Correlation between surface structure and slippage

Marcus Müller

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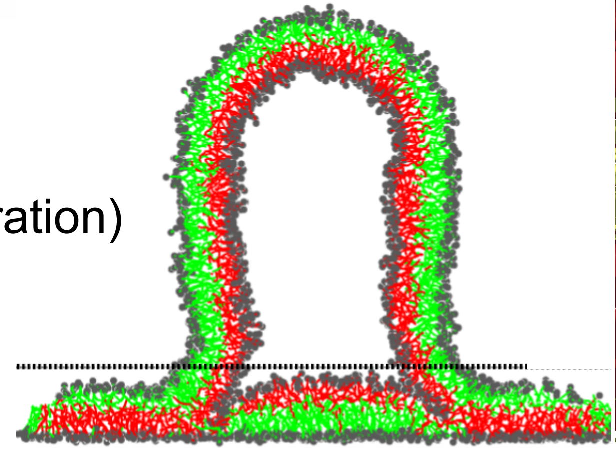
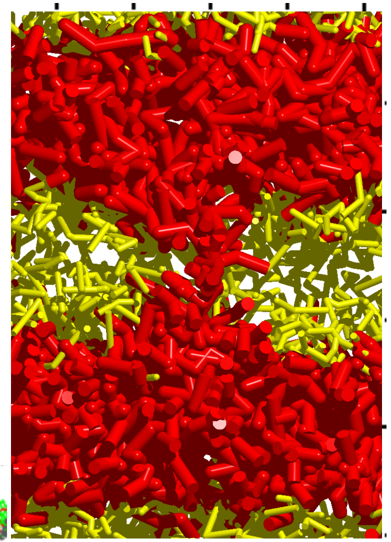
background:

- collective phenomena in membranes
  (fusion, spreading, lateral phase separation)

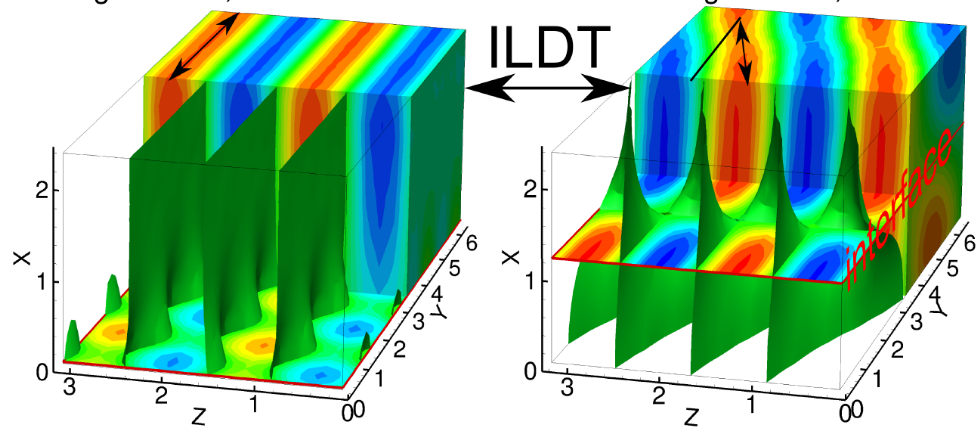




- directed self-assembly of block
  copolymer materials

twist angle α=90°, localized at bottom

twist angle α=28°, delocalized



- parameter-passing techniques and
  simulation techniques for polymers

MARIE CURIE ACTIONS

SFB 937

KITP Santa Barbara, March 19, 2014

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outline:

- intro: from particle models to a continuum description
  What determines the static and dynamic behavior of droplets on surfaces?
- statics: wetting behavior, Young's equation and interface potential
  Léonforte, Müller, JCP **135**, 214703 (2011)
  Tretyakov, Müller, Todorova, Thiele, JCP. **138** , 064905 (2013)
- dynamics: hydrodynamic boundary conditions of hard, soft and structured surfaces
  Servantie, Müller, PRL **101**, 026101 (2008), Pastorino, Müller, JCP **140**, 014901 (2014)
  Tretyakov, Müller, Soft Matter **9**, 3613 (2013)
- directed motion on asymmetric, vibrating substrates
  Tretyakov, Müller, Soft Matter, submitted

thanks to **Fabien Leonforte, Claudio Pastorino, Cem Servantie, and Nikita Tretyakov**

MARIE CURIE ACTIONS

SFB 937

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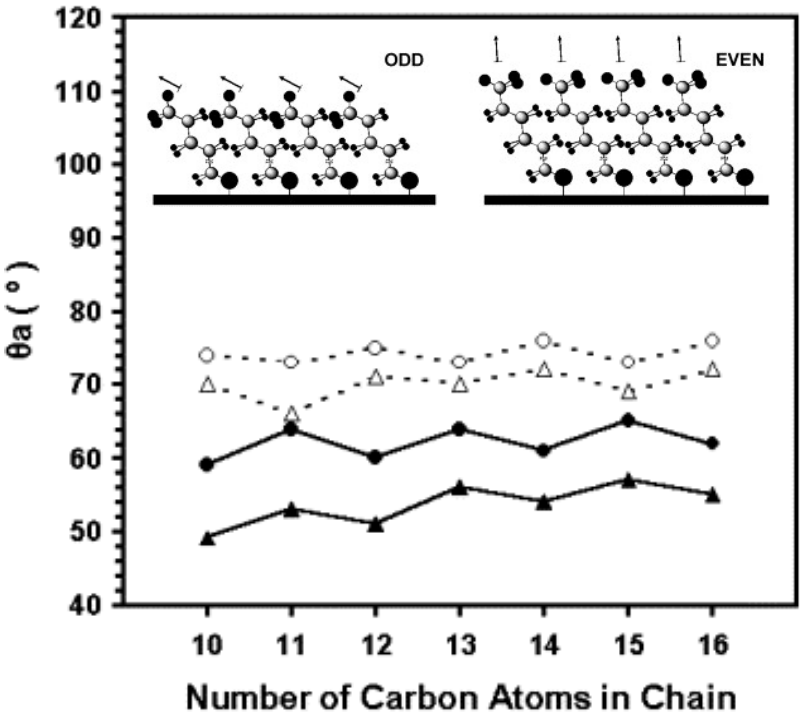
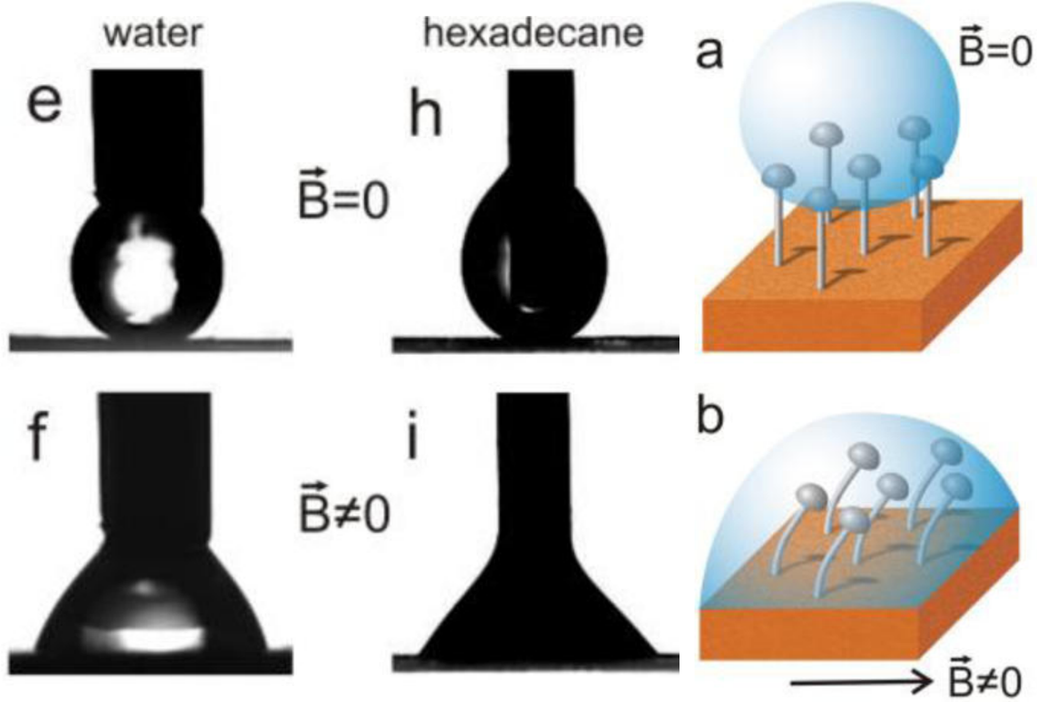
Controlling surface structure, one can tailor wettability and friction

molecular control by chemistry:
even-odd effects of the surface tension of fluorinated self-assembled monolayers – packing and chain lengths dictates orientation of dipole moments

macroscopic control by topography:
surface with overhangs ("nails") is amphiphobic, ie polar and non-polar liquids exhibit a large contact angle (Gibbs' criterion)



Barriet, Lee, Curr. Opin. Colloid Interface Sci. 8 236 (2003)



Grigoryev, Tokarev, Kornev, Luzinov, Minko, JACS **134**, 12916 (2012)

Controlling surface structure, one can tailor wettability and friction

molecular control by chemistry:
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macroscopic control by topography:
surface with overhangs ("nails") is amphiphobic, ie polar and non-polar liquids exhibit a large contact angle

role of modeling and computer simulation:
relate molecular structure to macroscopic behavior (wettability and friction)

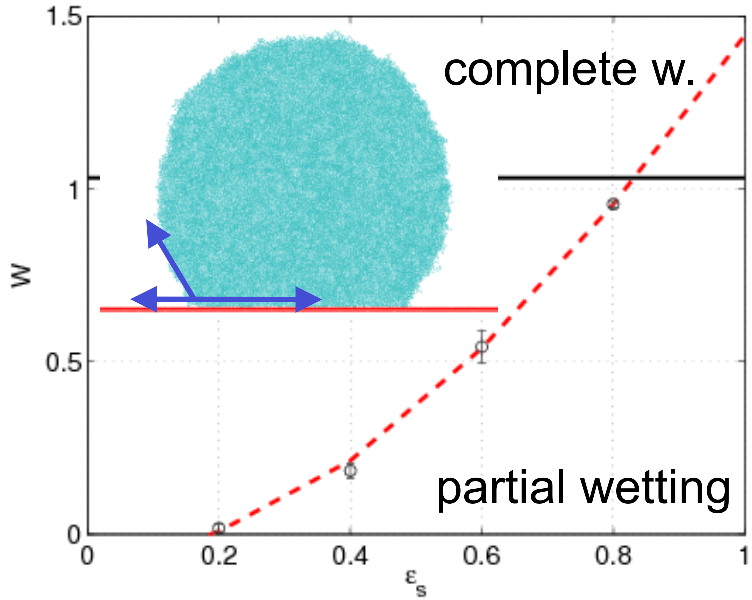
- identify microscopic parameters (e.g., surface tension) that pass information about the molecular structure onto macroscopic phenomenological descriptions
- devise computational strategies for extracting these parameters from molecular models
- assess the validity of macroscopic descriptions on small scales
  reasons for breakdown: interplay of "macroscopic" length scales (e.g., droplet size, scale of topography) with microscopic length scales (e.g., interface width, slip length, or correlation length of thermal fluctuations)

What dictates the statics and dynamics of macroscopically large drops?

parameters that characterize the drop shape?
volume, V, of drop and contact angle, Θ

$$W = (\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})/\gamma = \cos\theta$$

Young 1805



parameters that dictate the dissipation of drops driven by a body force on a "slippery surface" ?
bulk viscosity, η, and slip length slip, δ

$$\eta \frac{\partial v_y}{\partial x}\bigg|_{x_\mathrm{b}} = \frac{\eta}{\delta_\mathrm{b}} v_y\bigg|_{x_\mathrm{b}}$$

HBC: viscous *vs* friction stress

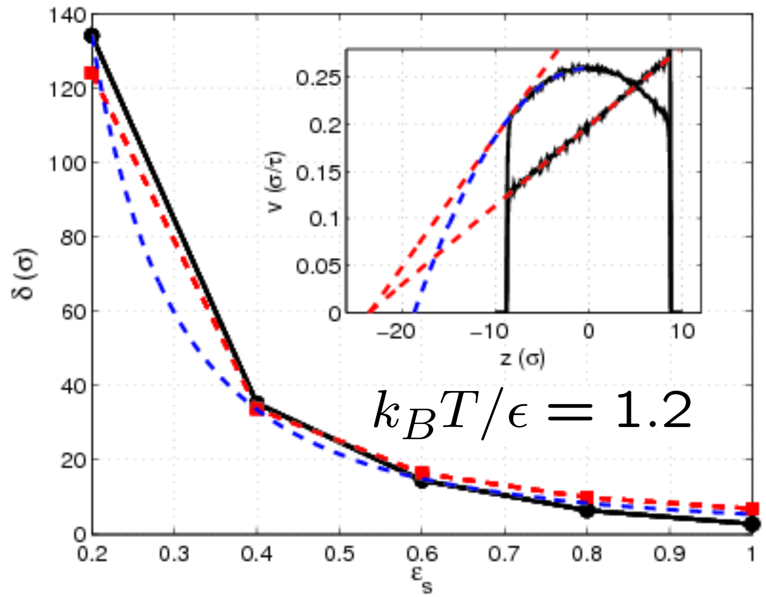
Navier 1823

combine information from Couette flow and Poiseuille flow to determine x_b and δ_b

$$\delta_\mathrm{b} \sim \frac{D^*_{q||}}{S_1(q_{||})\epsilon_s^2 \rho_c}$$

Barrat, Bocquet 1999

x_b and δ_b are materials parameter that characterize the surface independent from the type and strength of the flow



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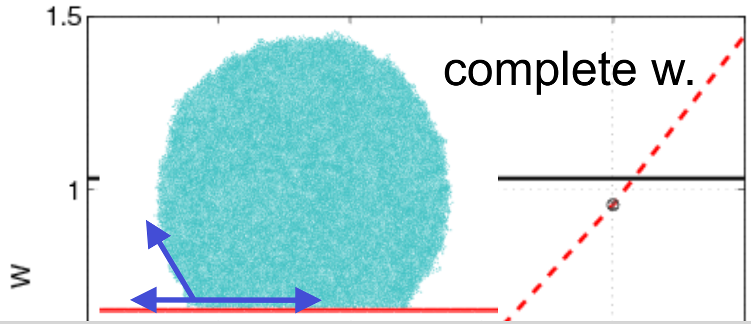


parameters that dictate the dissipation of drops

Goal: *parameter passing* – use molecular simulations to compute parameters that encode the microscopic properties of a material in a continuum description (thin film equation or Navier-Stokes equation)

Which parameters?

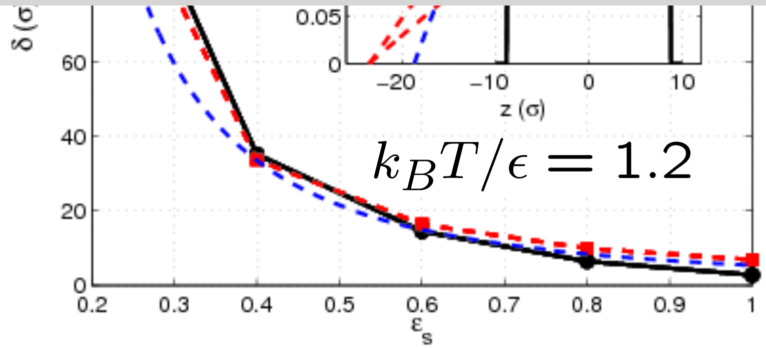
- contact angle and interface potential
- slip length and position of the hydrodynamic boundary

How to efficiently compute these parameters?

