

Micro-Macro Modelling and Simulation of Liquid-Vapour Flows (Uni Freiburg)

Surface tension and molecular dynamics

Hans Wilhelm Alt (TU Munich, Germany)

- The continuum definition
- Measurement of surface tension
- Discrete approximation
- What does molecular dynamics say ?

Surface Tension



“Surface tension preventing a paper clip from submerging”

“Water striders stay atop the liquid because of surface tension”

Definition of Surface Tension

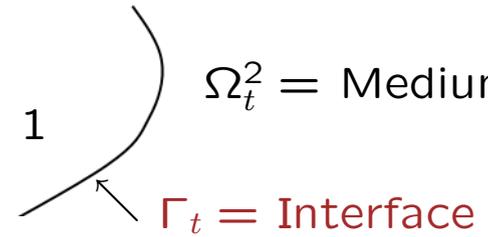
Π^s surface tension tensor on the surface Γ

Ω^1, Ω^2 two open sets

Π^m pressure tensor in Ω^m

$\Omega_t^1 = \text{Medium 1}$

$\Omega_t^2 = \text{Medium 2}$



Mass and momentum equation (simplest case):

$$\begin{cases} \partial_t(\varrho^m \boldsymbol{\mu}_{\Omega^m}) + \operatorname{div}(\varrho^m v \boldsymbol{\mu}_{\Omega^m}) = 0 \text{ for } m = 1, 2 \text{ in } \mathcal{D}'(\mathbb{R} \times \mathbb{R}^n) \\ \partial_t(\sum_m \varrho^m v \boldsymbol{\mu}_{\Omega^m}) + \operatorname{div}(\sum_m (\varrho^m v \otimes v + \Pi^m) \boldsymbol{\mu}_{\Omega^m} + \Pi^s \boldsymbol{\mu}_{\Gamma}) = \sum_m \mathbf{f}^m \boldsymbol{\mu}_{\Omega^m} \text{ in } \mathcal{D}'(\mathbb{R} \times \mathbb{R}^n) \\ v_{tan} \text{ continuous on } \Gamma \text{ (for two fluids)} \end{cases}$$

$$\left(\langle \zeta, \boldsymbol{\mu}_{\Sigma} \rangle := \int_{\mathbb{R}} \int_{\Sigma_t} \zeta(t, x) dH^M(x) dt, \quad \Sigma \text{ (} M\text{-dimensional)} = \begin{cases} \Omega^m \subset \mathbb{R} \times \mathbb{R}^3 \text{ (3-dimensional)} \\ \Gamma \subset \mathbb{R} \times \mathbb{R}^3 \text{ (2-dimensional)} \end{cases} \right)$$

$$\Leftrightarrow \begin{cases} \partial_t \varrho^m + \operatorname{div}(\varrho^m v) = 0 & \text{in } \Omega^m \text{ for } m = 1, 2 \\ \partial_t(\varrho^m v) + \operatorname{div}(\varrho^m v \otimes v + \Pi^m) = \mathbf{f}^m & \text{in } \Omega^m \text{ for } m = 1, 2 \\ v \text{ continuous on } \Gamma \text{ (for two fluids) and on } \Gamma: \\ \operatorname{div}(\Pi^s \boldsymbol{\mu}_{\Gamma}) = \mathbf{f}^s \boldsymbol{\mu}_{\Gamma}, \quad \mathbf{f}^s := \sum_m \Pi^m \nu_{\Omega^m} = (\Pi^1 - \Pi^2) \nu, \quad \nu := \nu_{\Omega^1} = -\nu_{\Omega^2} \end{cases}$$

The generalized Laplace law is

$$\operatorname{div}(\Pi^s \boldsymbol{\mu}_{\Gamma}) = \mathbf{f}^s \boldsymbol{\mu}_{\Gamma} \Leftrightarrow \begin{cases} \Pi^s \nu = 0 \text{ for normal } \nu \\ \operatorname{div}^{\Gamma} \Pi^s = \mathbf{f}^s = (\Pi^1 - \Pi^2) \nu \end{cases}$$

Definition of Surface Tension

Π^s surface tension tensor on the surface Γ

γ surface tension

$$\Pi^s = -\gamma(\text{Id} - \nu \otimes \nu) \implies \begin{cases} \Pi^s \nu = 0 \\ \text{div}^\Gamma \Pi^s = -\nabla^\Gamma \gamma + \gamma \text{div}^\Gamma (\nu \otimes \nu) \\ (\text{div}^\Gamma \nu) \nu = -\kappa_\Gamma \bullet \nu \nu = -\kappa_\Gamma \end{cases}$$

The Laplace law is therefore

$$\text{div}^\Gamma \Pi^s = (\Pi^1 - \Pi^2) \nu \iff \nabla^\Gamma \gamma + \gamma \kappa_\Gamma + (\Pi^1 - \Pi^2) \nu = 0$$

$$\iff \gamma \kappa_\Gamma \bullet \nu + \nu \bullet (\Pi^1 - \Pi^2) \nu = 0, \quad \partial_\tau \gamma + \tau \bullet (\Pi^1 - \Pi^2) \nu = 0 \text{ for } \tau \bullet \nu = 0$$

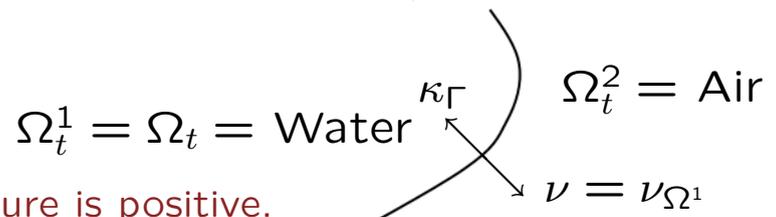
Consequence: All classical statements about fluid flow with surface will follow.

If $\Pi^1 = p \text{Id} - S$ and Ω^2 is occupied by air ($\rho^2 = 0$, $\Pi^2 = 0$), if $\gamma = \text{const}$:

$$\gamma \kappa_\Gamma \bullet \nu + p = \nu \bullet S \nu$$

If no flow ($v = 0$ hence $S = 0$): If γ is positive

and κ_Γ points inside the water, then the water pressure is positive.



