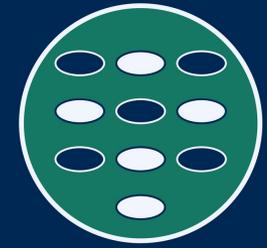


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# Sega's correction for the surface tension of fluid interfaces

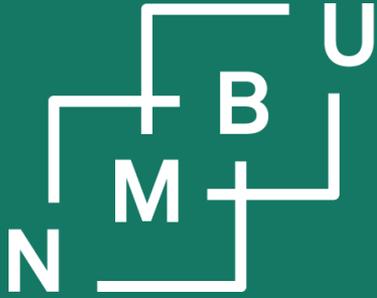
Martin Thomas Horsch

25. mai 2023

Seminar for materialinformatikk

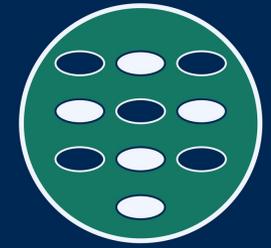
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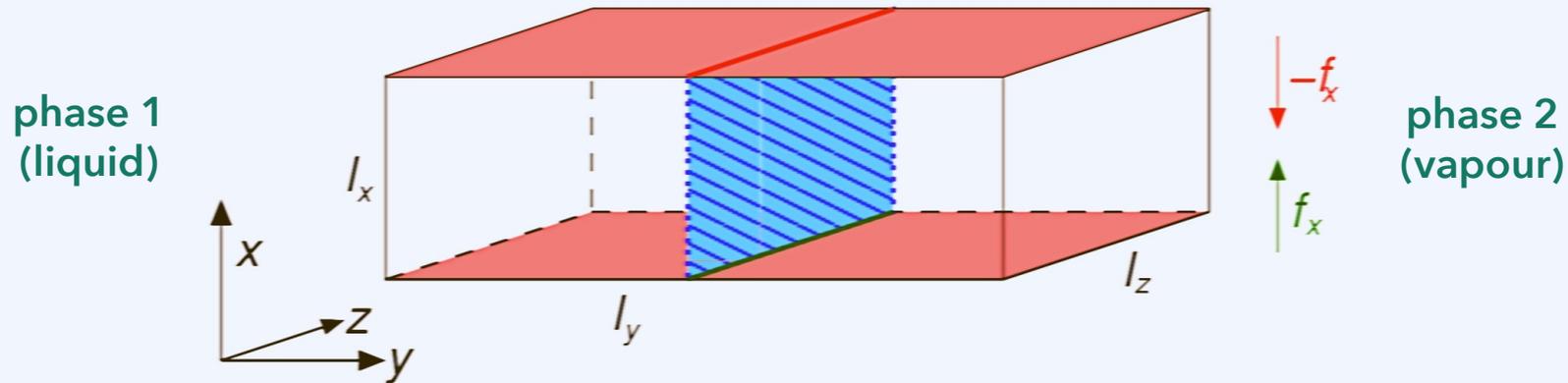
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# 1. Topic and introduction

## 2. Sega's argument

## 3. Discussion and evaluation

# Surface tension: Macromechanics



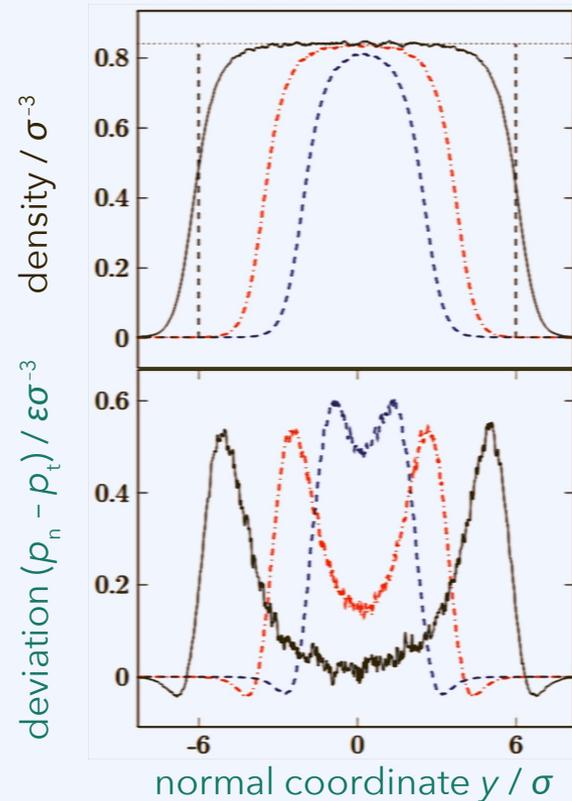
- Mechanical equilibrium  $\rightarrow$  fluid at rest, off-diagonal entries in pressure tensor are zero.
- The tangential pressure  $p_t = p_x = p_z$  deviates from the normal pressure  $p_n = p_y$ .
- Compared to the system boundaries perpendicular to  $y$  direction (normal direction), those in tangential 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,  $p_x - p_n = f_x / l_{yz} = -\gamma l_z / l_{yz} = -\gamma / l_y$ . Therefore,  $\gamma = l_y (p_n - p_x)$ .
- The same argument applies in  $z$  direction. So we can write  $\gamma = l_y (p_n - p_t)$ .