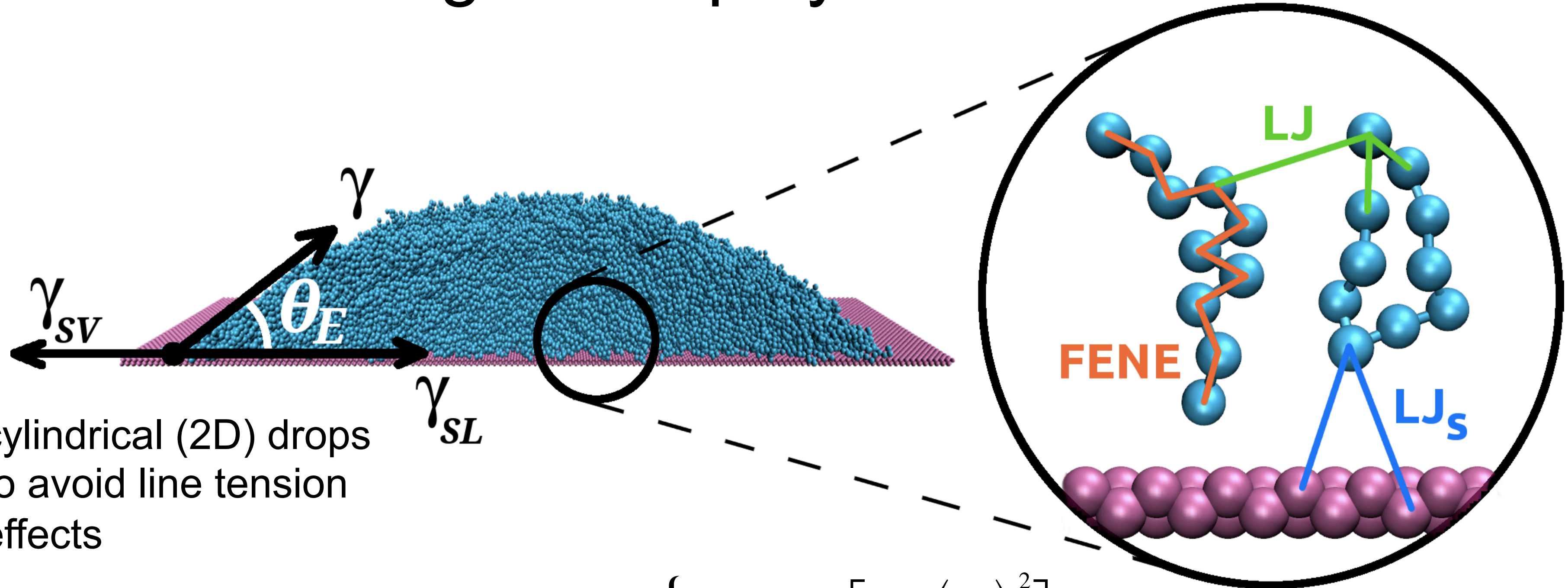
$$\delta_b \sim \frac{D^*_{q||}}{S_1(q_{||})\epsilon_s^2 \rho_c}$$

Barrat, Bocquet 1999

x_b and δ_b are materials parameter that characterize the surface independent from the type and strength of the flow



Coarse-grained polymer simulations



cylindrical (2D) drops to avoid line tension effects

$$U_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$U_{\mathrm{FENE}} = \begin{cases} -\frac{1}{2}kR_0^2\,\ln\left[1-\left(\frac{r}{R_0}\right)^2\right] & \text{for } r < R_0 \\ \infty & \text{for } r \geq R_0 \end{cases}$$

relevant polymer properties:

1. connectivity along the chain
2. excluded volume
3. thermal interaction (fluid-fluid, fluid-wall)

model: Grest, Kremer 1986

Lennard-Jones monomers (N=10,R_e=3.66σ)

FENE potential along bonds

2 layers FCC LJ solid

methods:

MD simulations, DPD thermostat

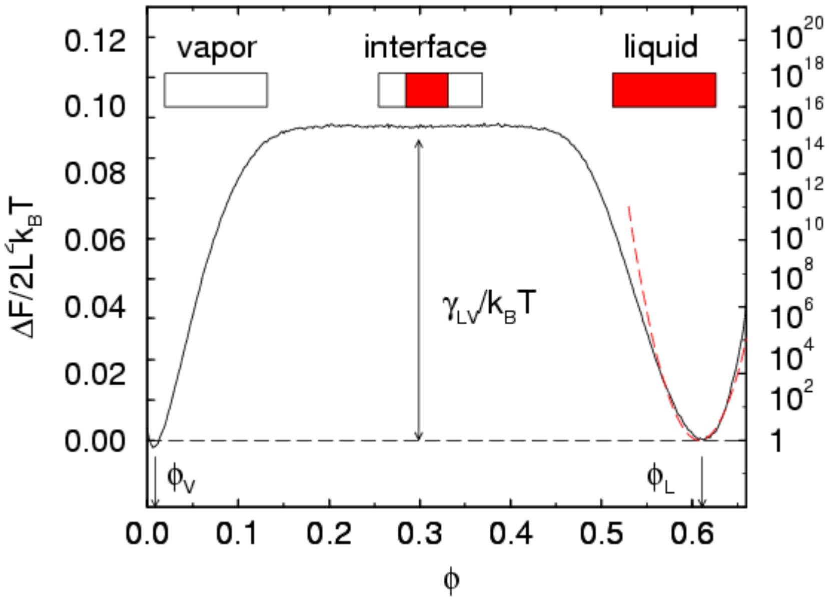
Static behavior of droplets: calculation of tensions

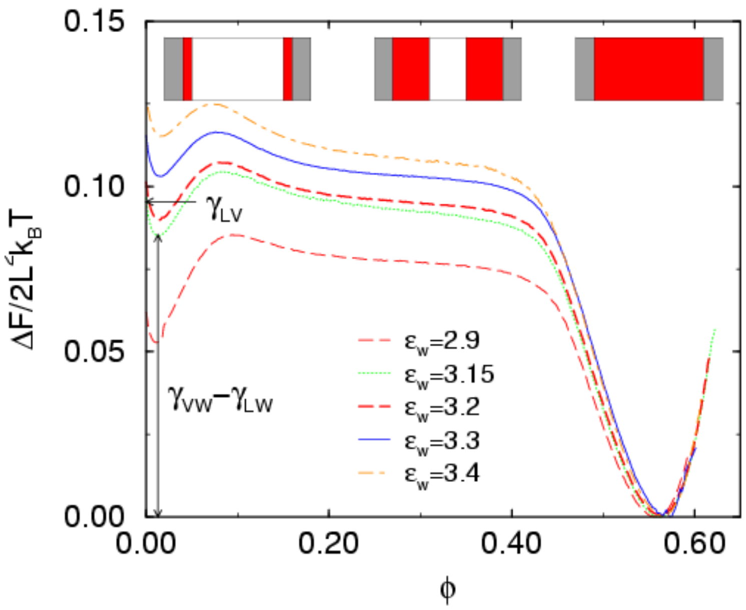
What parameters characterize the macroscopic shape of a droplet?
volume, V, and contact angle, Θ

$$W = (\gamma_{SV} - \gamma_{SL})/\gamma = \cos\theta$$

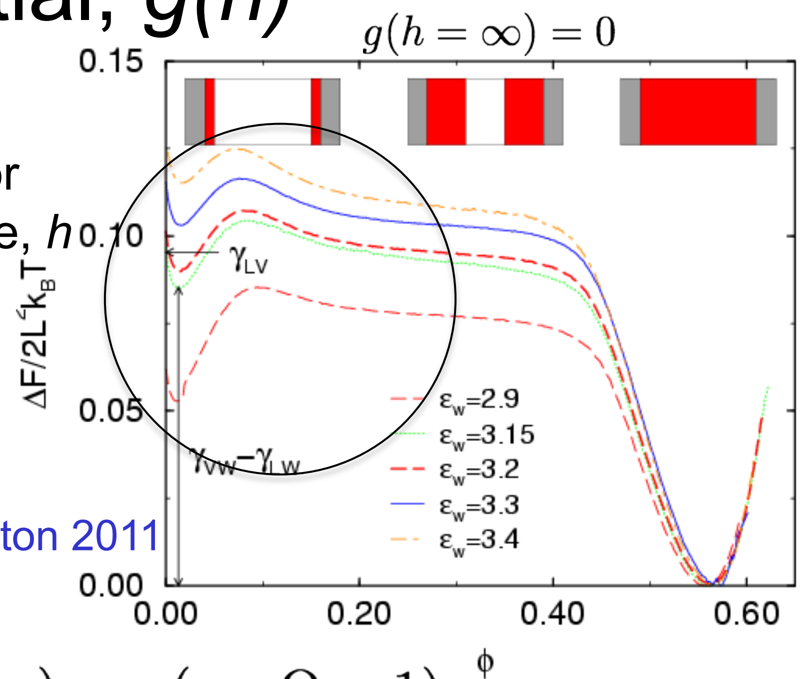
computational benefits of **Young's equation** (compared to measuring Θ):

- separate calculation of planar liquid-vapor and solid-liquid interface allows for small system sizes (compared to drops),
  no interaction between interfaces and no curvature effects
- changes of γ_{sl} and γ_{sv} with respect to T or ε_{wall} can be calculated by TDI
- accurate computational techniques available based on e.g., reweighting techniques in **grandcanonical ensemble** or **anisotropy of pressure** (virial)





Interface potential, *g(h)*



interface potential:
Interaction between solid-liquid and liquid-vapor interface per area as a function of their distance, *h*

$$g(h) = -\frac{k_B T}{A} \ln P(h) + \text{const}$$

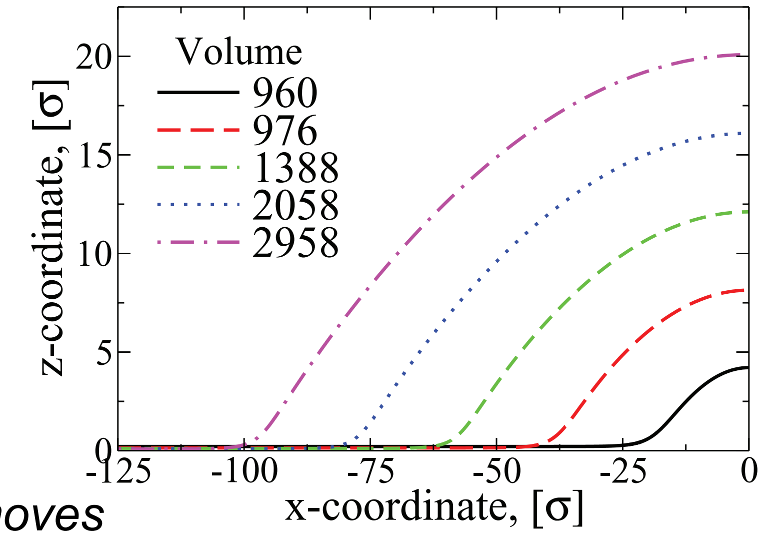
in grandcanonical (μVT) simulations

Müller, MacDowell 2000, MacDowell, Müller 2006
Grzelak, Errington 2008, 2010, Rane, Kumar, Errington 2011

provides information about contact angle,

$$\gamma_{SV} = \gamma_{SL} + \gamma + g(h_{\min}) \quad \Rightarrow \quad g(h_{\min}) = \gamma(\cos\Theta - 1)$$

line tension and deviations from cap-shaped droplet profile in the vicinity of the three-phase contact line

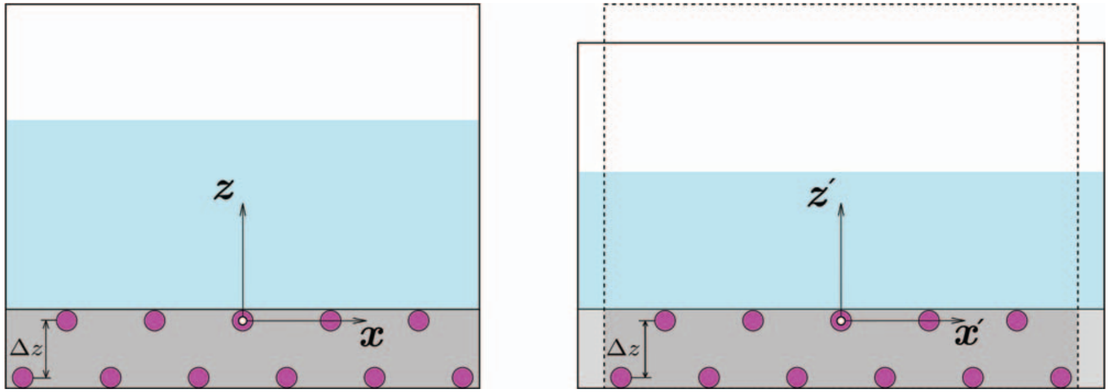


important for parameter-passing scheme from particle-based models to continuum description

$$F[h] = \gamma_{SL} L_y \int dx \; + L_y \int dx \sqrt{1 + (\partial_x h)^2}\, [\gamma + g(h)]$$

➡ **problem**: *grandcanonical insertion/deletion moves*

Measuring *g(h)* in the canonical ensemble



virtual deformation that changes area, A, but not volume of the liquid

$$\frac{1}{A}\left.\frac{\mathrm{d}F(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=1} = \gamma_{\mathrm{SL}} + \gamma + g(h) - \frac{\mathrm{d}g(h)}{\mathrm{d}h}h$$

Legendre transform of interface potential

$$\frac{1}{A}\left.\frac{\mathrm{d}F(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=1} = \int \mathrm{d}z\ [p_{\mathrm{n}}(z) - p_{\mathrm{t}}(z)]$$

anisotropy of virial pressure

$$+\frac{1}{A}\left\langle \sum_{s,i}\left[f^{\mathrm{s}}_{z,is}z_{is} - \frac{1}{2}(f^{\mathrm{s}}_{x,is}x_i + f^{\mathrm{s}}_{y,is}y_i)\right] - \sum_{s_2,i} f^{\mathrm{s}}_{z,is_2}\Delta z\right\rangle$$

contribution of non-deformed solid-liquid interactions

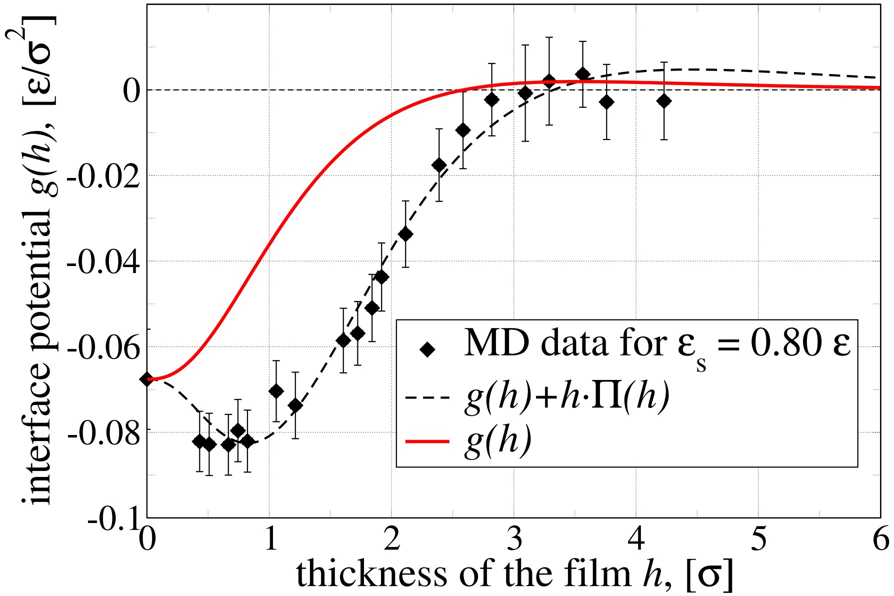
1) measure $\frac{1}{A}\left.\frac{\mathrm{d}F(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda=1}$ in MD simulation as a function of film thickness h