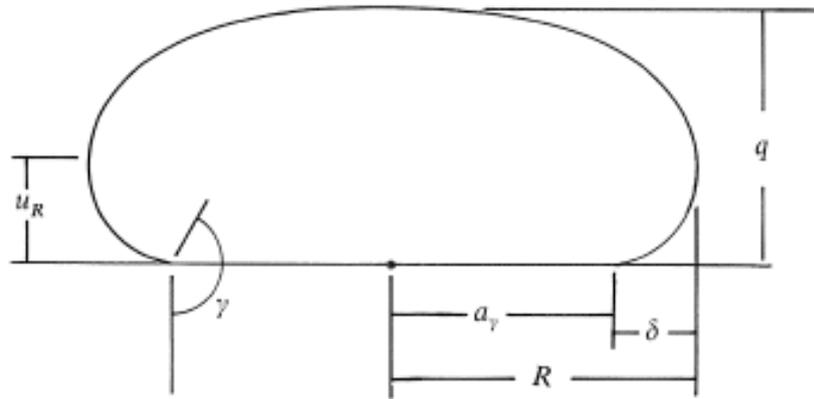
If flow is incompressible ($\rho^1 = \rho_0$), inviscid ($S = 0$), stationary, and irrotational,

Bernoulli's equation is besides $\text{div} v = 0$ that

$$\frac{\rho_0}{2} |v|^2 + p - \rho_0 \phi = \text{const}, \quad \mathbf{f}^1 = \rho_0 \nabla \phi \quad (\text{e.g. } \phi = -cx_3)$$

Liquid drops

Sessile drops



[Wikipedia]

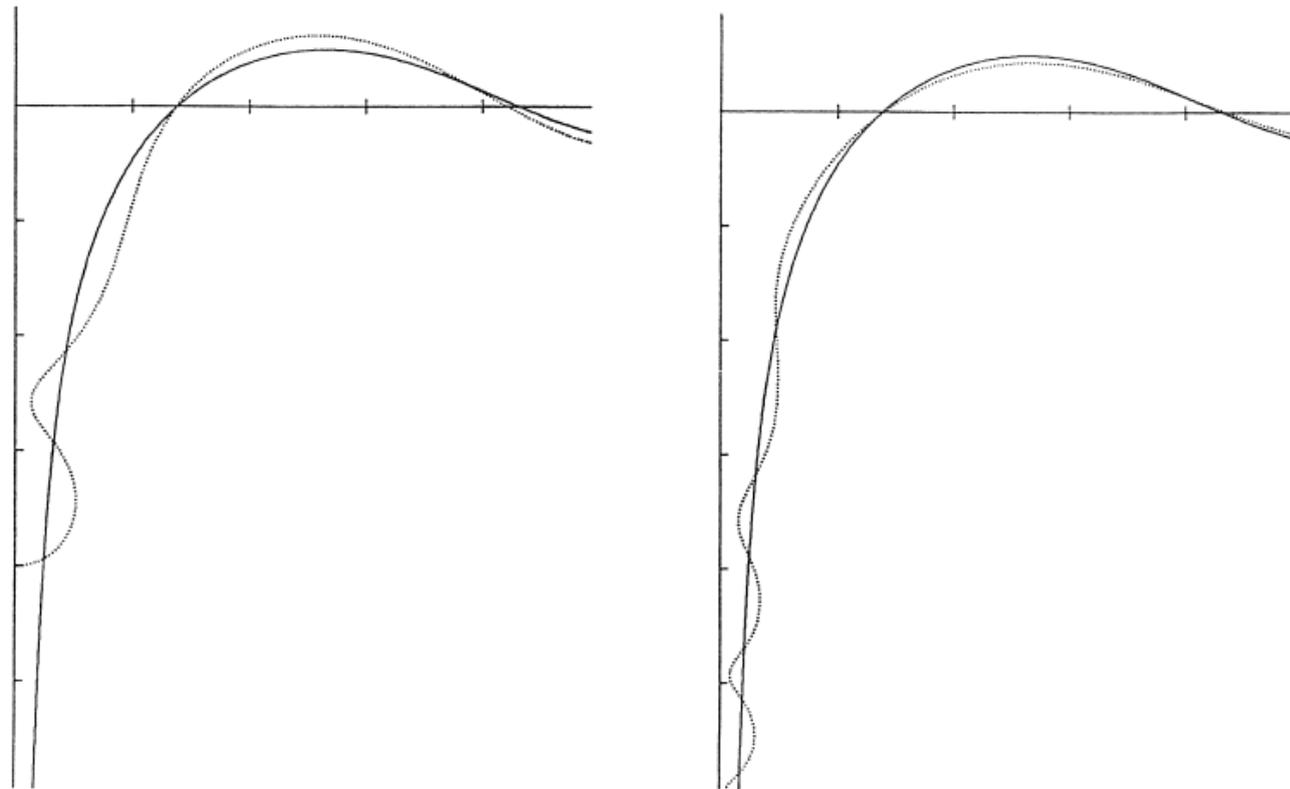
Corollary 3.1. *Corresponding to any value of the parameter u_0 , there is exactly one sessile drop making boundary angle γ , for any γ in $0 < \gamma \leq \pi$.*

[R. Finn. *Equilibrium Capillary Surfaces*

Grundlehren der mathematischen Wissenschaften 284, Springer 1986]

Liquid drops

Pendent drops



[Wikipedia]

Locale existence:

Theorem 4.1. *For any prescribed $u_0 \leq 0$, there exists $R_0 = R(u_0)$, such that a solution $u(r; u_0)$ of (4.2) exists in $0 < r < R_0$, with $\lim_{r \rightarrow 0} u(r; u_0) = u_0$.*

[R. Finn. *Equilibrium Capillary Surfaces*

Grundlehren der mathematischen Wissenschaften 284, Springer 1986]

Liquid drops



[de.m.wikipedia.org/wiki/Tropfen]