# Surface tension: 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:

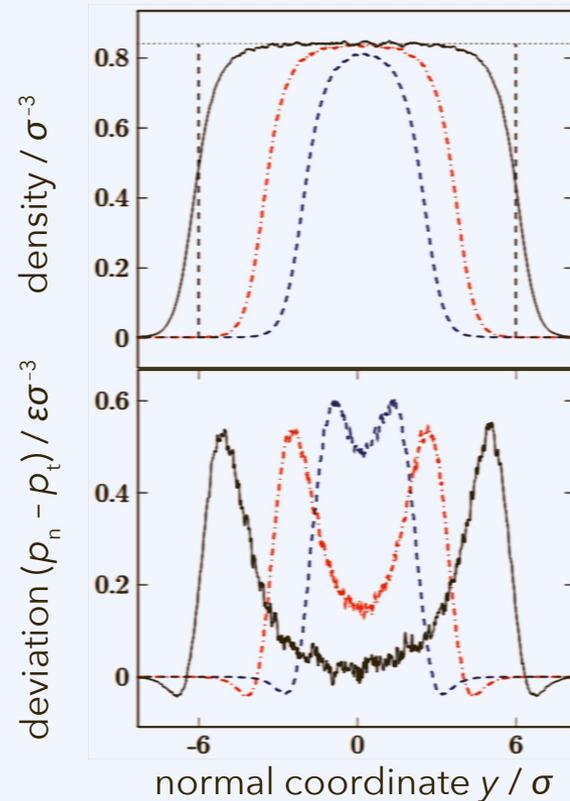
- For x direction,  $p_x - p_n = f_x / l_{yz} = -\gamma l_z / l_{yz} = -\gamma / l_y$ . Therefore,  $\gamma = l_y (p_n - p_x)$ .
- The same argument applies in z direction. So we can write  $\gamma = l_y (p_n - p_t)$ .

# Surface tension: 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  $\gamma$  is as well - in the case of a planar interface.



**LJ fluid**

$T = 0.7 \epsilon$

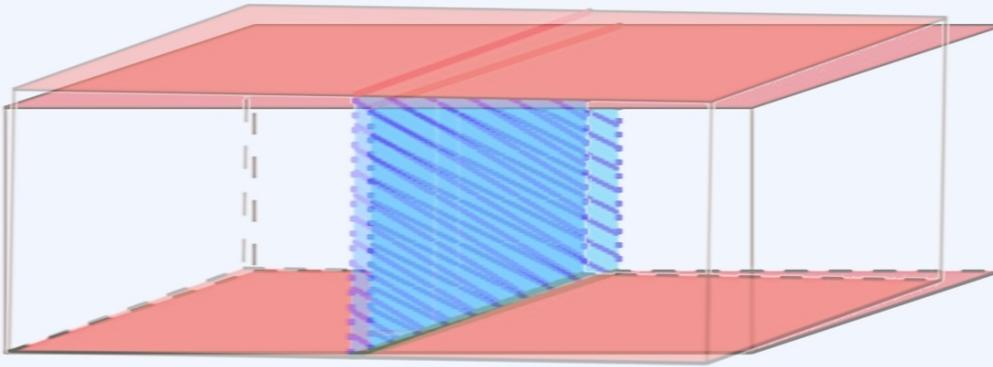
from S. Werth  
*et al.*, *Phys. A*  
392: 2359,  
2013.

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,  $\Pi$  is the virial,  $\Pi_n = \Pi_y = \sum_{\langle i, j \rangle} f_{ij,y} r_{ij,y}$  and  $\Pi_t = \Pi_x = \sum_{\langle i, j \rangle} f_{ij,x} r_{ij,x}$ .
- Since  $V = l_y F$ , where  $F$  is the surface area,  $\gamma = F^{-1} (\langle \Pi_n \rangle - \langle \Pi_t \rangle)$ . **Note that  $\rho T$  cancels out!**
- While the virial for the whole system is uniquely defined, the local profiles are not.

# Surface tension: 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  $F$  changes

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

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

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,  $\Pi$  is the virial,  $\Pi_n = \Pi_y = \sum_{\{i,j\}} f_{ij,y} r_{ij,y}$  and  $\Pi_t = \Pi_x = \sum_{\{i,j\}} f_{ij,x} r_{ij,x}$ .
- Since  $V = lF$ , where  $F$  is the surface area,  $\gamma = F^{-1} (\langle \Pi_n \rangle - \langle \Pi_t \rangle)$ . **Note that  $\rho T$  cancels out!**
- While the virial for the whole system is uniquely defined, the local profiles are not.

# Rigid multisite models

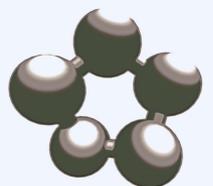
## Geometry

Types and positions of interaction sites



## Dispersion and repulsion

Lennard-Jones (or Mie) potential:  
Size and energy ( $m, n$ ) parameters

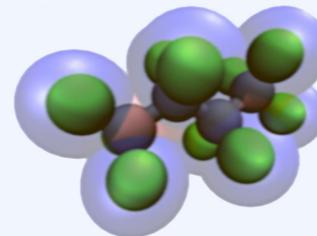


cyclopentane

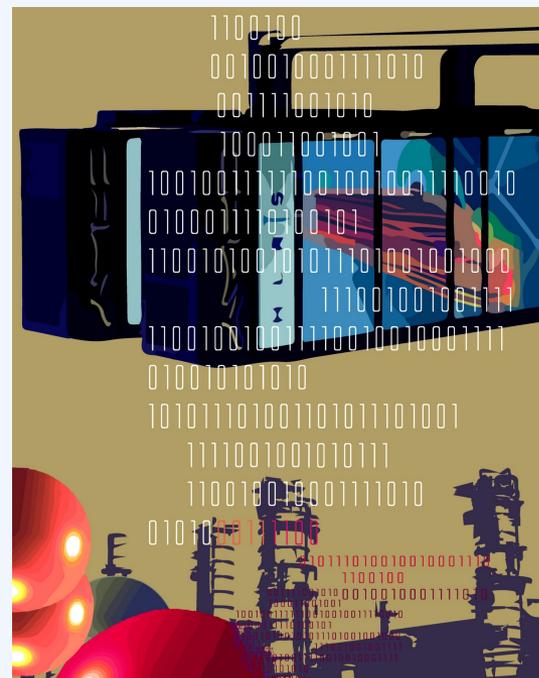
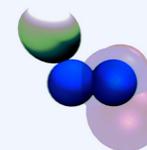
## Electrostatics