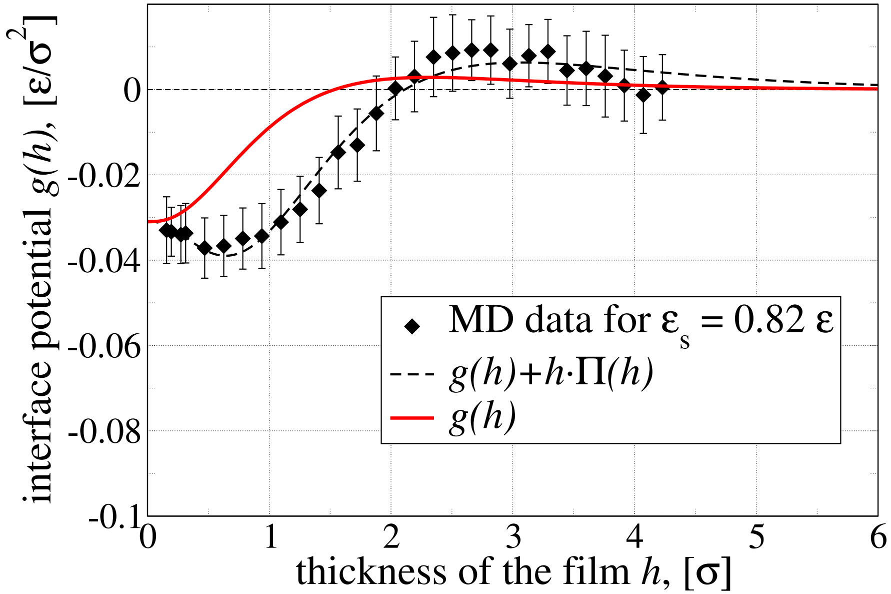
2) fit result by series of exponential (appropriate for short-ranged, cut-off interactions)

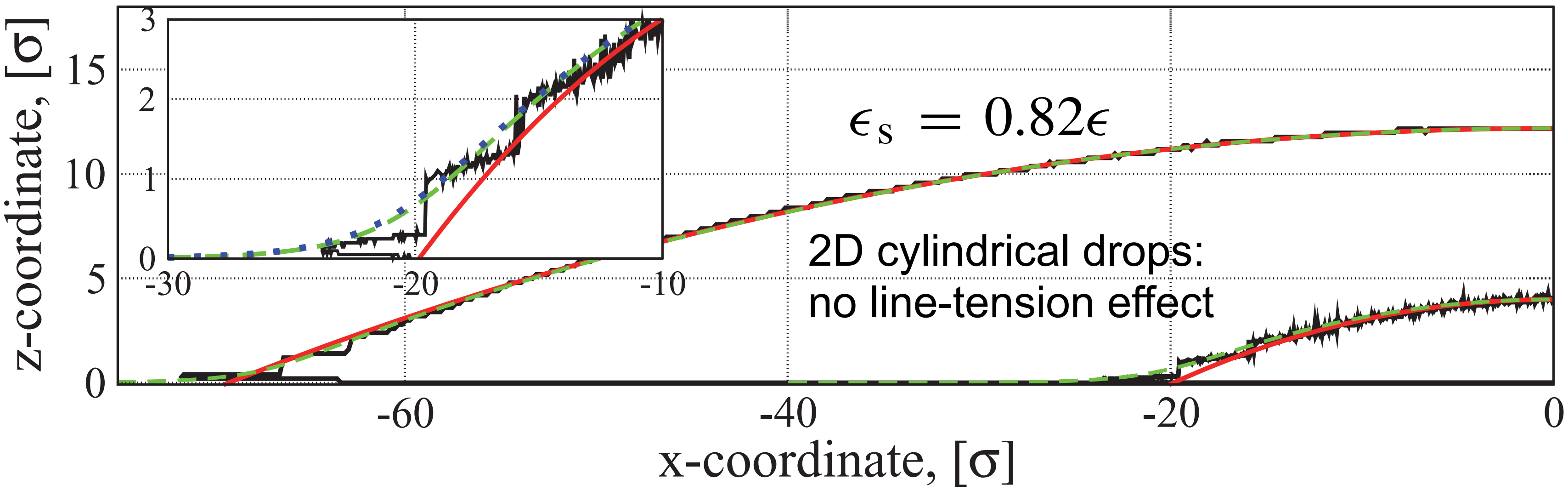
3) invert Legendre transform

Tretyakov, Müller, Todorova, Thiele, JCP **138**, 064905 (2013)

Results







➡ good description of the average deviation from cap-shape but liquid layering

Tretyakov, Müller, Todorova, Thiele, JCP **138**, 064905 (2013)

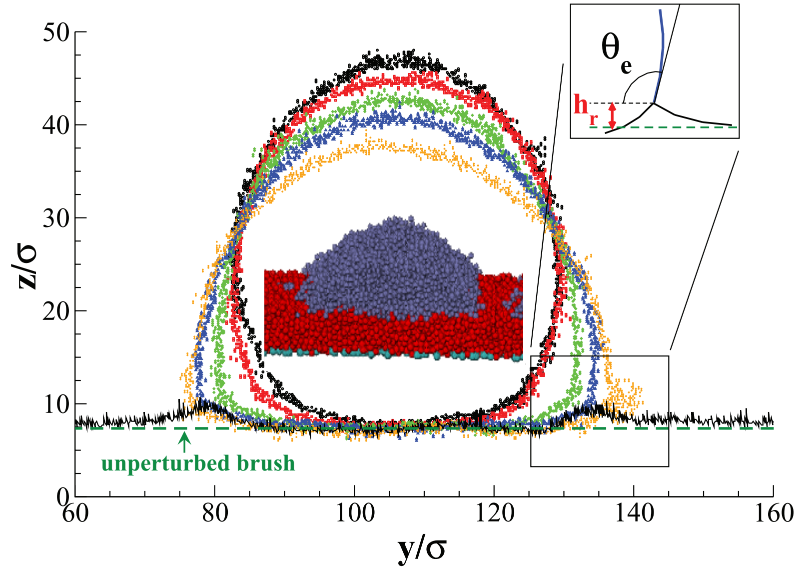
Droplets on deformable substrates

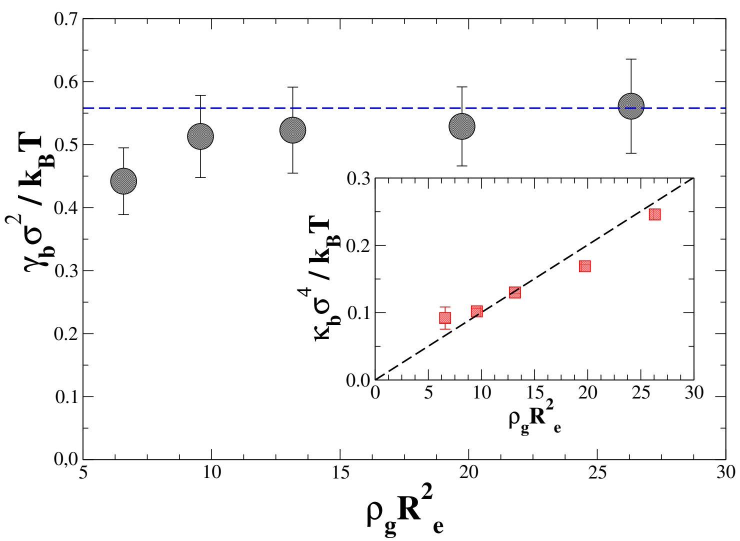
droplets on a polymer brush

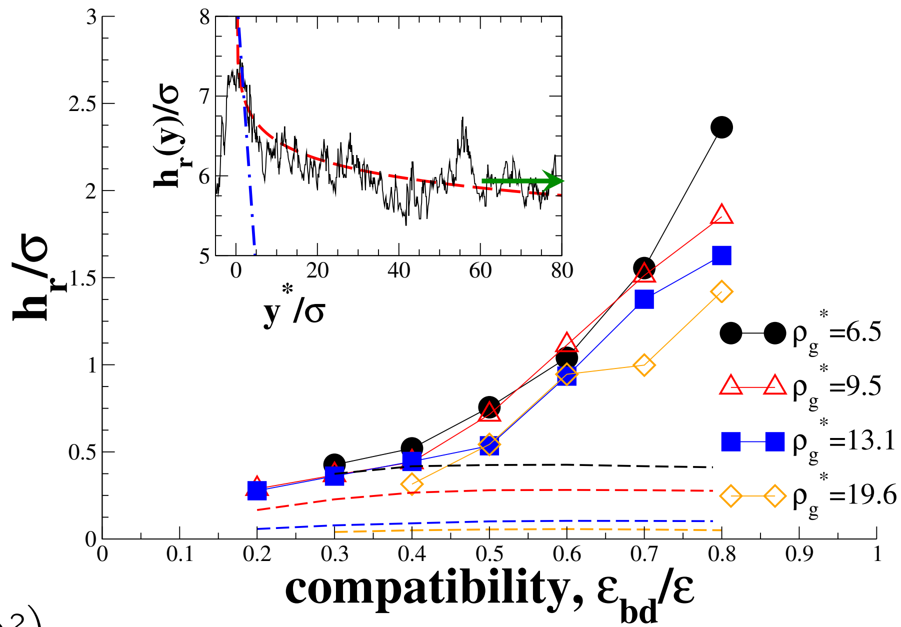
controlling the incompatibility between polymer liquid and brush, one independently tailors wettability and softness

➡

- rich wetting behavior
- deformation at the three-phase contact line ridge Shanahan, Carré, Langmuir **10**, 1647 (1994); Carré, Shanahan, Langmuir **11**, 24 (1995)







$$\mathcal{H}_{\text{cap}}[z_{\text{int}}(x,y)] = \frac{1}{2}\int \mathrm{d}^2(x,y)\left(\gamma_b\,[\nabla z_{\text{int}}]^2 + \kappa_b\,(z_{\text{int}} - \bar{z}_{\text{int}})^2\right)$$

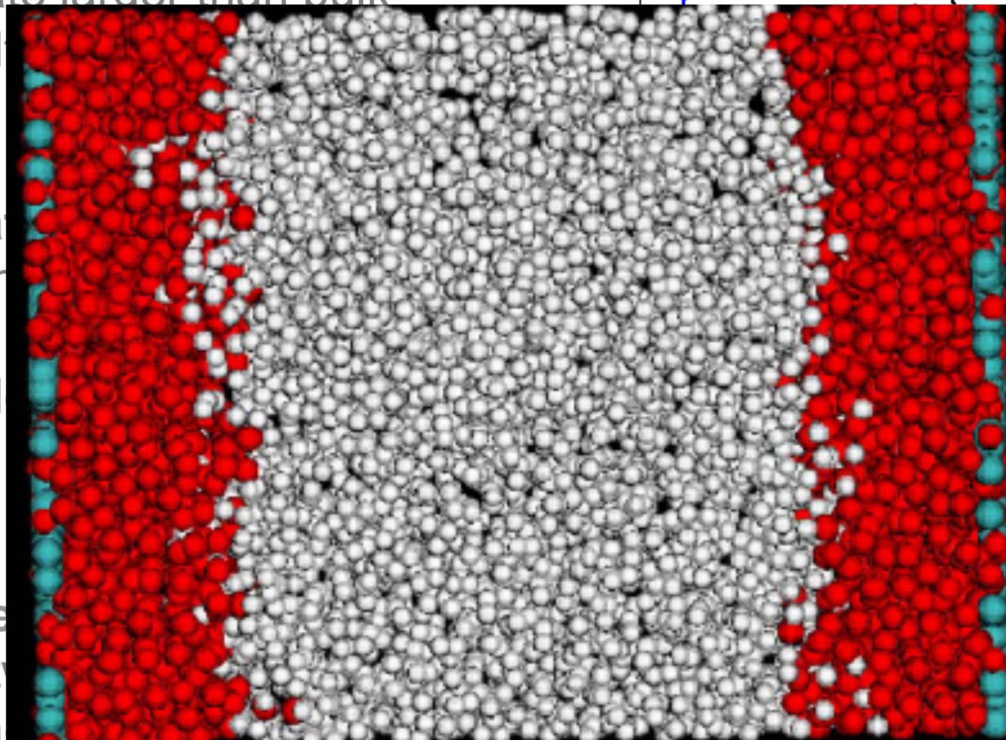
Léonforte, Müller, JCP **135**, 214703 (2011)

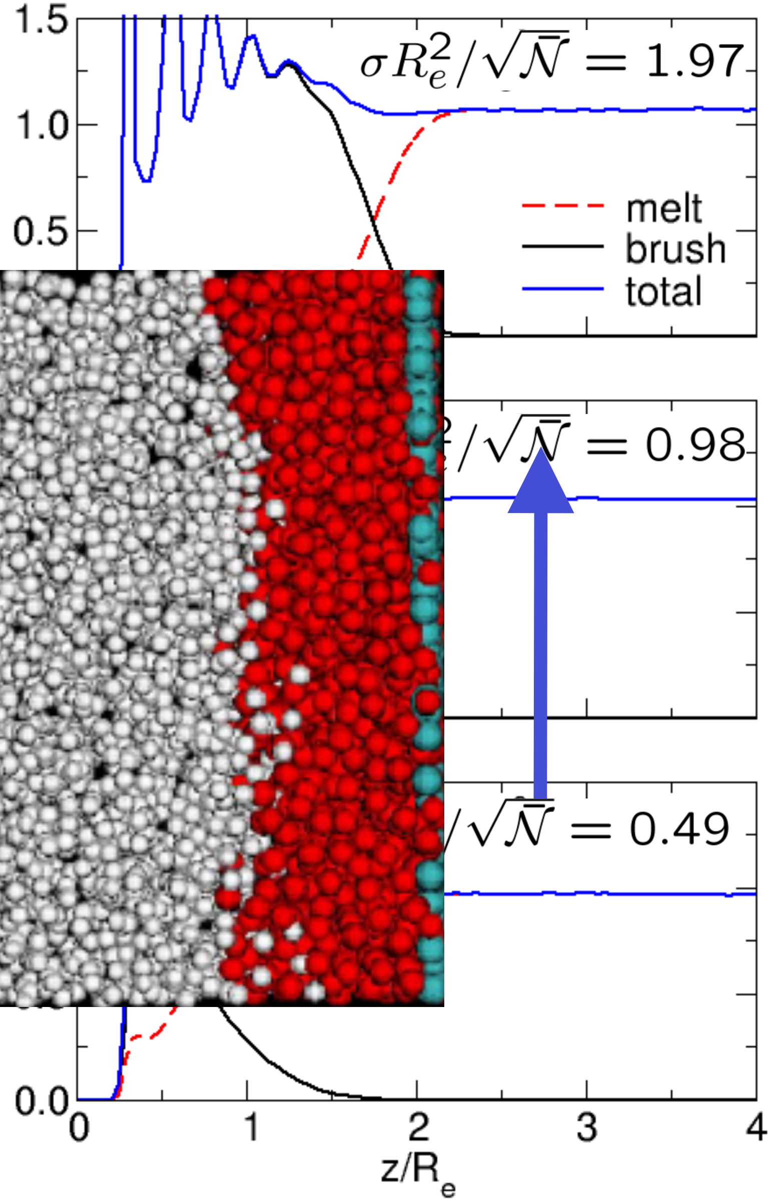
Flow past polymer brush

- **high grafting density**: **autophobicity**, strong layering, density at substrate larger than bulk narrow brush-mel