Measurement of Surface Tension

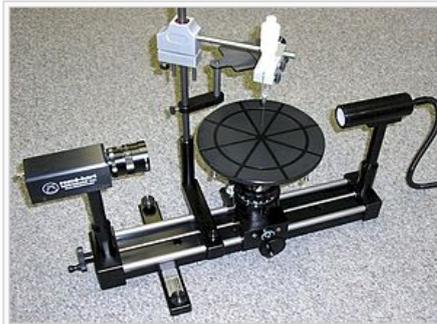
Surface tension of various liquids in dyn/cm (\iff millinewton/meter) against air

Liquid	Temperature °C	Surface tension, γ
Acetic acid	20	27.60
Acetic acid (40.1%) + Water	30	40.68
Acetic acid (10.0%) + Water	30	54.56
Acetone	20	23.70
Diethyl ether	20	17.00
Ethanol	20	22.27
Ethanol (40%) + Water	25	29.63
Ethanol (11.1%) + Water	25	46.03
Glycerol	20	63.00
<i>n</i> -Hexane	20	18.40
Hydrochloric acid 17.7M aqueous solution	20	65.95
Isopropanol	20	21.70
Liquid helium II	-273	[24] 0.37
Liquid nitrogen	-196	8.85
Mercury	15	487.00
Methanol	20	22.60
<i>n</i> -Octane	20	21.80
Sodium chloride 6.0M aqueous solution	20	82.55
Sucrose (55%) + water	20	76.45
Water	0	75.64
Water	25	71.97
Water	50	67.91
Water	100	58.85
Toluene	25	27.73

[en.m.wikipedia.org/wiki/Surface_Tension]

Because surface tension manifests itself in various effects, it offers a number of paths to its measurement. Which method is optimal depends upon the nature of the liquid being measured, the conditions under which its tension is to be measured, and the stability of its surface when it is deformed.

- **Du Noüy Ring method:** The traditional method used to measure surface or interfacial tension. Wetting properties of the surface or interface have little influence on this measuring technique. Maximum pull exerted on the ring by the surface is measured.^[10]
- **Du Noüy-Padday method:** A minimized version of Du Noüy method uses a small diameter metal needle instead of a ring, in combination with a high sensitivity microbalance to record maximum pull. The advantage of this method is that very small sample volumes (down to few tens of microliters) can be measured with very high precision, without the need to correct for [buoyancy](#) (for a needle or rather, rod, with proper geometry). Further, the measurement can be performed very quickly, minimally in about 20 seconds. First commercial multichannel tensiometers [CMCeeker] were recently built based on this principle.
- **Wilhelmy plate method:** A universal method especially suited to check surface tension over long time intervals. A vertical plate of known perimeter is attached to a balance, and the force due to wetting is measured.^[11]
- **Spinning drop method:** This technique is ideal for measuring low interfacial tensions. The diameter of a drop within a heavy phase is measured while both are rotated.
- **Pendant drop method:** Surface and interfacial tension can be measured by this technique, even at elevated temperatures and pressures. Geometry of a drop is analyzed optically. For details, see [Drop](#).^[11]
- **Bubble pressure method** (Jaeger's method): A measurement technique for determining surface tension at short surface ages. Maximum pressure of each bubble is measured.
- **Drop volume method:** A method for determining interfacial tension as a function of interface age. Liquid of one density is pumped into a second liquid of a different density and time between drops produced is measured.^[12]
- **Capillary rise method:** The end of a capillary is immersed into the solution. The height at which the solution reaches inside the capillary is related to the surface tension by the equation [discussed below](#).^[13]
- **Stalagmometric method:** A method of weighting and reading a drop of liquid.
- **Sessile drop method:** A method for determining surface tension and [density](#) by placing a drop on a substrate and measuring the [contact angle](#) (see [Sessile drop technique](#)).^[14]
- **Vibrational frequency of levitated drops:** The natural frequency of vibrational oscillations of magnetically levitated drops has been used to measure the surface tension of superfluid ^4He . This value is estimated to be 0.375 dyn/cm at $T = 0 \text{ K}$.^[15]
- **Resonant oscillations of spherical and hemispherical liquid drop:** The technique is based on measuring the resonant frequency of spherical and hemispherical pendant droplets driven in oscillations by a modulated electric field. The surface tension and viscosity can be evaluated from the obtained resonant curves.^{[16][17][18]}



Surface tension can be measured using the [pendant drop method](#) on a [goniometer](#).

Molecular Dynamics

Consider particle system (without external force): For α

$$m_\alpha \ddot{x}_\alpha(t) = -\sum_{\beta:\beta \neq \alpha} F_{\alpha,\beta}(t), \quad F_{\alpha,\beta}(t) = \nabla V_{\alpha,\beta}(x_\alpha(t) - x_\beta(t))$$

$$V_{\beta,\alpha}(z) = V_{\alpha,\beta}(-z)$$

e.g. Lennard-Jones potential

This ODE-system is equivalent to a distributional mass-momentum system.

Define for curves $t \rightarrow x(t)$, $t \rightarrow y(t)$

$$\langle \zeta, \boldsymbol{\mu}_x \rangle := \int_{\mathbb{R}} \zeta(t, x(t)) dt, \quad \langle \zeta, \boldsymbol{\mu}_{x,y} \rangle := \int_{\mathbb{R}} \int_0^1 \zeta(t, (1-s)x(t) + sy(t)) ds dt$$

Mass-momentum-energy conservation:

$$\partial_t \left(\sum_{\alpha} m_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) + \operatorname{div} \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) = 0$$

$$\partial_t \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) + \operatorname{div} \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \otimes \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} - \frac{1}{2} \sum_{\alpha,\beta} F_{\alpha,\beta} \otimes (x_{\alpha} - x_{\beta}) \boldsymbol{\mu}_{x_{\alpha},x_{\beta}} \right) = 0$$

$$\partial_t \left(\sum_{\alpha} f_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) + \operatorname{div} \left(\sum_{\alpha} f_{\alpha} \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} - \frac{1}{4} \sum_{\alpha,\beta} F_{\alpha,\beta} \bullet (\dot{x}_{\alpha} + \dot{x}_{\beta}) (x_{\alpha} - x_{\beta}) \boldsymbol{\mu}_{x_{\alpha},x_{\beta}} \right) = 0$$

$$\text{with } f_{\alpha} := \frac{m_{\alpha}}{2} |\dot{x}_{\alpha}|^2 + \frac{1}{2} \sum_{\beta:\beta \neq \alpha} V_{\alpha,\beta}(x_{\alpha} - x_{\beta})$$