Point charges or multipoles  
(point dipoles, point quadrupoles):  
Magnitude and orientation

perfluorobutane



methylhydrazine



Molecular model database (MolMod DB<sup>1</sup>)

<http://molmod.boltzmann-zuse.de/>

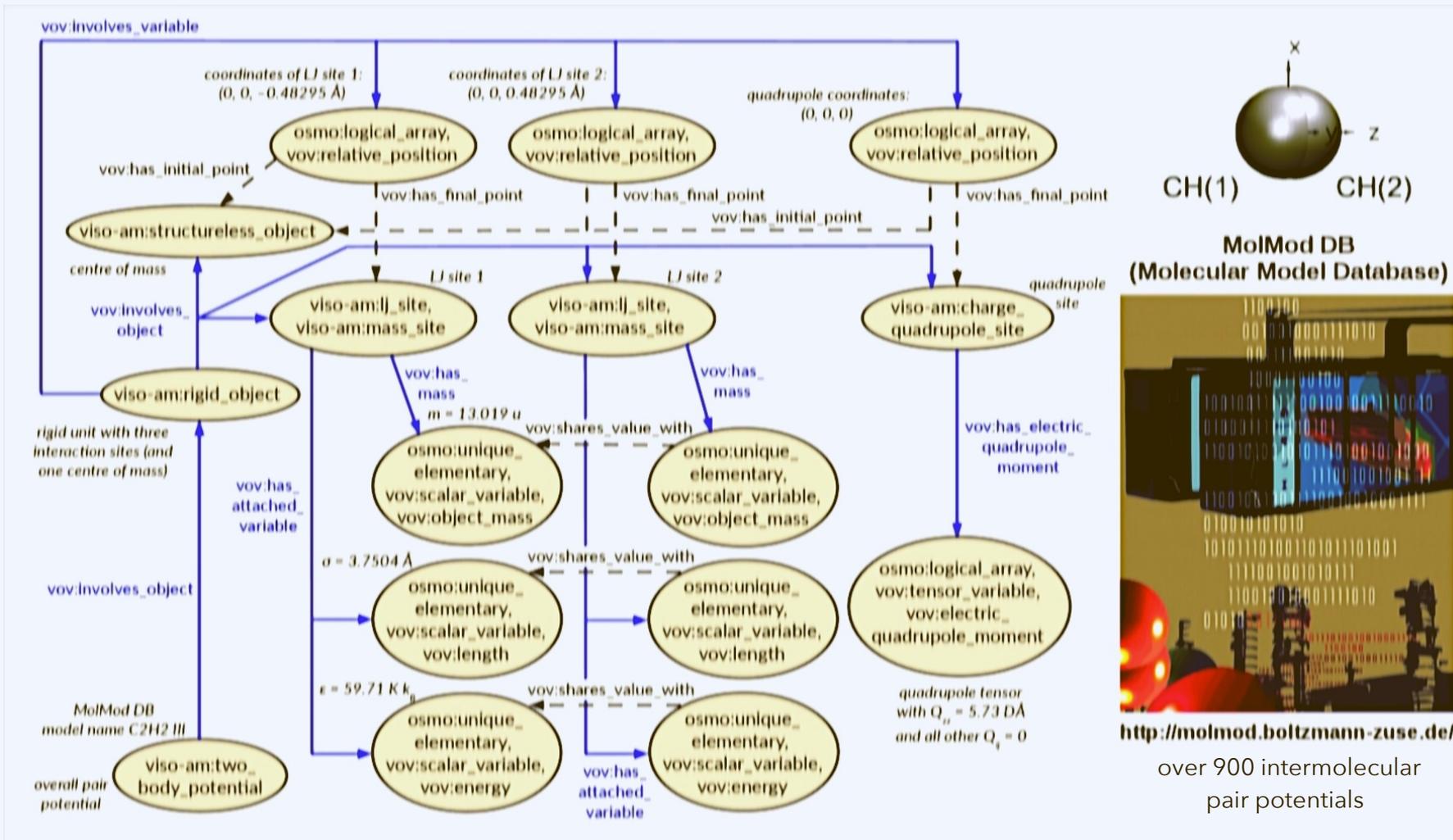
over 900 intermolecular pair potentials



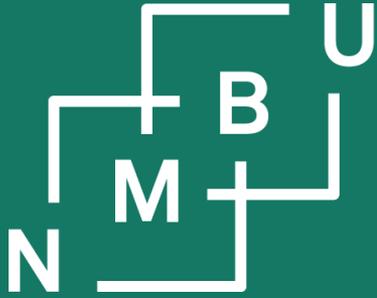
Computational  
Molecular Engineering

<sup>1</sup>S. Stephan *et al.*, *Mol. Sim.* 45, 806–814, 2019.

# Rigid multisite models: MolMod knowledge graph<sup>1,2</sup>

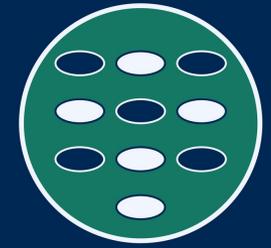


<sup>1</sup>S. Stephan et al., *Mol. Sim.* 45, 806-814, 2019. <sup>2</sup>M. Horsch et al., *Proc. ISWC*, 2020.