- **intermediate gra** wide brush melt i free chains reach total densit profil grafting

- **small grafting de** no separation bet brush-melt interfa





Pastorino et al, JCP **124**, 064902 (2006), Macromolecules **42**, 401 (2009)

Velocity profiles under shear (Couette flow)

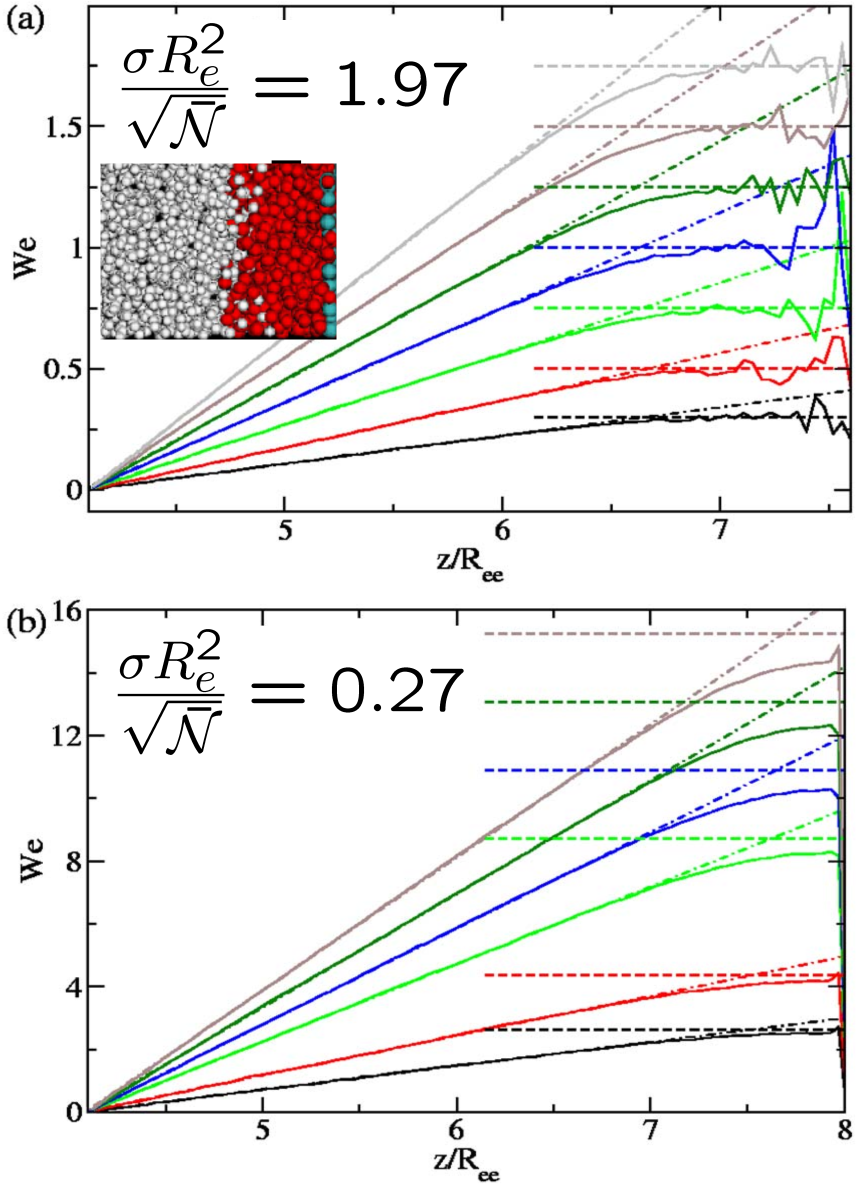
linear profile at center yields viscosity

- <u>very</u> high grafting densities:
  finite apparent slip (small overlap between brush and melt)
  Pastorino et al, Macro. **42**, 401 (2009)
- intermediate (high) grafting density:
  no apparent slip boundary condition, reduced effective width
- small grafting density:
  finite apparent slip

linear extrapolation of the velocity profile is insufficient at a soft surface

- negative slip length δ (inside the fluid) incompatible with Green-Kubo relation
- where is the boundary, x_b?

➡ use two type of flows: Couette & Poiseuille



Pastorino et al, JCP **124**, 064902 (2006)

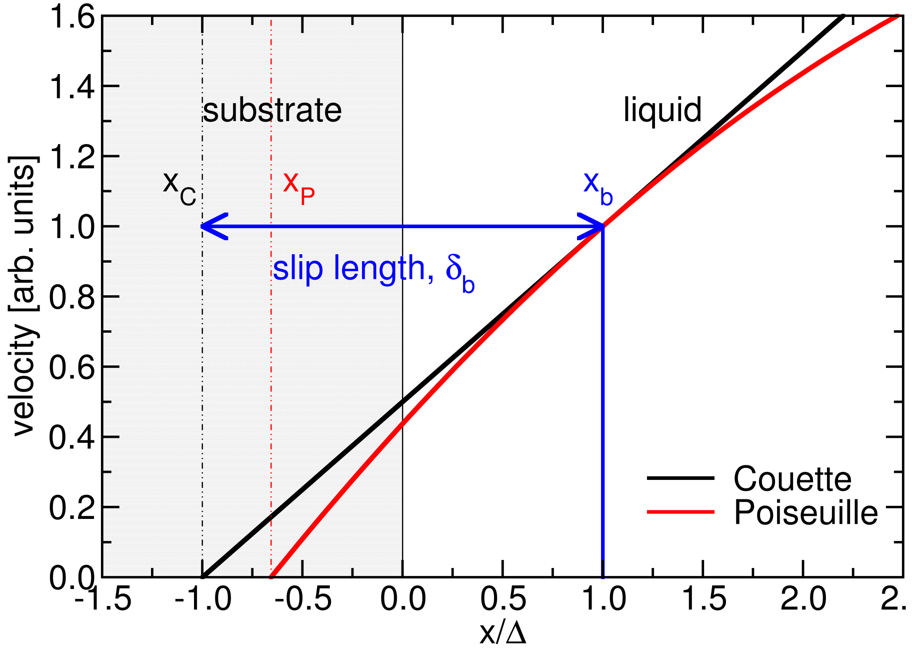
Navier slip boundary condition

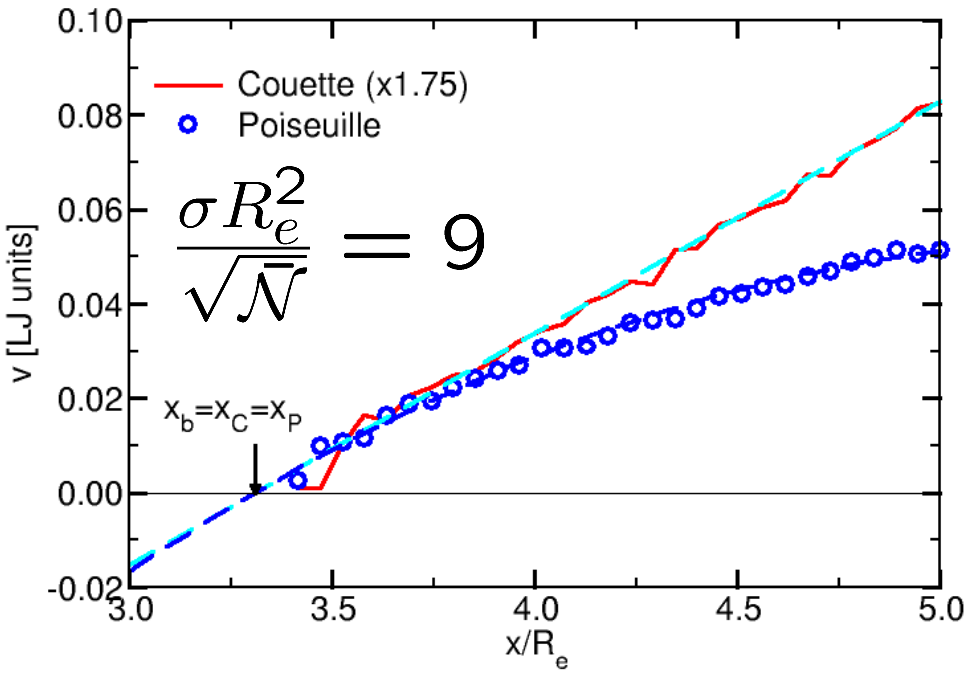
$$\eta \frac{\partial v_y}{\partial x}\bigg|_{x_b} = \frac{\eta}{\delta_{\mathrm{b}}} v_y\bigg|_{x_b}$$

hydrodynamic boundary condition:
parameterize microscopic information obtained from MD simulation as boundary condition for NS equation

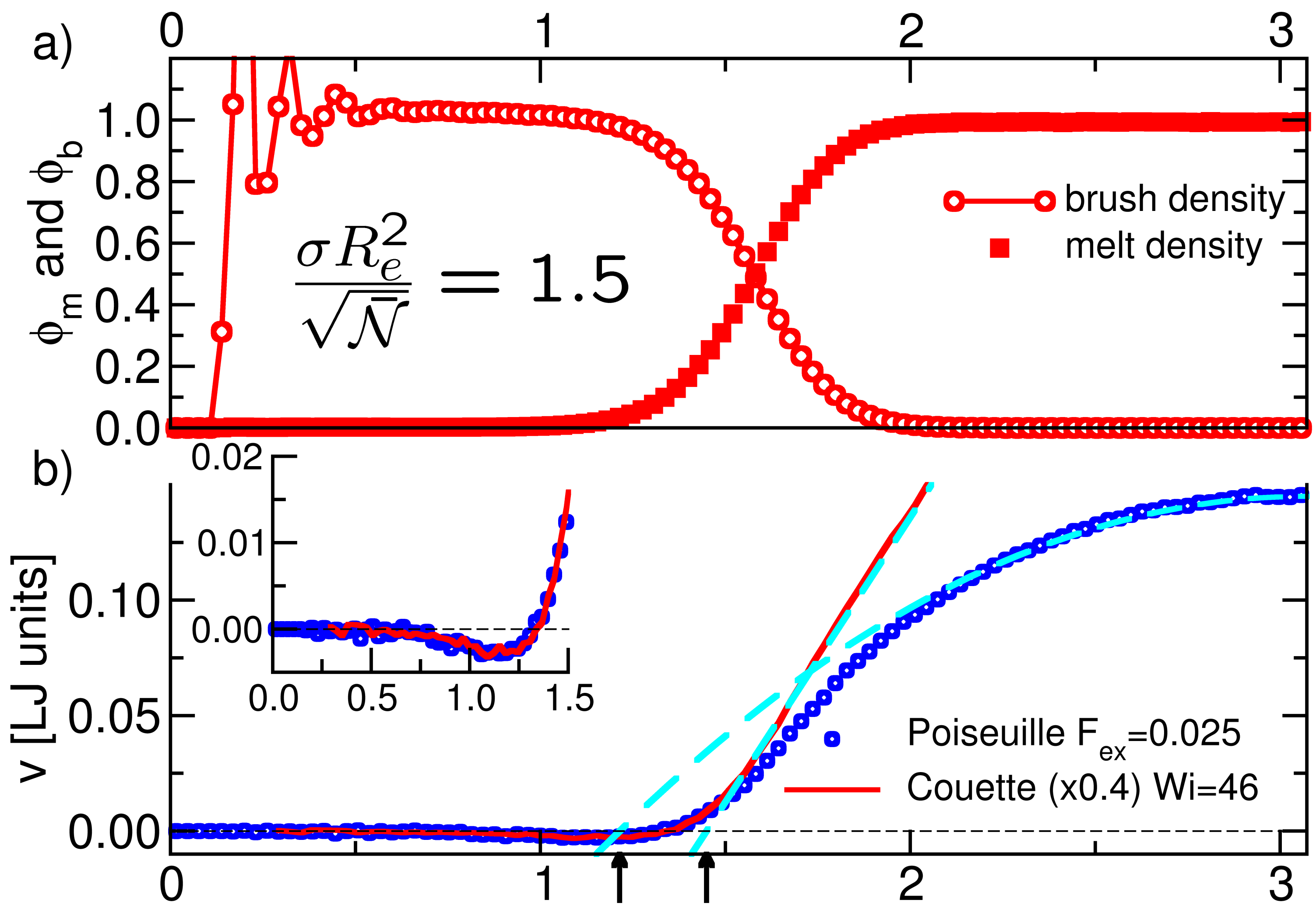
fit flow far away from surface by prediction of continuum hydrodynamics
(Couette flow – linear velocity profile and Poiseuille flow – parabolic profile)
and extrapolate these profiles to zero (x_C and x_P)

$$\delta_{\mathrm{b}} = \sqrt{(x_{\mathrm{P}} - x_{\mathrm{C}})(D - x_{\mathrm{C}} - x_{\mathrm{P}})} \quad \text{and} \quad x_b = x_{\mathrm{C}} + \delta_b$$





Poiseuille and Couette flow (MD)

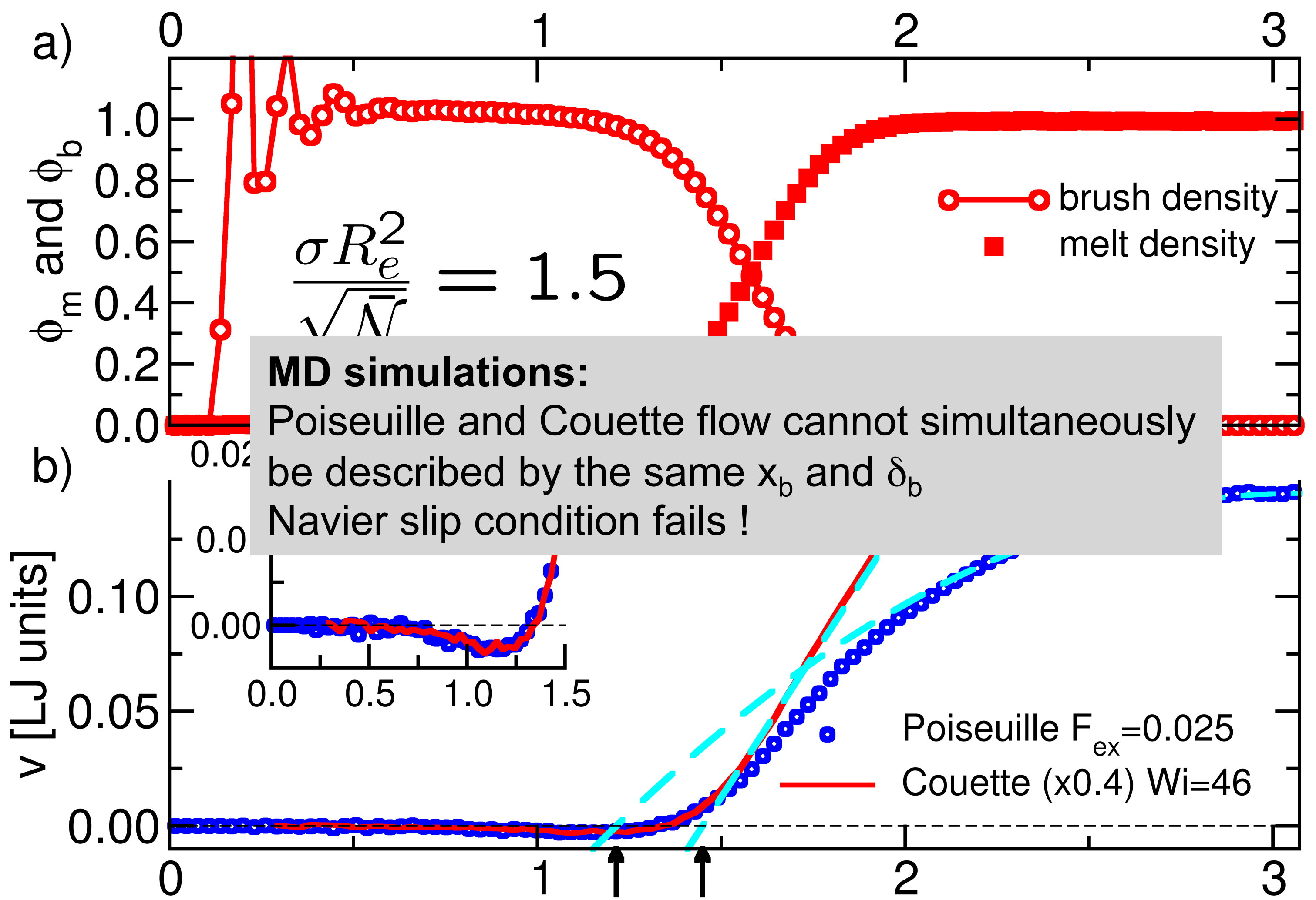


$x_P < x_C$

$\delta_b = \sqrt{(x_P - x_C)(D - x_C - x_P)}$

$x_b = x_C + \delta_b$

Poiseuille and Couette flow (MD)