[H.W. Alt. *Entropy principle and interfaces. Fluids and Solids. Section 7.*

AMSA Vol. 19, pp. 585-663, 2009]

Proof: For test functions $\eta \in C_0^\infty(\mathbb{R} \times \mathbb{R}^3; \mathbb{R})$ and $\zeta \in C_0^\infty(\mathbb{R} \times \mathbb{R}^3; \mathbb{R}^3)$

$$\begin{aligned}
 & \langle -\partial_t \eta, m_\alpha \boldsymbol{\mu}_{x_\alpha} \rangle + \langle -\nabla \eta, m_\alpha \dot{x}_\alpha \boldsymbol{\mu}_{x_\alpha} \rangle \\
 &= - \int_{\mathbb{R}} m_\alpha (\partial_t \eta(t, x_\alpha(t)) + \dot{x}_\alpha(t) \bullet \nabla \eta(t, x_\alpha(t))) dt = - \int_{\mathbb{R}} m_\alpha \frac{d}{dt} (\eta(t, x_\alpha(t))) dt = 0 \\
 & \langle -\partial_t \zeta, \sum_\alpha m_\alpha \dot{x}_\alpha \boldsymbol{\mu}_{x_\alpha} \rangle + \left\langle -\mathbf{D}\zeta, \sum_\alpha m_\alpha \dot{x}_\alpha \otimes \dot{x}_\alpha \boldsymbol{\mu}_{x_\alpha} - \frac{1}{2} \sum_{\alpha\beta} F_{\alpha,\beta} \otimes (x_\alpha - x_\beta) \boldsymbol{\mu}_{x_\alpha, x_\beta} \right\rangle \\
 &= - \int_{\mathbb{R}} \sum_{\alpha k} m_\alpha \frac{d}{dt} (\zeta_k(t, x_\alpha(t))) \dot{x}_{\alpha k}(t) dt + \frac{1}{2} \left\langle \mathbf{D}\zeta, \sum_{\alpha\beta} F_{\alpha,\beta} \otimes (x_\alpha - x_\beta) \boldsymbol{\mu}_{x_\alpha, x_\beta} \right\rangle \\
 &= \int_{\mathbb{R}} \sum_{\alpha k} \zeta_k(t, x_\alpha(t)) m_\alpha \ddot{x}_{\alpha k}(t) dt \\
 &+ \frac{1}{2} \int_{\mathbb{R}} \sum_{\alpha\beta} \int_0^1 \mathbf{D}\zeta(t, (1-s)x_\beta(t) + sx_\alpha(t)) \bullet (F_{\alpha,\beta}(t) \otimes (x_\alpha(t) - x_\beta(t))) ds dt \\
 &= \sum_{\alpha\beta} (\zeta(t, x_\alpha(t)) - \zeta(t, x_\beta(t))) \bullet F_{\alpha,\beta}(t) dt = 2 \sum_{\alpha\beta} \zeta(t, x_\alpha(t)) \bullet F_{\alpha,\beta}(t) dt \\
 &= \int_{\mathbb{R}} \sum_\alpha \zeta(t, x_\alpha(t)) \bullet \left(m_\alpha \ddot{x}_\alpha(t) + \sum_\beta F_{\alpha,\beta}(t) \right) = 0
 \end{aligned}$$

[H.W. Alt. *Entropy principle and interfaces. Fluids and Solids. Section 7.*
 AMSA Vol. 19, pp. 585-663, 2009]

Mass and momentum laws

For molecular dynamics:

$$\partial_t \left(\sum_{\alpha} m_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) + \operatorname{div} \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) = 0$$

$$\partial_t \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} \right) + \operatorname{div} \left(\sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \otimes \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} - \frac{1}{2} \sum_{\alpha, \beta} F_{\alpha, \beta} \otimes (x_{\alpha} - x_{\beta}) \boldsymbol{\mu}_{x_{\alpha}, x_{\beta}} \right) = 0$$

If $V_{\alpha, \beta}(z) = \tilde{V}_{\alpha, \beta}(r)$, $r = |z|$, the pressure tensor is symmetric:

$$F_{\alpha, \beta} = W_{\alpha, \beta} \cdot (x_{\alpha} - x_{\beta}), \quad W_{\alpha, \beta} := \frac{1}{r_{\alpha, \beta}} \frac{\partial \tilde{V}_{\alpha, \beta}}{\partial r}(r_{\alpha, \beta}), \quad r_{\alpha, \beta} := |x_{\alpha} - x_{\beta}|$$

For continuum physics:

$$\partial_t(\varrho \boldsymbol{\mu}_{\Omega}) + \operatorname{div}(\varrho v \boldsymbol{\mu}_{\Omega}) = 0$$

$$\partial_t(\varrho v \boldsymbol{\mu}_{\Omega}) + \operatorname{div}(\varrho v \otimes v \boldsymbol{\mu}_{\Omega} + \Pi \boldsymbol{\mu}_{\Omega} + \Pi^s \boldsymbol{\mu}_{\Gamma}) = 0$$

where the surface tension tensor is $\Pi^s = -\gamma(\operatorname{Id} - \nu \otimes \nu)$.