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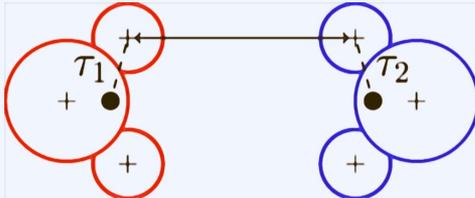
1. Topic and introduction
2. Sega's argument
3. Discussion and evaluation

# Long-range (cutoff) correction at planar interfaces

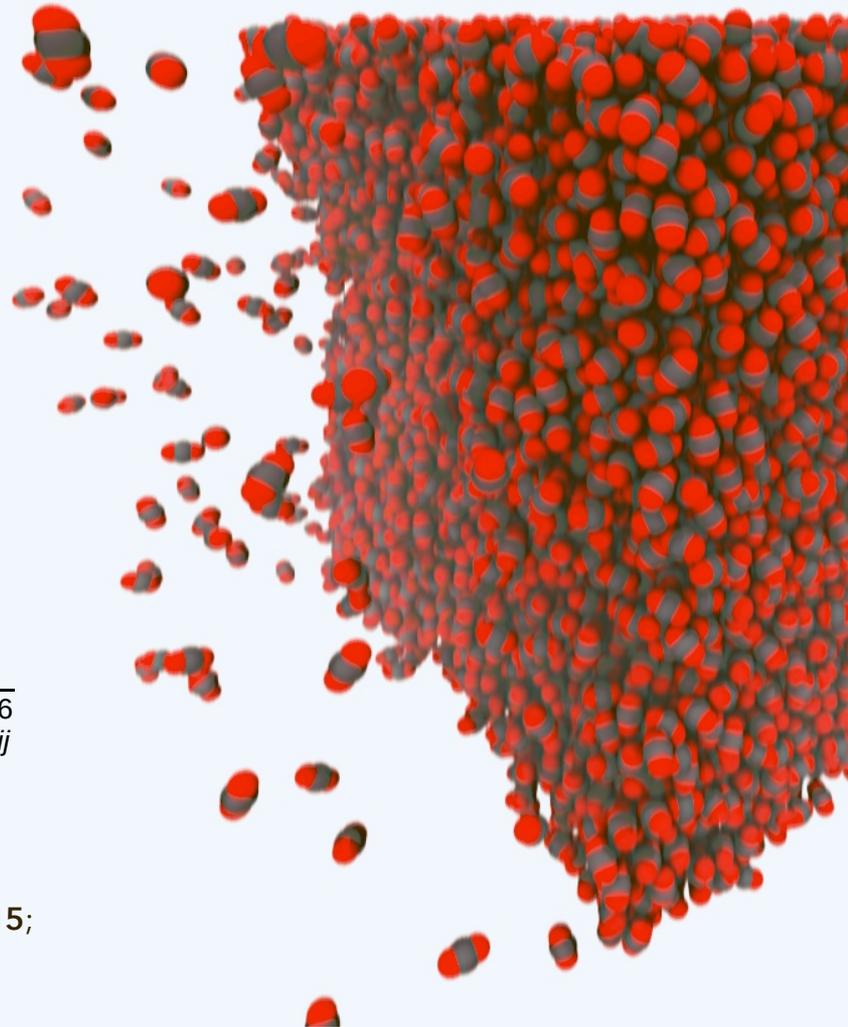
Dispersive long-range correction by Janeček<sup>1-4</sup>

$$U_i^{\text{LRC}} = 2\pi \int_0^L dy \rho(y) \int_{r_{\min}(y-y_i)}^{\infty} r dr u^{\text{LJ}}(r)$$

Angle averaging for multiple (dispersive) interaction sites in a rigid molecular model following Lustig<sup>2,5</sup>



Angle averaging for dipoles following Cook and Rowlinson<sup>4,6</sup>  $\langle u_{ij}^{\mu}(r_{ij}) \rangle = \frac{\mu_i^2 \mu_j^2}{3kT r_{ij}^6}$



<sup>1</sup>J. Janeček, *J. Phys. Chem. B* **110(12)**: 6264–6269, **2006**;

<sup>2</sup>S. Werth et al., *Mol. Phys.* **112(17)**: 2227–2234, **2014**;

<sup>3</sup>F. Goujon et al., *J. Chem. Theory Comput.* **11(10)**: 4573–4585, **2015**;

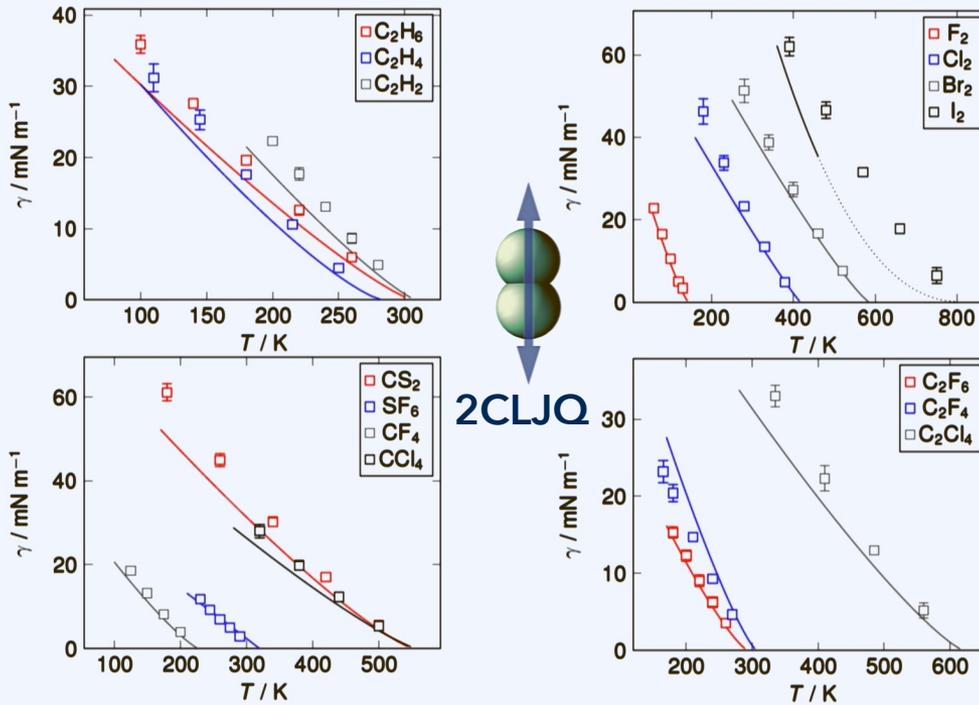
<sup>4</sup>S. Werth et al., *Mol. Phys.* **113(23)**: 3750–3756, **2015**;

<sup>5</sup>R. Lustig, *Mol. Phys.* **65(1)**: 175–179, **1988**;

<sup>6</sup>D. Cook, J. S. Rowlinson, *Proc. Roy. Soc. A* **219(1138)**: 405, **1953**.

