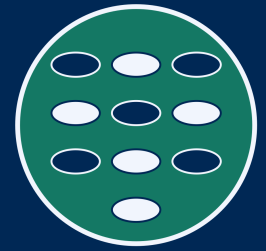
However, note that in our statistical-mechanical expressions, the momentum coordinates refer to molecular centres of mass as well as angular momenta.

¹M. Sega, B. Fábíán, P. Jedlovsky, *J. Phys. Chem. Lett.* **8**: 2608–2612, doi:10.1021/acs.jpcllett.7b01024, **2017**.



Noregs miljø- og
biovitenskapelige
universitet

Materialteori og -informatikk



Digitalisering på Ås

1. The established view
2. Apparent kinetic contribution
3. Interfacial properties: Open questions

What does this all mean for us?

The micromechanical pressure tensor is a standard literature expression, going back to Irving and Kirkwood.¹ It is the one implemented in GROMACS.²

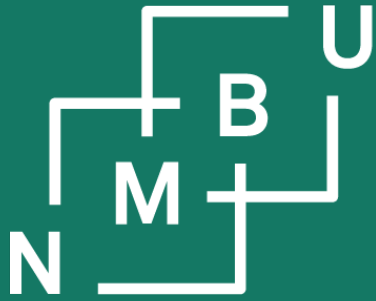
But our pressure and surface tension expressions are strictly the ones from statistical mechanics. **We don't need to add an apparent kinetic contribution.** But if we do it consistently over rigid units, it should be zero. The micro-mechanical pressure could be helpful for connecting to continuum mechanics.

There are two possibilities regarding codes using SHAKE, RATTLE, or similar:

- 1) The apparent kinetic contribution is really needed if rigid molecular models are analysed over effective forces acting on individual atoms.
This is possible, but a clear proof of it cannot be found in the literature.
- 2) But it is entirely possible that even then, the real γ is $\gamma^{\bar{}}$, and not γ^p .
While $\gamma^{\bar{}} \neq \gamma^p$ was shown, the literature contains no clear proof of $\gamma = \gamma^p$.

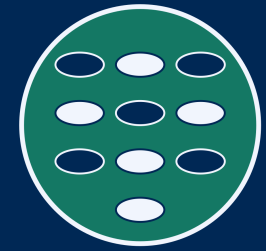
¹J. H. Irving, J. G. Kirkwood, *J. Chem. Phys.* **18(6)**: 817-829, **1950**; therein, see Eqs. (5.12) to (5.14).

²GROMACS manual, <https://manual.gromacs.org/>, section on "the global MD algorithm," **2023**.



Norges miljø- og
biovitenskapelige
universitet

Materialteori og -informatikk



Digitalisering på Ås

Role of the frame of reference in the apparent kinetic contribution to the surface tension

Martin Thomas Horsch
Norwegian University of Life Sciences

30th January 2025, UKRI STFC Daresbury Laboratory
CECAM Workshop on Interfacial Properties: Open Questions (IPOQ 2025)