Hence we compare

$$\tilde{\Pi}^{\text{molecular}} := \sum_{\alpha} m_{\alpha} \dot{x}_{\alpha} \otimes \dot{x}_{\alpha} \boldsymbol{\mu}_{x_{\alpha}} - \frac{1}{2} \sum_{\alpha, \beta} W_{\alpha, \beta} \cdot (x_{\alpha} - x_{\beta}) \otimes (x_{\alpha} - x_{\beta}) \boldsymbol{\mu}_{x_{\alpha}, x_{\beta}}$$

$$\tilde{\Pi}^{\text{continuum}} := \varrho v \otimes v \boldsymbol{\mu}_{\Omega} + \Pi \boldsymbol{\mu}_{\Omega} - \gamma(\operatorname{Id} - \nu \otimes \nu) \boldsymbol{\mu}_{\Gamma}$$

in the equilibrium case.

Numerical results

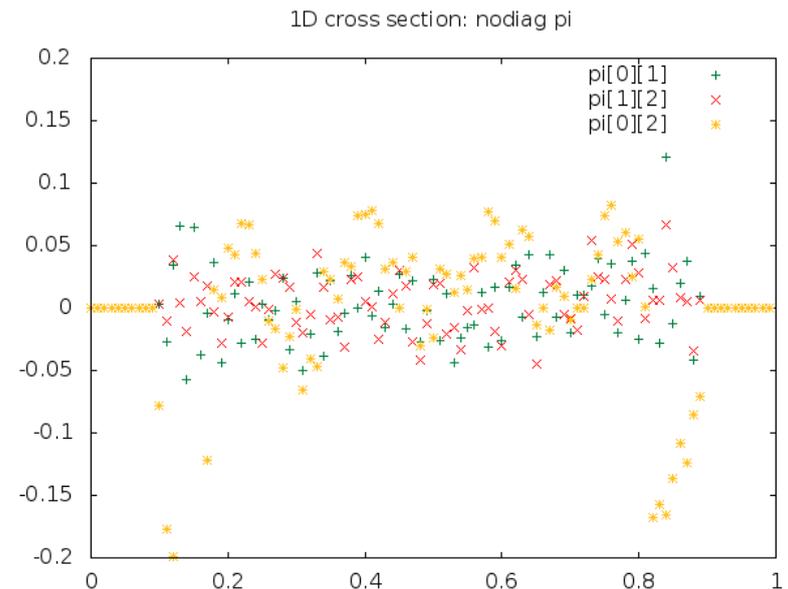
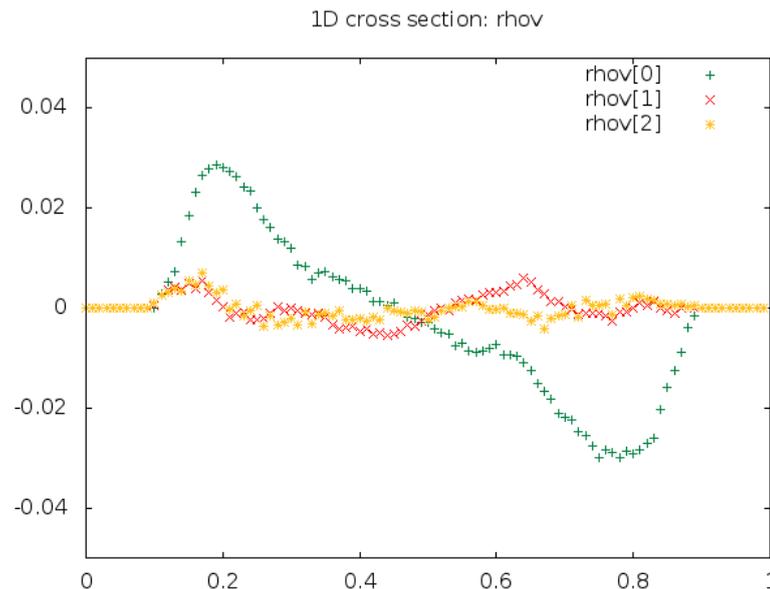
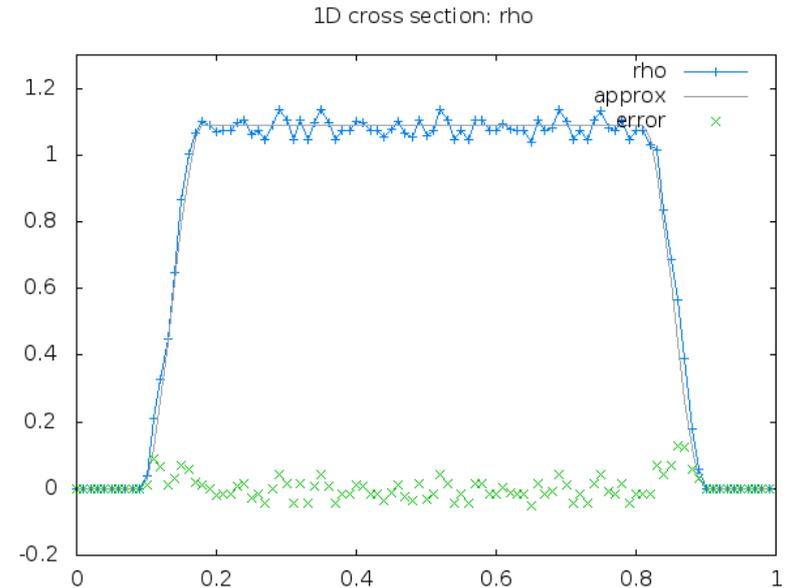
Results with 19683 molecules

Cross section in x_1 -direction through 0:

- Density (characteristic function)
- Distribution of ρv and
- nondiagonal elements of Π

with respect to a mollifier

[H.W.Alt 2014]