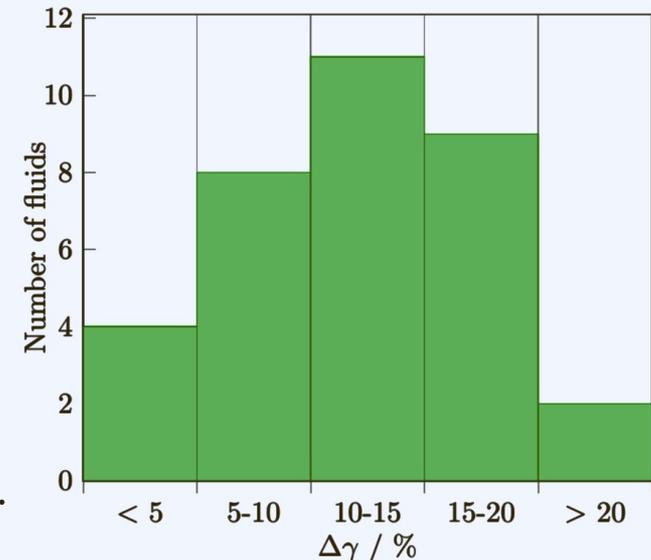
# Rigid multisite models: Surface tension

## 2 LJ centres + quadrupole<sup>1</sup>



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

## 2 LJ centres + dipole<sup>2</sup>

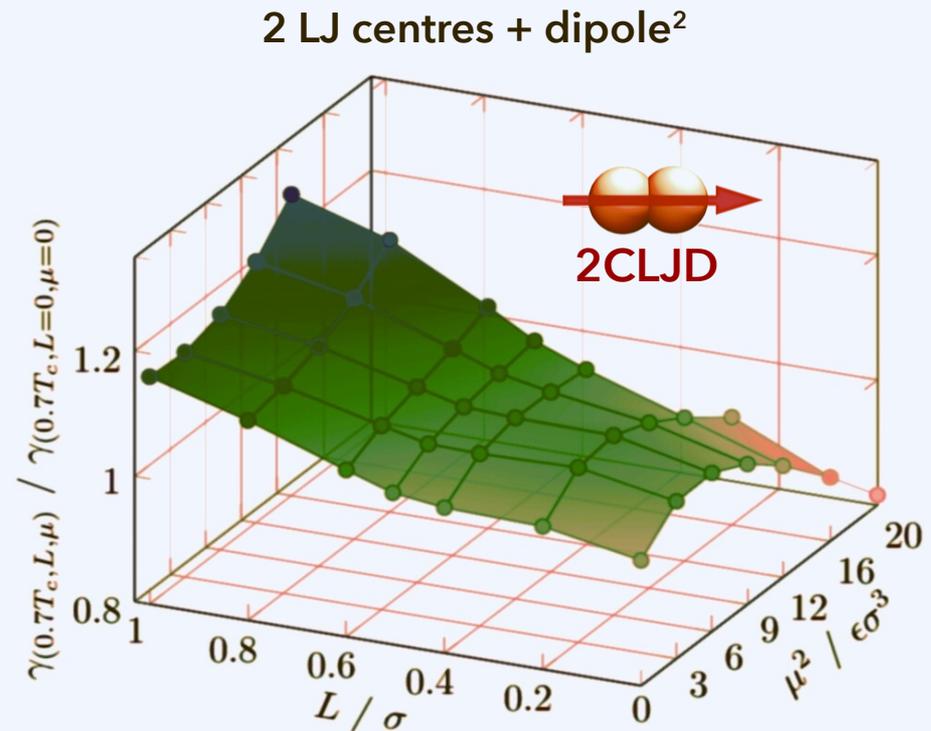
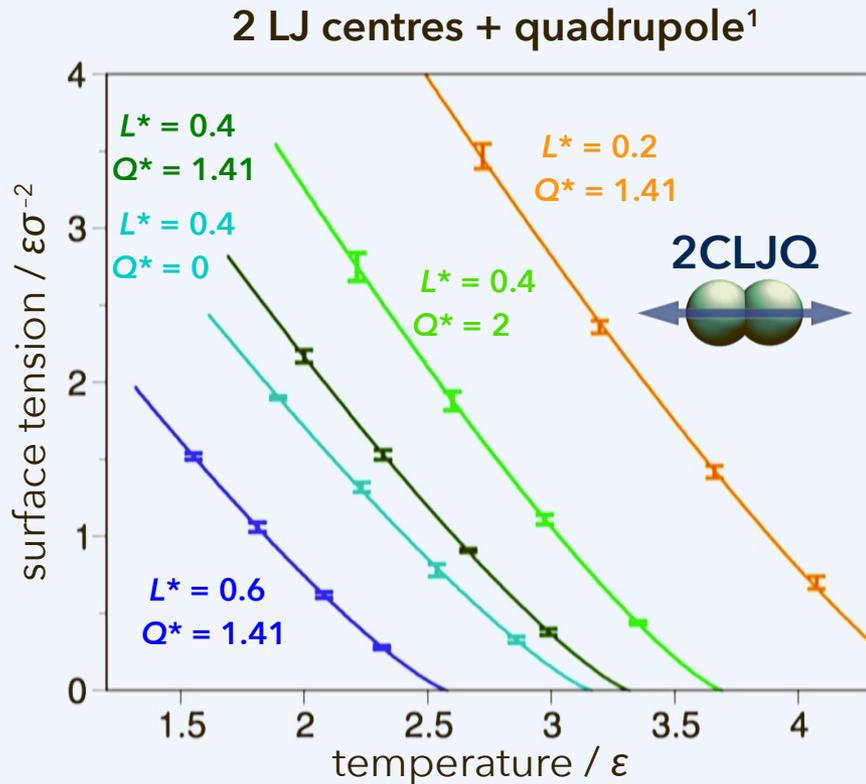