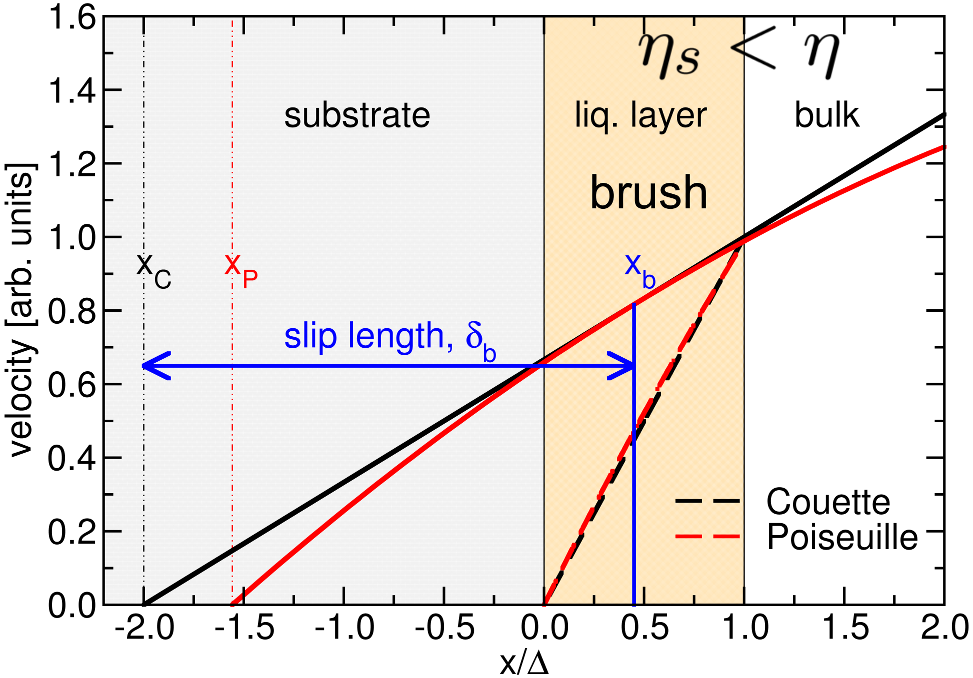
MD simulations:
Poiseuille and Couette flow cannot simultaneously be described by the same x_b and δ_b
Navier slip condition fails !

$x_P < x_C$

$$\delta_b = \sqrt{(x_P - x_C)(D - x_C - x_P)}$$

$$x_b = x_C + \delta_b$$

Schematic, two-layer model



$$v_{|x=0} = 0$$

$$v_{|x=\Delta^-} = v_{|x=\Delta^+}$$

$$\eta_s \frac{\partial v}{\partial x}_{|x=\Delta^-} = \eta \frac{\partial v}{\partial x}_{|x=\Delta^+}$$

$$v = \dot{\gamma} \frac{\eta}{\eta_s} x \qquad v = \frac{f}{2\eta_s} x(D-x)$$

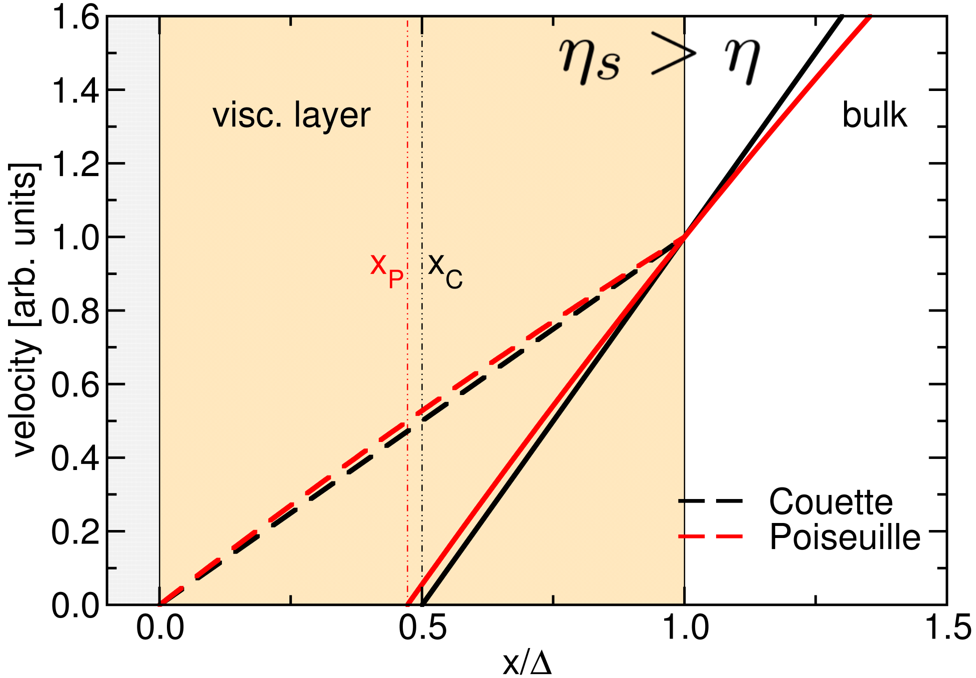
$$v = \dot{\gamma}(x - x_{\mathrm{C}}) \qquad v = \frac{f}{2\eta}(x - x_{\mathrm{P}})(D - x_{\mathrm{P}} - x)$$

$$x_{\mathrm{C}} = -\left(\frac{\eta}{\eta_s} - 1\right)\Delta \qquad x_P = \frac{D}{2} \pm \sqrt{\frac{D^2}{4} + \left(\frac{\eta}{\eta_s} - 1\right)\Delta(D - \Delta)}$$

$$\delta_{\mathrm{b}} = \Delta \sqrt{\frac{\eta}{\eta_s}\left(\frac{\eta}{\eta_s} - 1\right)}$$

Servantie, Müller, PRL **101**, 026101(2008)

Schematic, two-layer model



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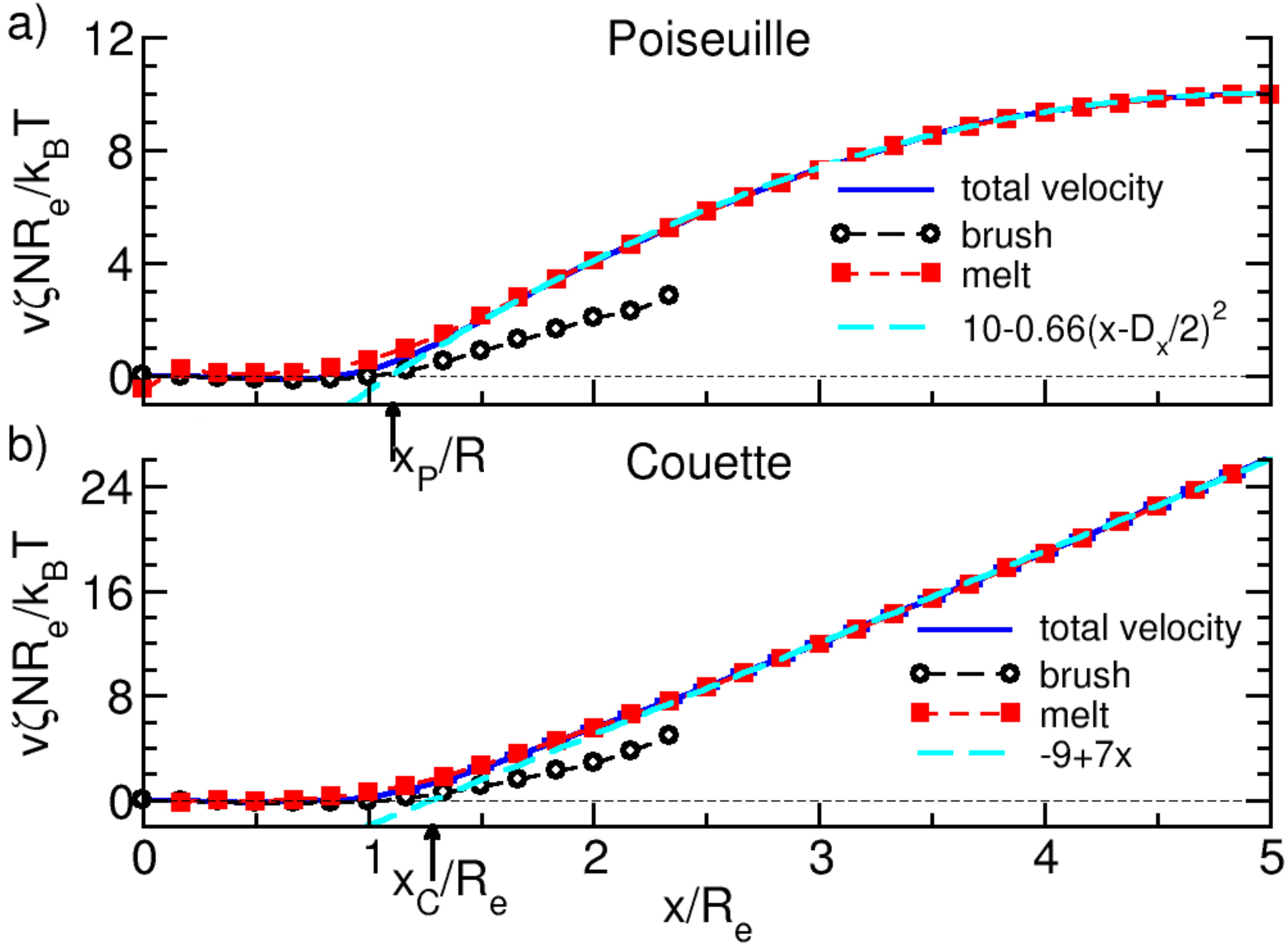
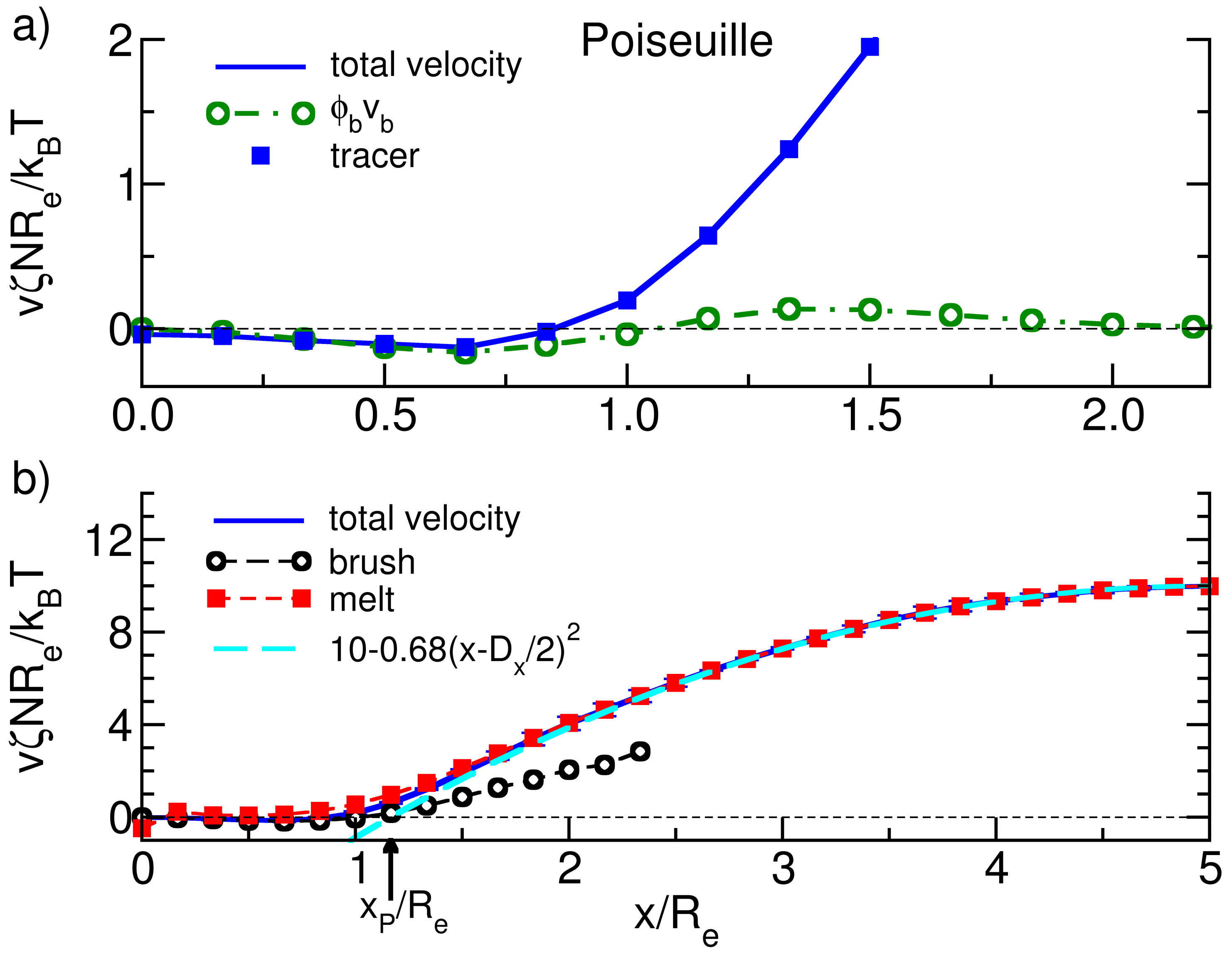
$$\delta_\mathrm{b} = \Delta\sqrt{\frac{\eta}{\eta_s}\left(\frac{\eta}{\eta_s} - 1\right)}$$

does not exist !