Numerical results

Results with 19683 molecules

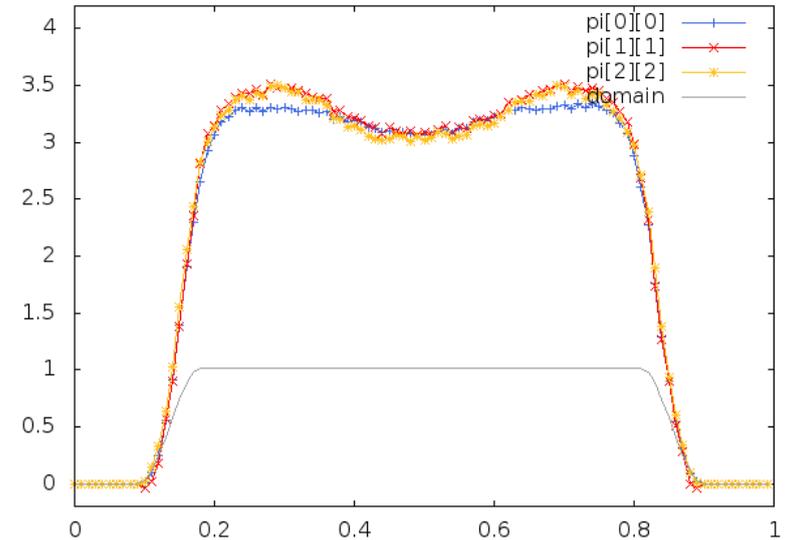
You see cross section

- in x_1 -direction (right side)
- in x_2 -direction (below left)
- in x_3 -direction (below right)

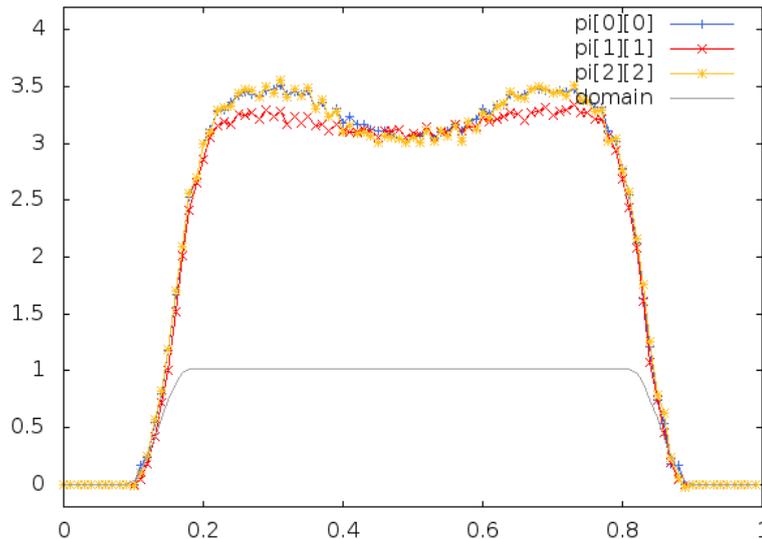
The diagonal elements of Π
and characteristic function
w.r.t. a mollifier

[H.W.Alt 2014]

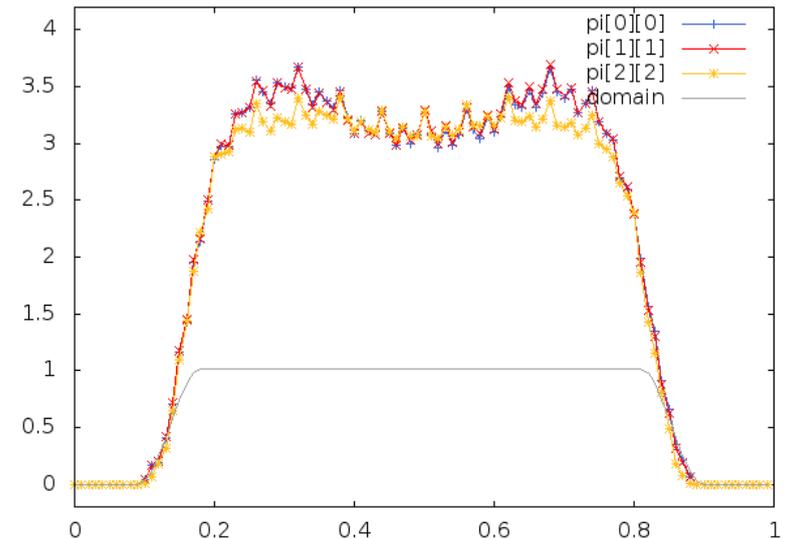
1D cross section: diag pi



1D cross section: diag pi



1D cross section: diag pi



Distributed Surface Tension

In the **equilibrium case** ($v = 0$, stationary) the equation to solve is

$$\operatorname{div} \tilde{\Pi} = 0 \quad \text{with} \quad \tilde{\Pi} \in \mathcal{D}'(\mathbb{R} \times \mathbb{R}^3)$$

Example: (with surface tension)

$$\tilde{\Pi} = p \operatorname{Id} \mu_{\Omega} - \gamma (\operatorname{Id} - \nu \otimes \nu) \mu_{\Gamma} \quad \text{where } \nu \text{ normal of } \Gamma$$

It is $\tilde{\Pi} = \Pi \mu_{\Omega} + \Pi^s \mu_{\Gamma}$ with $\Pi = p \operatorname{Id}$ and $\Pi^s = -\gamma (\operatorname{Id} - \nu \otimes \nu)$

Example: Let $r \mapsto p(r)$ be smooth, $r = |x|$. Then ($\tilde{\Pi} = \Pi \mu_{\mathbb{R} \times \mathbb{R}^3}$)

$$\Pi := p \operatorname{Id} + \frac{r p'(r)}{2} (\operatorname{Id} - \nu \otimes \nu) \quad \text{where } \nu := \frac{x}{r}$$

is a “**distributed surface tension**” solution.

Proof:

1) Take a discrete version of surface tension in Ω^k , $\partial\Omega^k = \Gamma^{k-1} \cup \Gamma^k$, for each k

$$0 = \operatorname{div} \left(\sum_k (p^k \operatorname{Id}) \mu_{\Omega^k} - \sum_k \gamma^k (\operatorname{Id} - \nu^k \otimes \nu^k) \mu_{\Gamma^k} \right)$$

and go to the limit $k \rightarrow \infty$.