**Models (squares) overestimate surface tension from experiment (lines: correlations from DIPPR).**

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

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

# Rigid multisite models: Surface tension



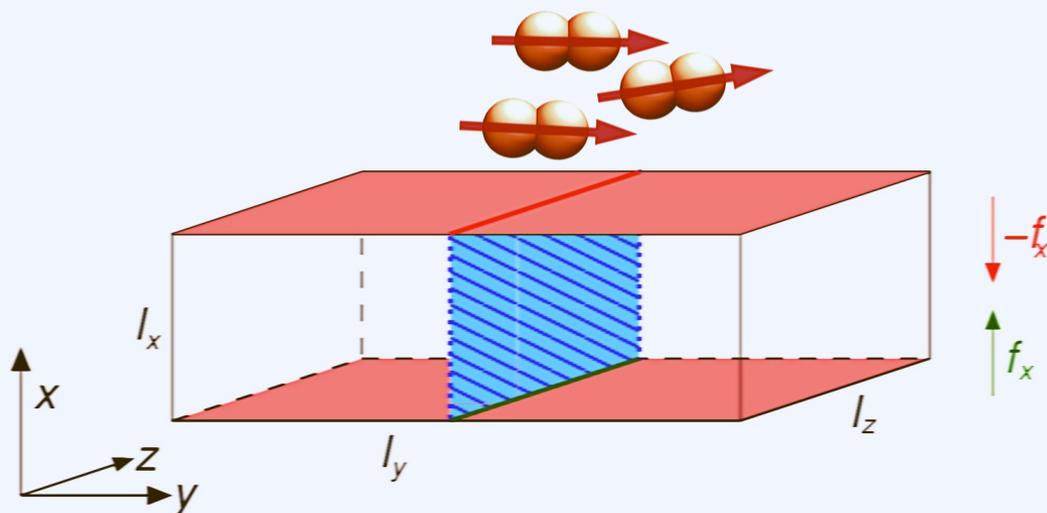
- Systematic exploration of the physically relevant part of the model parameter space
- Correlation of the 2LJQC and 2LJCD surface tension by critical-scaling expressions

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

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

# Sega's additional "ideal gas" short-range correction<sup>1</sup>

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



Sega *et al.*<sup>1,2</sup> distinguish:  
surface tension  $\gamma^{\Xi}$  computed using the **virial tensor** only (which, they claim, is inaccurate)  
surface tension  $\gamma^p$  computed using the **micromechanical pressure tensor**

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 Sega *et al.*<sup>2</sup>

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

- our **simulations were wrong**
- **models might become worse**

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

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

# Sega's argument<sup>1</sup> according to Lbadoui-Darvas<sup>2</sup>

The argument is presented by M. Lbadoui-Darvas *et al.*<sup>2</sup> 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, which might lead to erroneous surface tension values. 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.*<sup>1</sup> distinguish:

surface tension  $\gamma^{\bar{}}$  which, using the **statistical-mechanical** pressure, is  $l_y(p_n - p_t)$

surface tension  $\gamma^p$  which, using the **micromechanical** pressure, is  $l_y(p_n - p_t)$

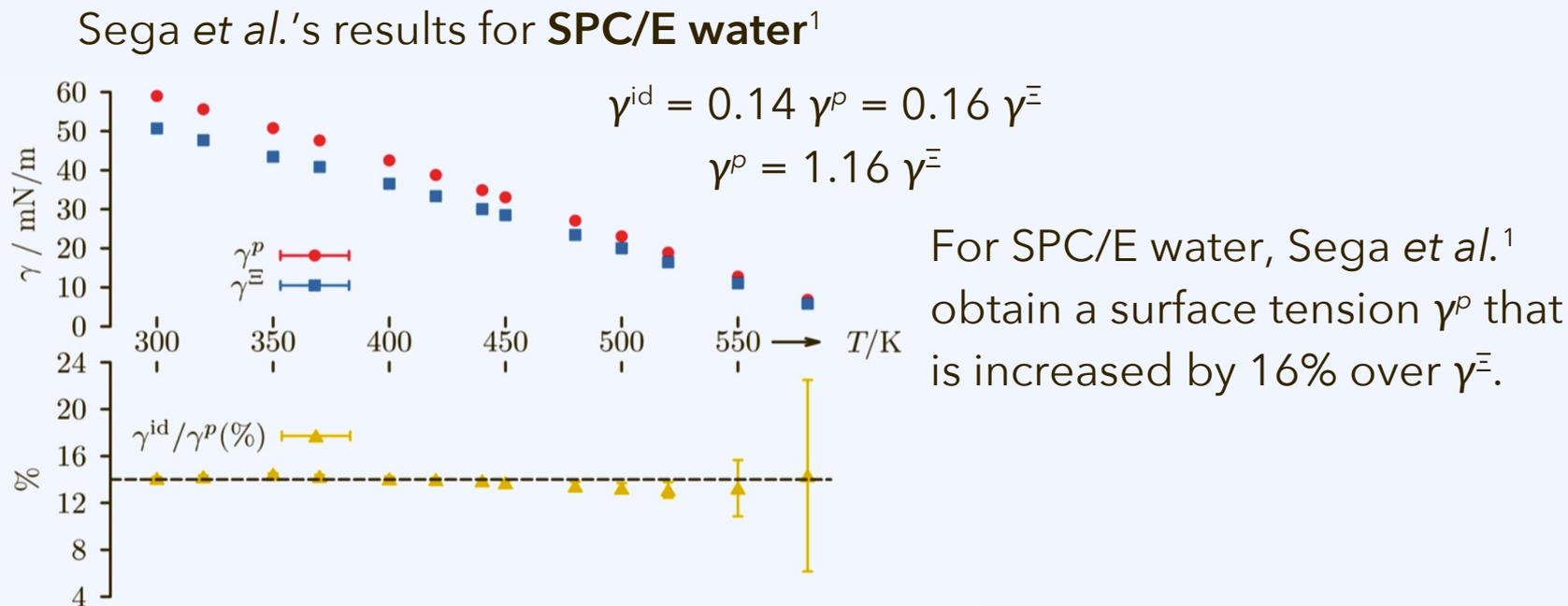
pressure tensor following Lbadoui-Darvas *et al.*<sup>2</sup>

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

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

<sup>2</sup>M. Lbadoui-Darvas *et al.*, *J. Phys. Chem. B* **126(4)**: 751–765, doi:10.1021/acs.jpccb.1c08553, **2022**.