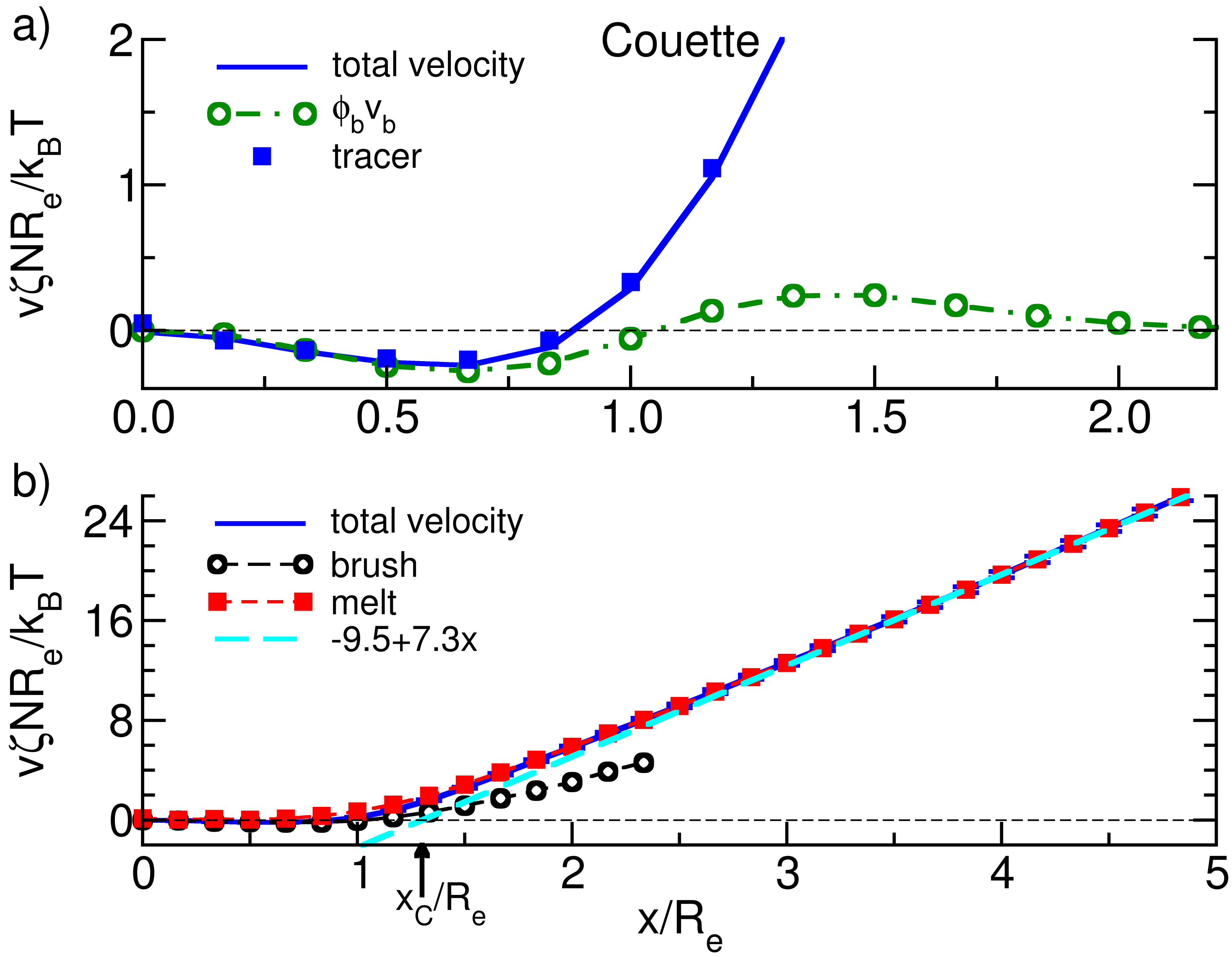
Velocity profiles (SCMF)
Poiseuille and Couette flow



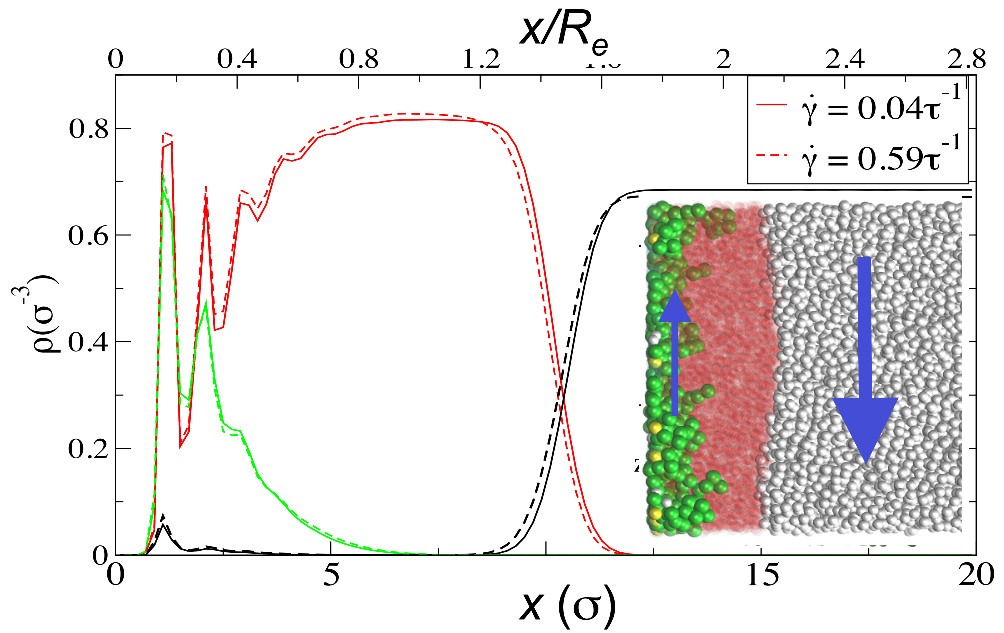
Velocity profiles (SCMF)
inversion of flow direction inside the brush

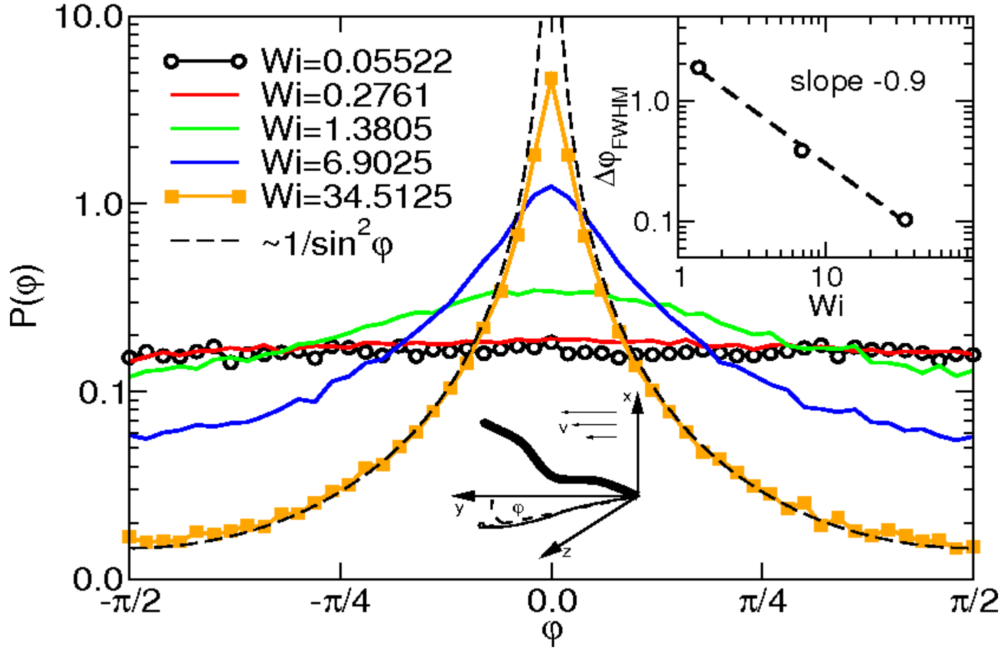


Velocity profiles (dynamic SCMF simulations) inversion of flow direction inside the brush



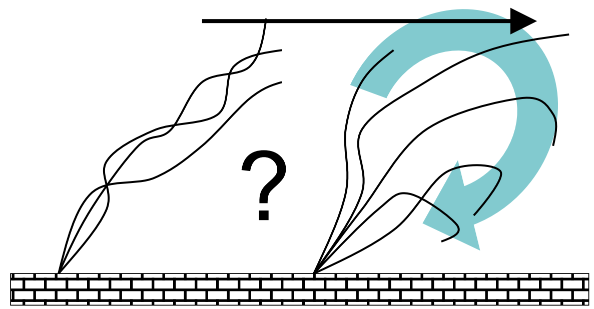
Microscopic flow at the surface





back to flow past polymer brushes: mixed brush of long irreversibly grafted and short end-physisorbed chains in a explicit bad solvent

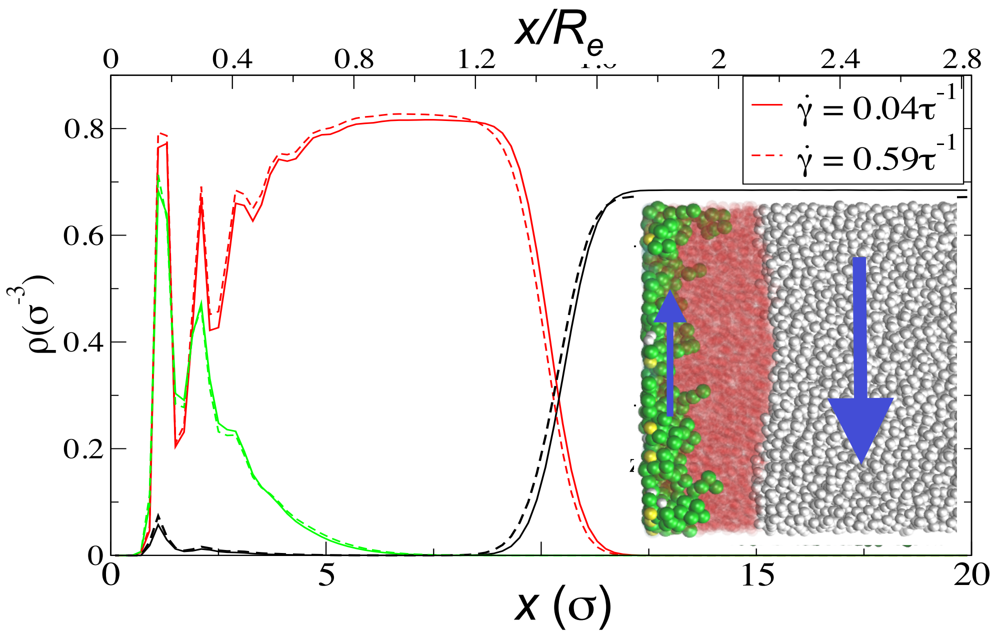
Is the flow inside the brush similar to the one in a porous medium?
Milner, Macromolecules **24**, 3704 (1991)



static tilt vs cyclic motion

Gerashchenko, Steinberg, 2006,
Delgado-Buscaliono 2006,
Winkler, 2006

Microscopic flow at the surface



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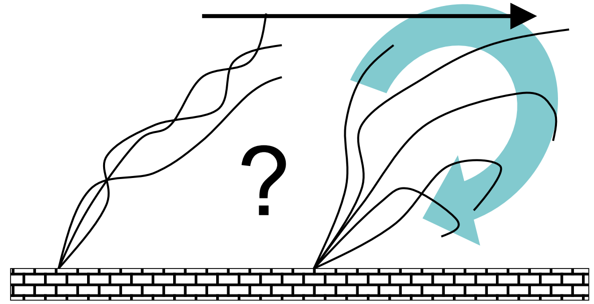
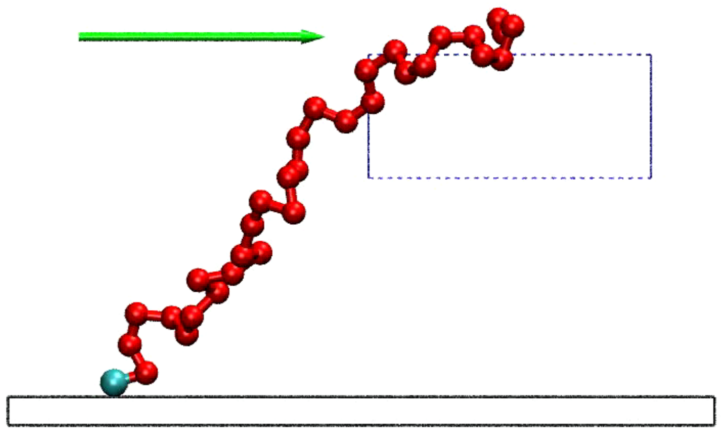


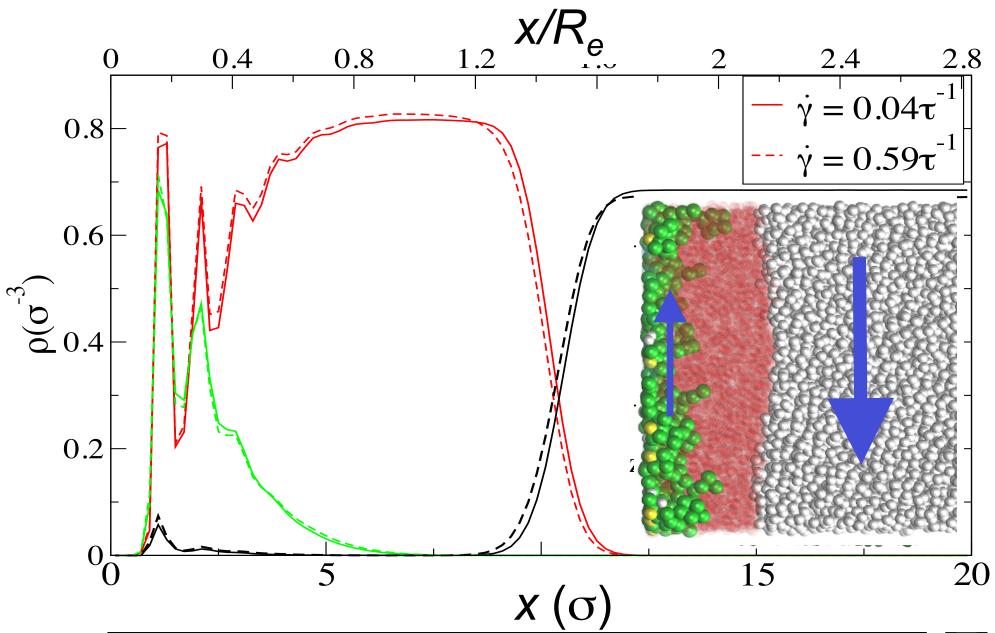
static tilt vs cyclic motion

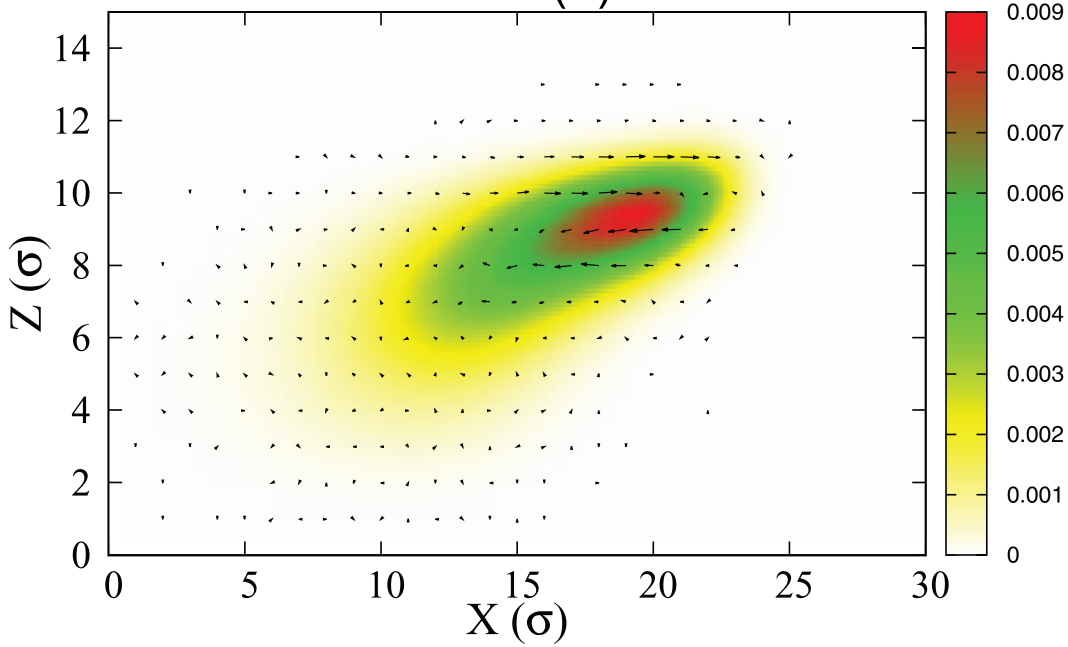


➡ collective tumbling motion of the long grafted chains results in an inversion of the direction of the near-surface flow
$v_{inv}=\alpha R_e \dot{\gamma}$ with $\alpha=10^{-5}$