Distributed Surface Tension

2) Direct computation in Euclidean coordinates. If

$$\Pi - p\text{Id} = -\gamma(r)(\text{Id} - \nu \otimes \nu) = -\frac{\gamma(r)}{r^2} \begin{bmatrix} x_2^2 + x_3^2 & -x_1x_2 & -x_1x_3 \\ -x_1x_2 & x_1^2 + x_3^2 & -x_2x_3 \\ -x_1x_3 & -x_2x_3 & x_1^2 + x_2^2 \end{bmatrix}$$

we compute $\nabla\left(\frac{\gamma(r)}{r^2}\right) = \left(\frac{\gamma(r)}{r^2}\right)_{,r} \nabla r = \left(\frac{\gamma(r)}{r^2}\right)_{,r} \frac{x}{r}$ and

$$\begin{aligned} \text{div}(\Pi - p\text{Id}) &= -\left(\frac{\gamma(r)}{r^2}\right)_{,r} \frac{1}{r} \underbrace{\begin{bmatrix} x_2^2 + x_3^2 & -x_1x_2 & -x_1x_3 \\ -x_1x_2 & x_1^2 + x_3^2 & -x_2x_3 \\ -x_1x_3 & -x_2x_3 & x_1^2 + x_2^2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}}_{=0} \\ &\quad - \frac{\gamma(r)}{r^2} \begin{bmatrix} \text{div}(x_2^2 + x_3^2, -x_1x_2, -x_1x_3) \\ \text{div}(-x_1x_2, x_1^2 + x_3^2, -x_2x_3) \\ \text{div}(-x_1x_3, -x_2x_3, x_1^2 + x_2^2) \end{bmatrix} = \frac{2\gamma(r)}{r^2} x = \frac{2\gamma(r)}{r} \nu \end{aligned}$$

Therefore

$$0 = \text{div}\Pi = \underbrace{\text{div}(p\text{Id})}_{= \nabla p} + \frac{2\gamma(r)}{r} \nu = \left(p_{,r}(r) + \frac{2\gamma(r)}{r}\right) \nu$$

\iff

$$\gamma(r) = -\frac{rp_{,r}(r)}{2} \quad (\text{which is an approximation of Laplace' formula})$$

Distributed Surface Tension

Theorem. If a sequence of distributed surface tension solutions p^k satisfies $p^k \rightarrow p \mathcal{X}_{\mathbb{R} \times D}$ for $k \rightarrow \infty$ with $p = \text{const}$ and $D = B_R(0)$ then

$$\tilde{\Pi}^k := \left(p^k \text{Id} + \frac{r p_{/r}^k}{2} (\text{Id} - \nu \otimes \nu) \right) \mu_{\mathbb{R} \times \mathbb{R}^3} \quad \text{with } \nu := \mathbf{e}_r = \frac{x}{r}$$

$$\longrightarrow \tilde{\Pi} := p \text{Id} \mu_{\mathbb{R} \times D} - \gamma (\text{Id} - \nu \otimes \nu) \mu_{\mathbb{R} \times \partial D} \quad \text{with } \gamma := \frac{R p|_{\mathbb{R} \times \partial D}}{2}$$

(Laplace law)

pointwise in the space of distributions.

Proof: For test functions $\xi \in C_0^\infty(\mathbb{R}^3; \mathbb{R}^{3 \times 3})$

$$\begin{aligned} \int_{\mathbb{R}^3} \xi \bullet (r p_{/r}^k (\text{Id} - \nu \otimes \nu)) \, dL^3 &= \int_{\mathbb{R}^3} \eta r p_{/r}^k \, dL^3 \quad \left(\text{if } \eta := \xi \bullet (\text{Id} - \nu \otimes \nu) \right) \\ &= \int_{\mathbb{R}^3} \eta r \mathbf{e}_r \bullet \nabla p^k \, dL^3 = - \int_{\mathbb{R}^3} p^k \text{div}(\eta r \mathbf{e}_r) \, dL^3 \longrightarrow - \int_{B_R(0)} p \text{div}(\eta r \mathbf{e}_r) \, dL^3 \\ &= - \int_{\partial B_R(0)} p \eta r \underbrace{\mathbf{e}_r \bullet \nu_{B_R(0)}}_{=1} \, dH^2 + \int_{B_R(0)} \eta r \mathbf{e}_r \bullet \underbrace{\nabla p}_{=0} \, dL^3 \\ &= \int_{\partial B_R(0)} \xi \bullet (-pR(\text{Id} - \nu \otimes \nu)) \, dH^2 \end{aligned}$$