# Sega's correction:<sup>1</sup> Quantitative impact

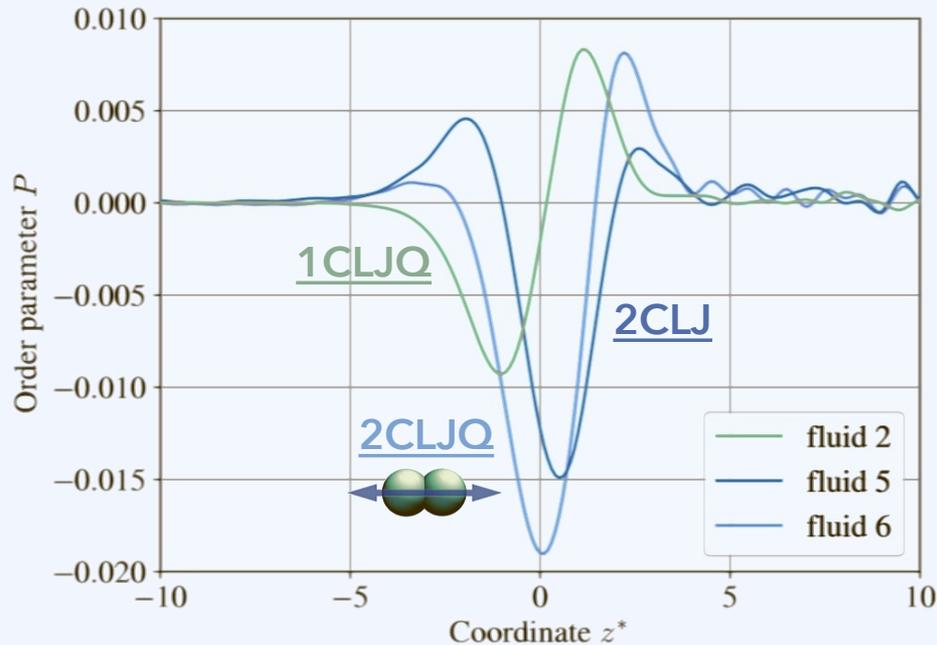


**Figure 3.** Upper panel: surface tension  $\gamma^{\text{p}}$  and virial contribution  $\gamma^{\text{E}}$  as a function of temperature. Lower panel: ratio  $\gamma^{\text{id}}/\gamma^{\text{p}} = 1 - \gamma^{\text{E}}/\gamma^{\text{p}}$ . Error bars are always smaller than the symbols in the upper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

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

# Sega's correction:<sup>1</sup> Quantitative impact

Homes *et al.*'s results for the **2CLJQ fluid**<sup>3</sup>



**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<sup>2,3</sup>

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

(evaporation, not equilibrium)

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

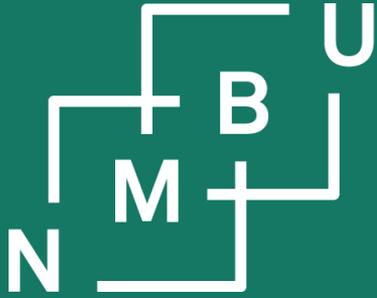
Orientation profiles for Stockmayer and 2CLJD done by Mecke *et al.*<sup>2</sup> long ago.

**Latest news from Homes *et al.*<sup>3</sup> on 2CLJ and 2CLJQ.**

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

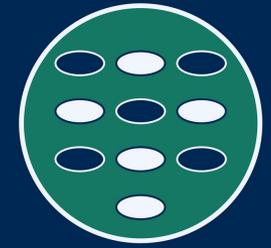
<sup>2</sup>M. Mecke, J. Fischer, J. Winkelmann, *J. Chem. Phys.* **114(13)**: 5842–5852, doi:10.1063/1.1349177, **2001**.

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



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1. Topic and introduction
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# Sega's argument: Plausibility (pressure tensor)

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

statistical-mechanical

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

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

micromechanical

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

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

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

However, note that in our statistical-mechanical expressions, the momentum coordinates refer to molecular centres of mass as well as angular momenta. It is clear that for centre-of-mass momenta, Sega's deviation will disappear again.

(Sega is working with the *coordinates of individual atoms* or interaction sites.)

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

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$$\text{where } \mathbf{\Pi} = \sum_{\{i,j\}} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij}^T$$

micromechanical

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

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

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

This *could have led Sega et al.*<sup>1</sup> to abandon micromechanics and rely on the expression grounded in statistical mechanics. *But ... they did the opposite.*

Why would they do this? **Are any subsequent papers providing a justification?**

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

# Sega's argument: Plausibility (equipartition theorem)

Lbadoui-Darvas *et al.*<sup>1</sup> claim that following the **equipartition theorem**, “*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.*” Does this make any sense, and is it correct?

At first, **it does not make sense**, since energy is a scalar. It does not have a direction. *Maybe they mean:* Energy associated with each *microscopic DOF*.

It is generally impossible to associate *potential energy* with “directions” or individual microscopic degrees of freedom. Exception: *Internal degrees of freedom*, if they are implemented as independently additive (e.g., harmonic).