Pastorino, Müller, JCP **140**, 014901 (2014)

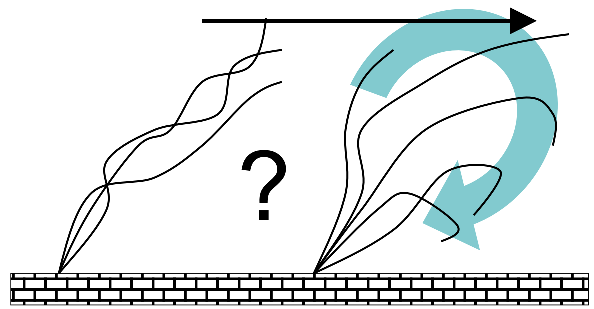
Microscopic flow at the surface





back to flow past polymer brushes: mixed brush of long irreversibly grafted and short end-physisorbed chains in a explicit bad solvent

Is the flow inside the brush similar to the one in a porous medium?
Milner, Macromolecules **24**, 3704 (1991)



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Pastorino, Müller, JCP **140**, 014901 (2014)

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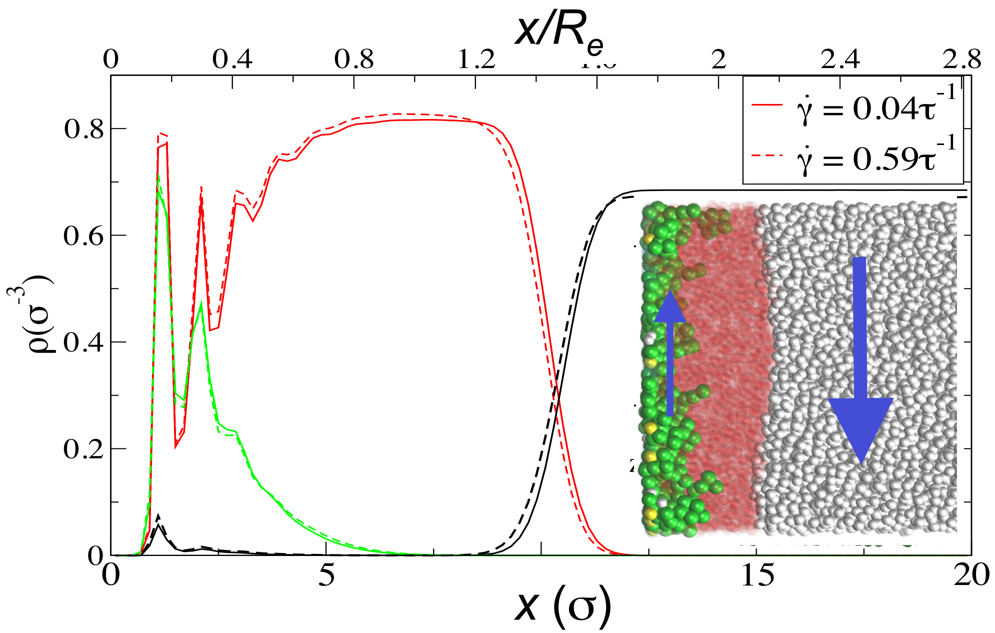

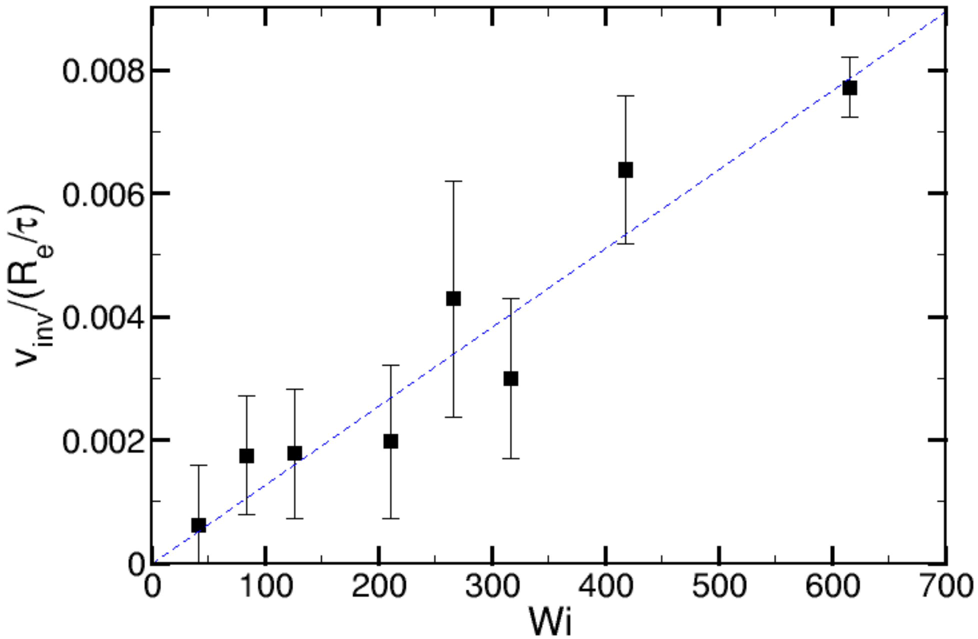

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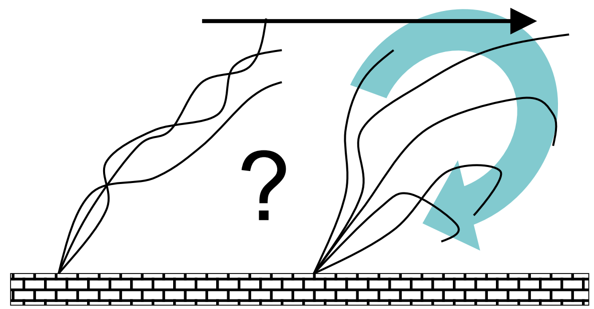

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Pastorino, Müller, JCP **140**, 014901 (2014)

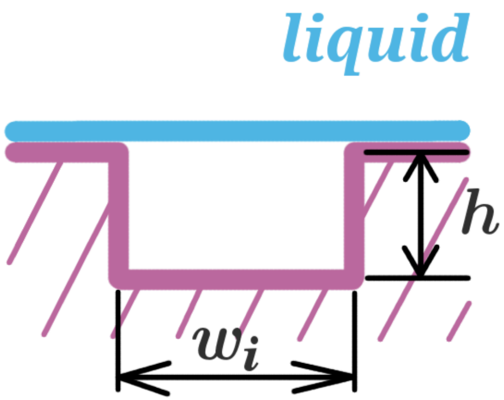
Topographically structured substrates

tailor wettability and surface flow by topographical structure of substrate

system: **2D grooves**

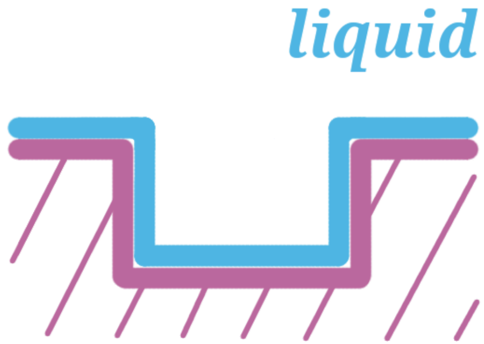
macroscopic description:

Cassie state



$$\cos\Theta_{\mathrm{fill}} = -\frac{1}{1+2h/w}$$

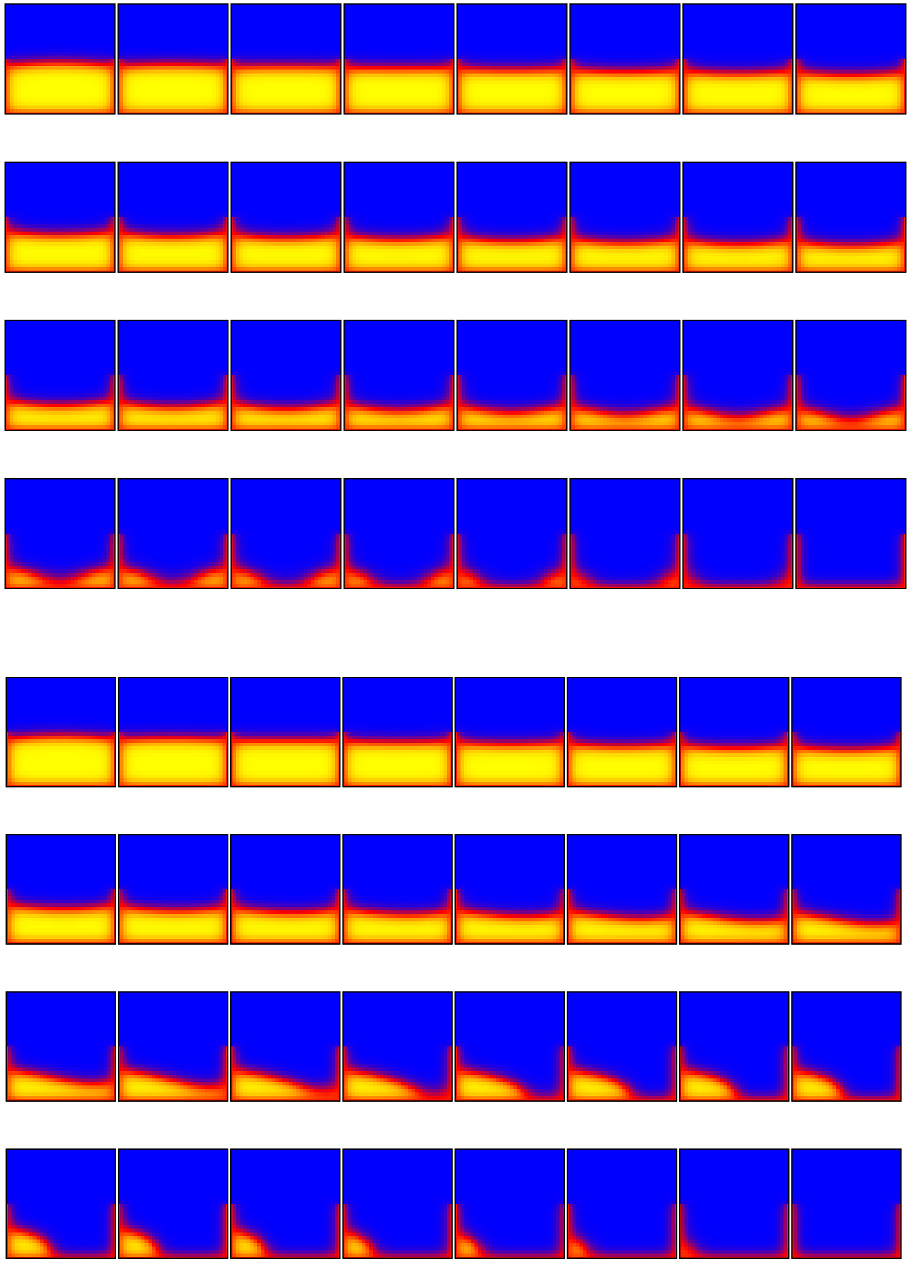
Wenzel state

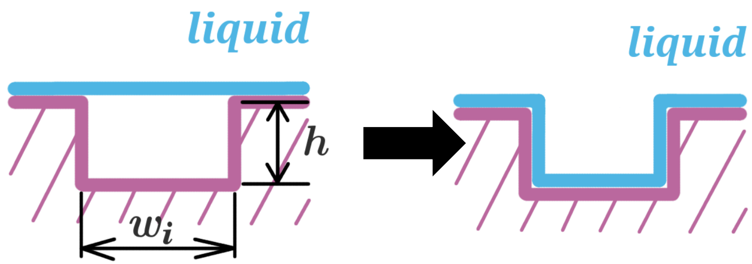


macroscopic expectation:
Cassie state gives rise to lower friction,
only the liquid in contact with the solid gives rise to friction

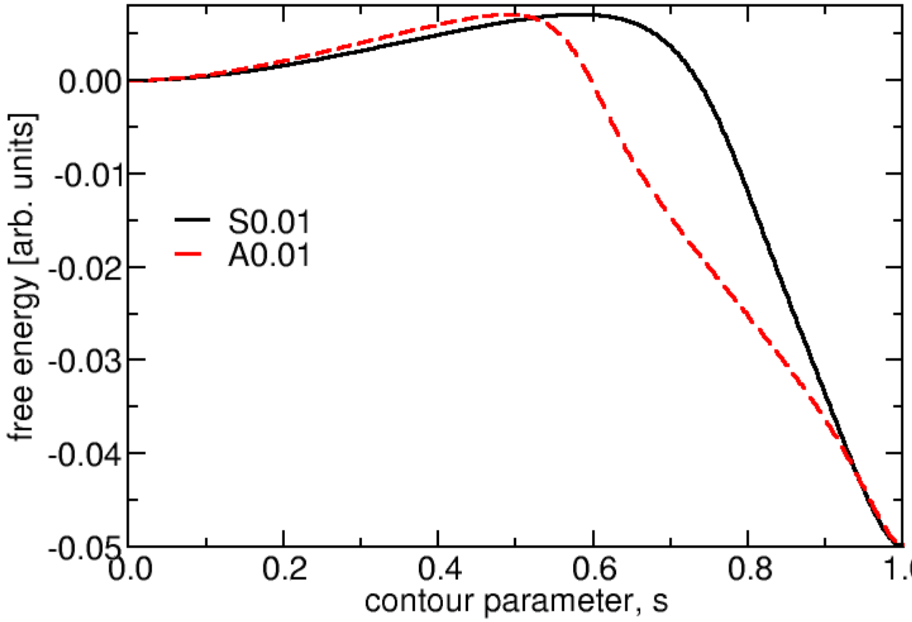
Cottin-Bizonne, Barrat, Bocquet, Charlaix,
Nat. Mater. 2, 237 (2003)

Topographically structured substrates





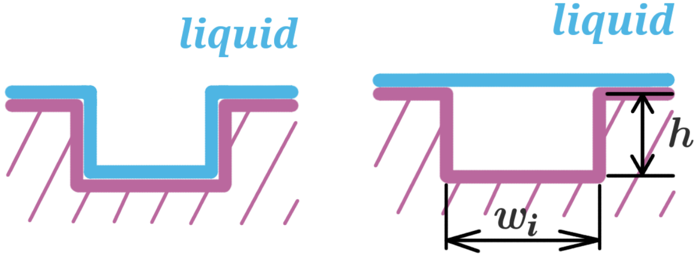
minimum free energy path of filling:
most probable path of filling the groove