Numerical and theoretical results

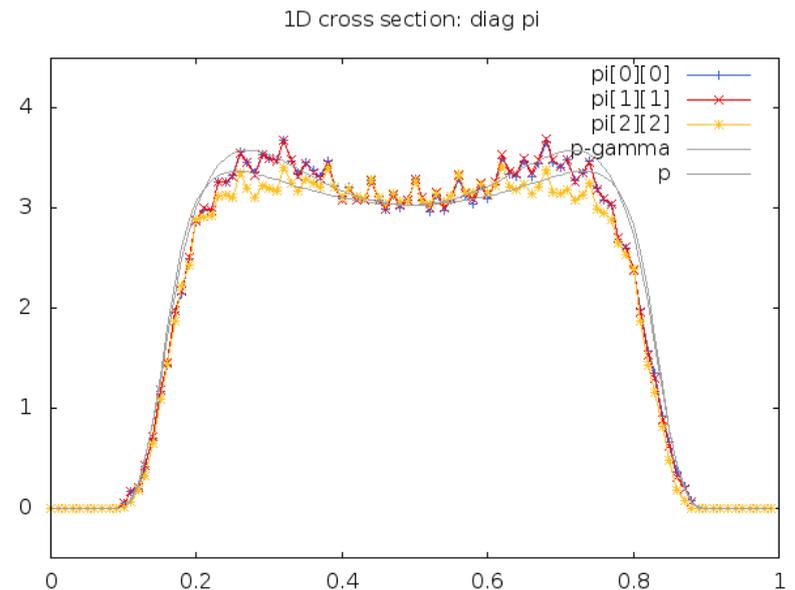
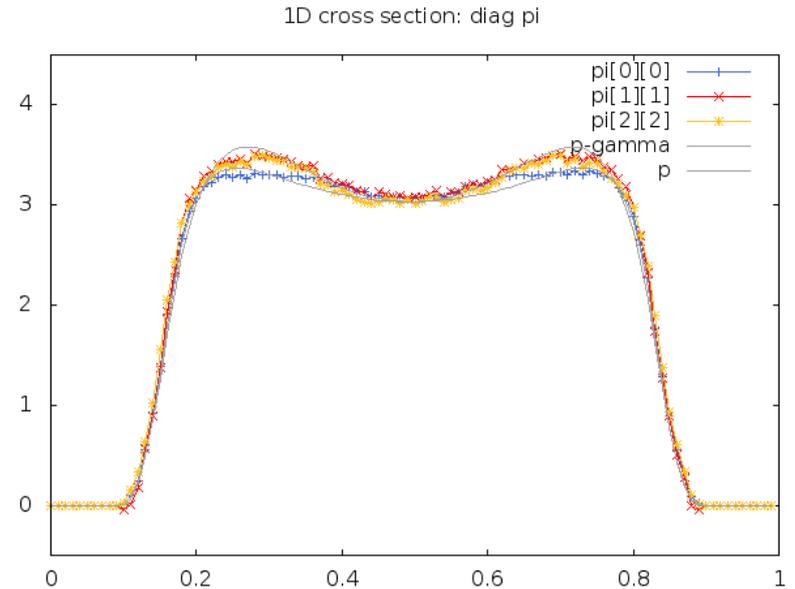
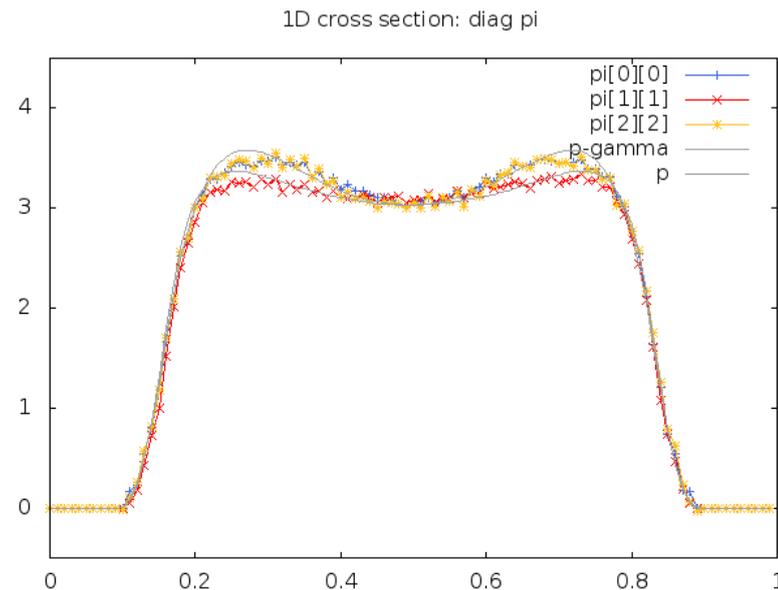
Results with 19683 molecules

You see cross section

- in x_1 -direction (right side)
- in x_2 -direction (below left)
- in x_3 -direction (below right)

and a corresponding approximation
of a continuum solution
w.r.t. a mollifier

[H.W.Alt 2014]

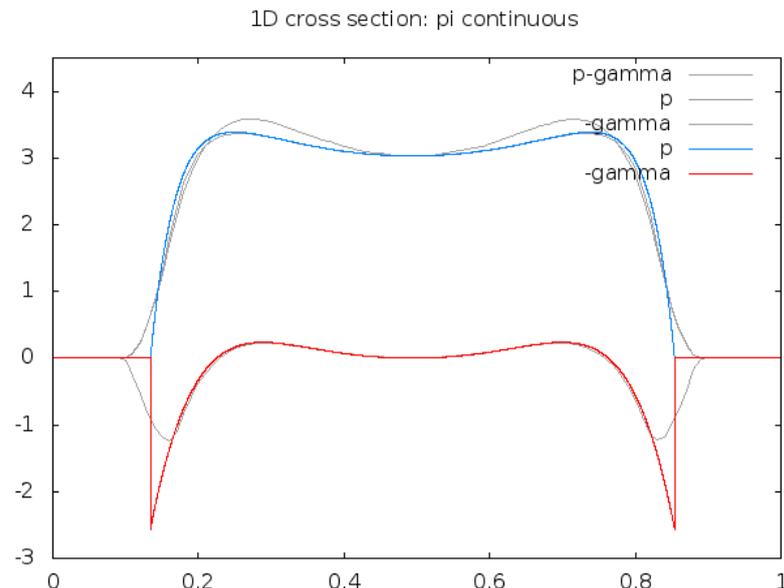


Numerical and theoretical results

Continuum solution as approximation

- w.r.t. a mollifier (black)
- the pressure p (blue)
- the approximative surface tension (red)
- $p = p_0 + p_1 r^2 + p_2 r^4 - p_3 r^6 - p_6 r^{12}$
 $p_0 = 3, p_1 = 8, p_2 = 10, p_3 = 600,$
 $p(R) = 0, R = 1.$

[H.W.Alt 2014]



From the theoretical result

$$\tilde{\Pi}^k := \left(p^k \text{Id} + \frac{r p_r^k}{2} (\text{Id} - \nu \otimes \nu) \right) \mu_{\mathbb{R} \times \mathbb{R}^3}$$

$$\longrightarrow \tilde{\Pi} := p \text{Id} \mu_{\mathbb{R} \times \mathbb{B}_R(0)} - \gamma (\text{Id} - \nu \otimes \nu) \mu_{\mathbb{R} \times \partial \mathbb{B}_R(0)}$$

$$\text{with } \gamma := \frac{R p|_{\mathbb{R} \times \overline{\mathbb{B}_R(0)}}}{2} \quad (\text{Laplace law})$$

Conclusion

- On a micro-scale one has to switch to distributed surface tension.
- On a large scale the effect of surface tension indeed takes place on the boundary.
- The method of comparing molecular dynamics and conservation laws is applicable in general.
- The method generalizes for example to membranes (concurrency of two interfaces).