In that case, in the zero-density limit, both the kinetic energy and the potential energy of the IDF independently *each* contribute  $T/2$  to the energy. Therefore, *if we try to make sense of the claim* from Lbadoui-Darvas *et al.*,<sup>1</sup> **it is incorrect**.

<sup>1</sup>M. Lbadoui-Darvas *et al.*, *J. Phys. Chem. B* **126(4)**: 751–765, doi:10.1021/acs.jpccb.1c08553, **2022**.



# Sega's correction: Follow-up work<sup>1-7</sup>

As of now, 14 citations of Sega *et al.*'s work are found in journal papers.

Seven out of the 14 citing papers are **self-citations**.<sup>1-7</sup>

They continue to use Sega's method, claiming that not doing so is mistaken:<sup>3</sup>

*"As we have **shown in a previous work** [...] the configurational part of the pressure (i.e., the virial) is **not enough** to describe the average value of the surface tension of liquid interfaces, because of the preferential orientation of molecules at the boundaries. [...] The **anisotropy of the kinetic energy tensor** at interfaces (which, by the way, constitutes no violation of the equipartition theorem) **can contribute in considerable amount to the surface tension.**"*

Used for SPC/E water<sup>1, 2, 4</sup> and mixtures with formamide<sup>2</sup> and methyllamine.<sup>4</sup>

**None of these seven papers justifies the use of the micromechanical pressure.**

<sup>1</sup>B. Kiss, ..., P. Jedlovsky, doi:10.1021/acs.jpcc.8b05874, **2018**. <sup>2</sup>M. Sega, G. Horvai, P. Jedlovsky, doi:10.1016/j.molliq.2018.04.004, **2018**. <sup>3</sup>M. Sega, P. Jedlovsky, doi:10.1039/c8cp02046a, **2018**. <sup>4</sup>R. A. Hórvath, ..., P. Jedlovsky, doi:10.1016/j.molliq.2019.110978, **2019**. <sup>5</sup>B. Fábíán, ..., P. Jedlovsky, doi:10.1021/acs.jpcc.9b10642, **2020**. <sup>6</sup>G. Hantal, ..., P. Jedlovsky, doi:10.1021/acs.jpcc.0c09989, **2021**. <sup>7</sup>M. Lbadoui-Darvas, A. Idrissi, P. Jedlovsky, doi:10.1021/acs.jpcc.1c08553, **2022**.



# Sega's correction: Uptake<sup>2-5,7</sup>

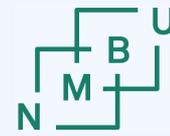
As of now, 14 citations of Sega *et al.*'s work are found in journal papers.

Seven out of the 14 citing papers are from **work by others**.<sup>1-7</sup> Two of these<sup>1,6</sup> are by M. Lbadoui-Darvas (close collaborator of Sega *et al.*). On the other five:

- Longford *et al.*<sup>2</sup> cite Sega, but only simulate single-centre LJ systems.
- Malek *et al.*<sup>3</sup> neglect  $m\mathbf{v}\cdot\mathbf{v}^T$  “regardless of the concerns raised by Sega”.
- García Martínez *et al.*<sup>4</sup> use the micromechanical pressure tensor, but don't attribute it to Sega; they even misrepresent Sega *et al.*'s work.
- Zhao *et al.*<sup>5</sup> don't use (or even discuss) Sega's method at all.
- Shi *et al.*<sup>7</sup> wrote a review, commenting on Sega's work approvingly.

To summarize, as of now, **nobody actively claims that Sega's method is wrong.**

<sup>1</sup>G. Ergin, M. Lbadoui-Darvas, S. Takahama, doi:10.1021/acs.langmuir.7b03346, **2017**. <sup>2</sup>F. G. J. Longford *et al.*, doi:10.1063/1.5055241, **2018**. <sup>3</sup>S. M. A. Malek *et al.*, doi:10.1088/1361-648x/aab196, **2018**. <sup>4</sup>M. García Martínez *et al.*, doi:10.1080/08927022.2019.1619930, **2019**. <sup>5</sup>Y. Zhao *et al.*, doi:10.1016/j.physb.2022.414178, **2022**. <sup>6</sup>M. Lbadoui-Darvas *et al.*, doi:10.1080/08927022.2021.1980215, **2023**. <sup>7</sup>K. Shi *et al.*, doi:10.1063/5.0132487, **2023**.



# What does this all mean for us?

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

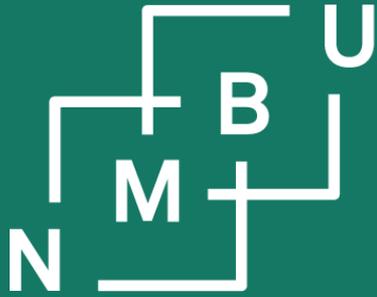
Our pressure and surface tension expressions are strictly the ones from statistical mechanics. **We do not need to add an “ideal-gas contribution” to  $\gamma$ .** But if we do it consistently (over molecular centres of mass), it will be zero. For non-equilibria, implementing the micromechanical pressure could be helpful.

There are two possibilities regarding Sega & collaborators' own results:

- 1) Their method is in fact correct for the case where rigid molecular models are analysed over effective forces acting on individual atoms. *However, none of their papers contains the theory to establish this.*
- 2) It is entirely possible that even in their own system,  $\gamma = \bar{\gamma}$  and not  $\gamma^p$ . They only observe that  $\bar{\gamma} \neq \gamma^p$ , without showing which is the right one.

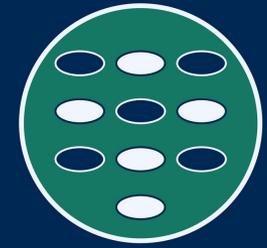
<sup>1</sup>J. H. Irving, J. G. Kirkwood, *J. Chem. Phys.* **18(6)**: 817-829, **1950**; therein, see Eqs. (5.12) to (5.14).

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



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Digitalisering på Ås

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Seminar for materialinformatikk

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