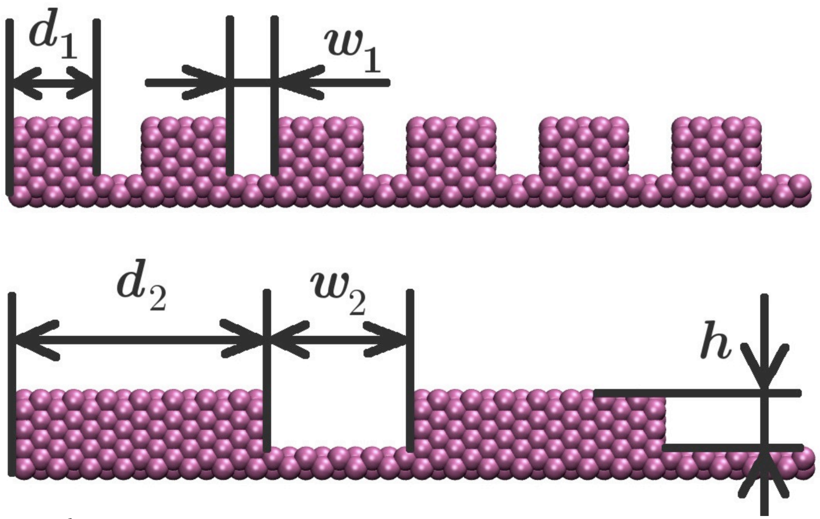


with A. Giacomello and S. Melloni

Microscopically structured substrates

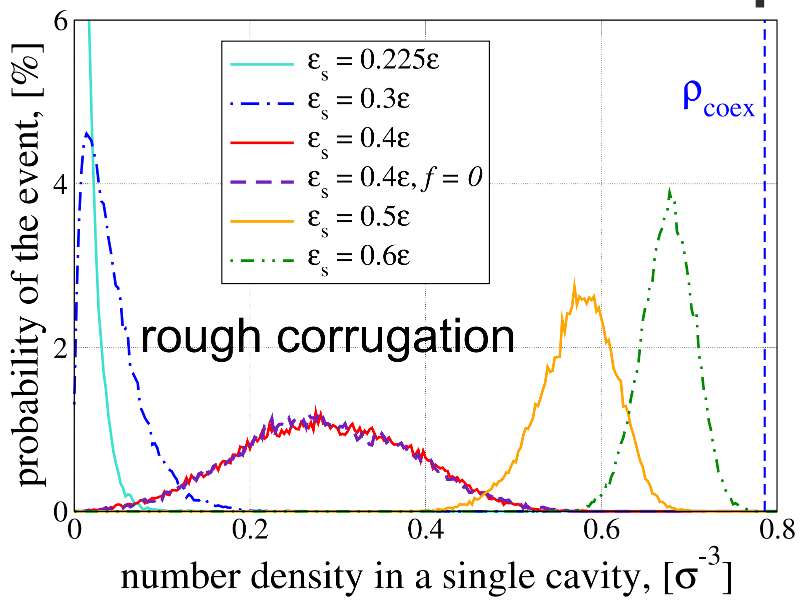
crossover between macroscopically structured substrates (Wenzel and Cassie states) and intrinsic surface roughness





→ no sharp transition between Cassie and Wenzel state but rather gradual crossover

liquid-vapor interface exhibits very large vertical fluctuations

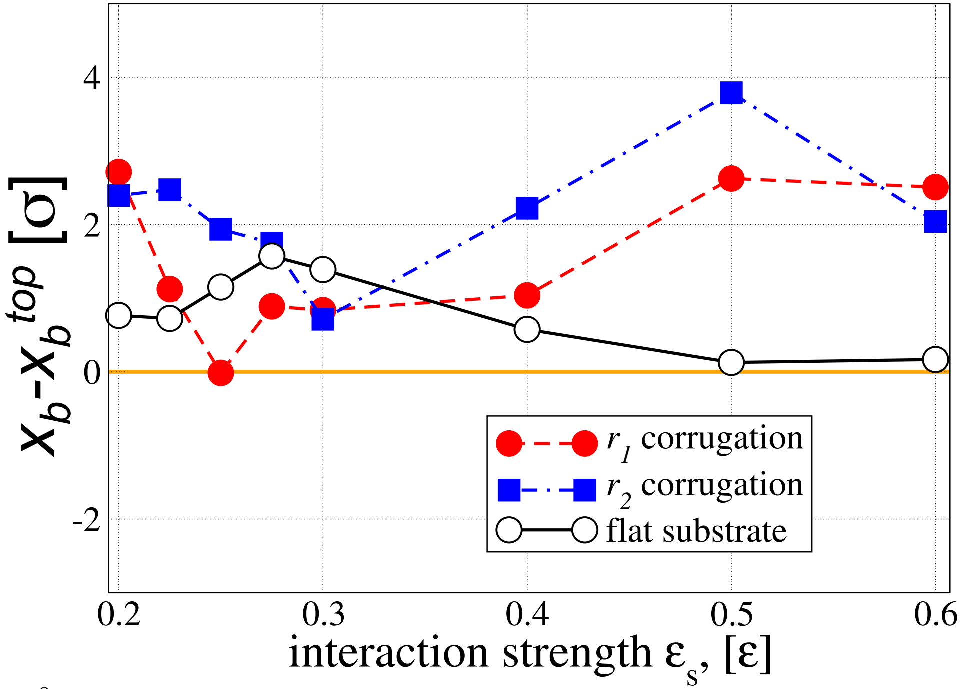


Tretyakov, Müller, Soft Matter **9**, 3613 (2013)

Questions:

- Where is the position x_b of the hydrodynamic boundary condition?
- How does friction change due to topographical structure?

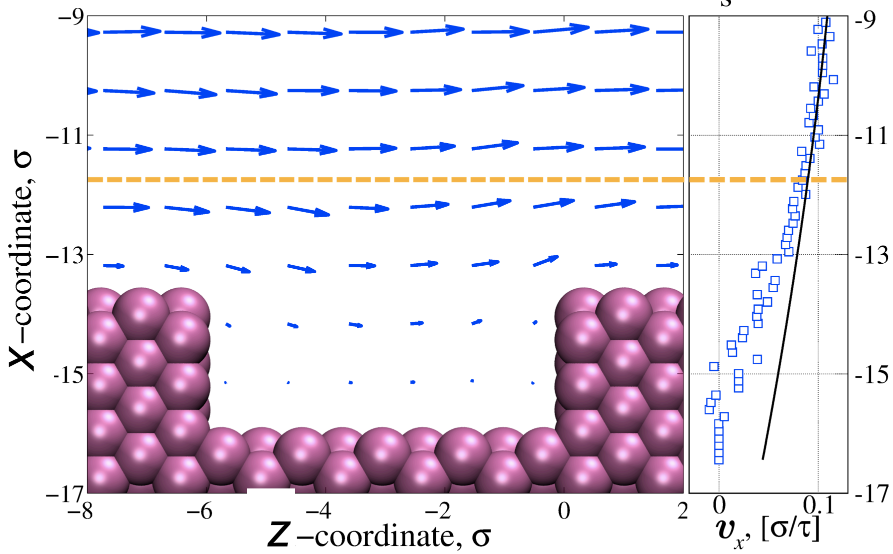
Where is the hydrodynamic boundary position?

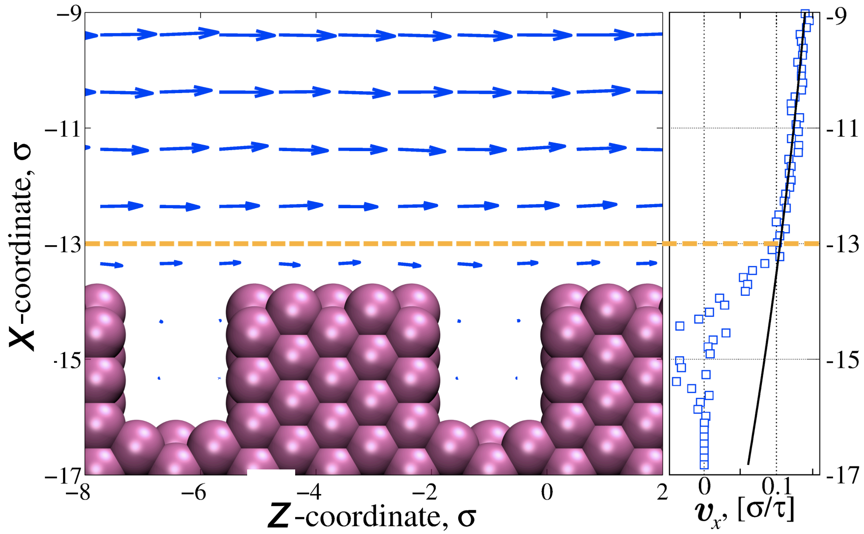


x_b is **above** the grooves

position of the hydrodynamic boundary coincides with the distance where the oscillating perpendicular velocity component has decayed

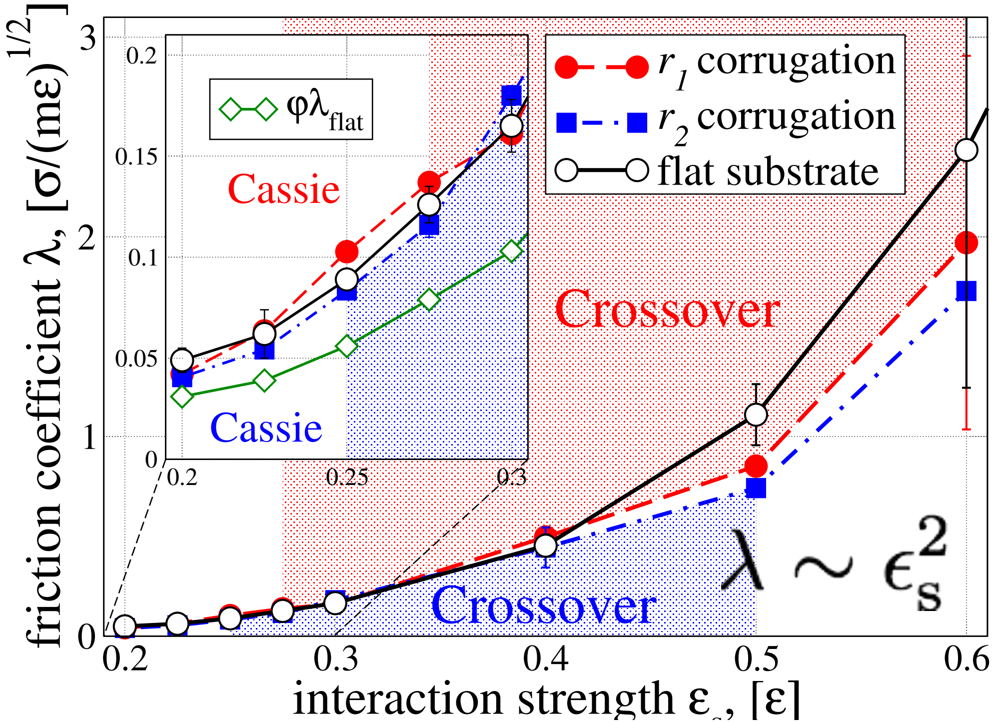
larger periodicity of corrugation results in larger decay length and higher hydrodynamic boundary position





Tretyakov, Müller, Soft Matter **9**, 3613 (2013)

How does friction change due to topo. structure?

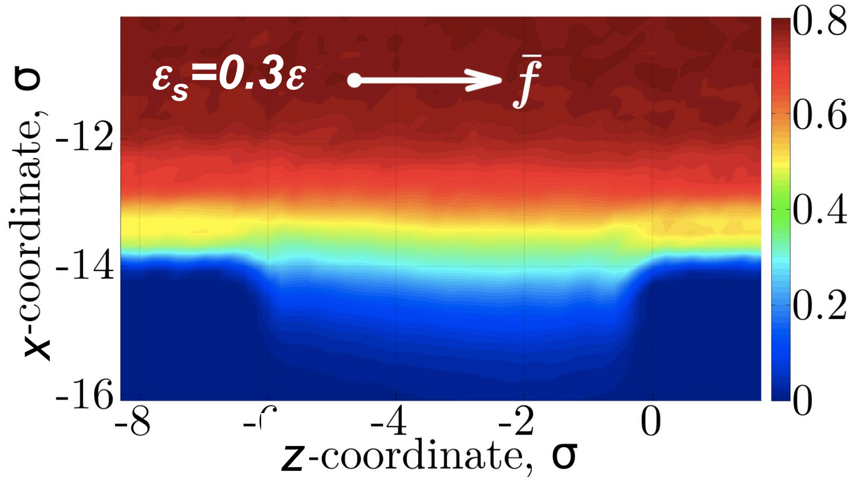


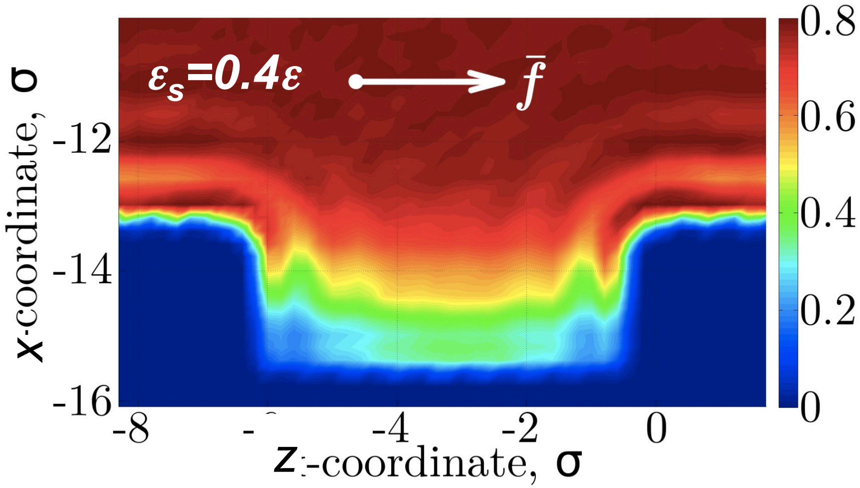
→ macroscopic prediction for the Cassie state $\lambda=\phi\lambda_{flat}$ is not appropriate but the friction does not strongly depend on topography

Cassie state = reduced friction
intrinsic roughness = increased friction

data compatible with

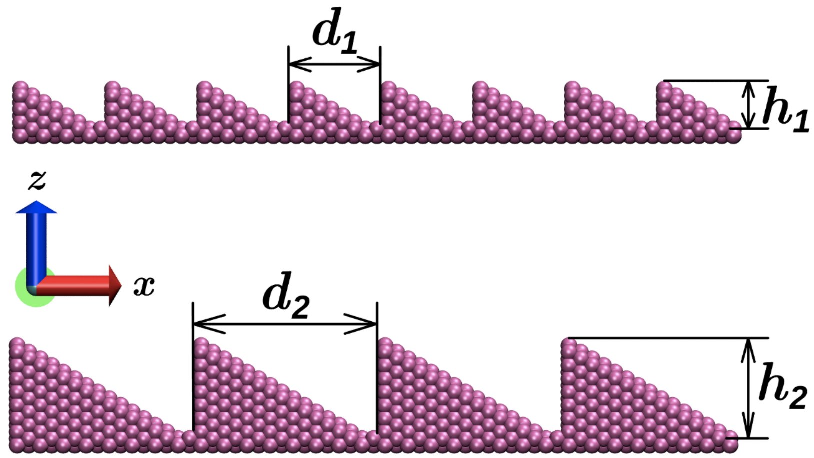
$$\lambda=\phi\lambda_{flat} + (n_{edge}/A)\ \lambda_{edge}$$

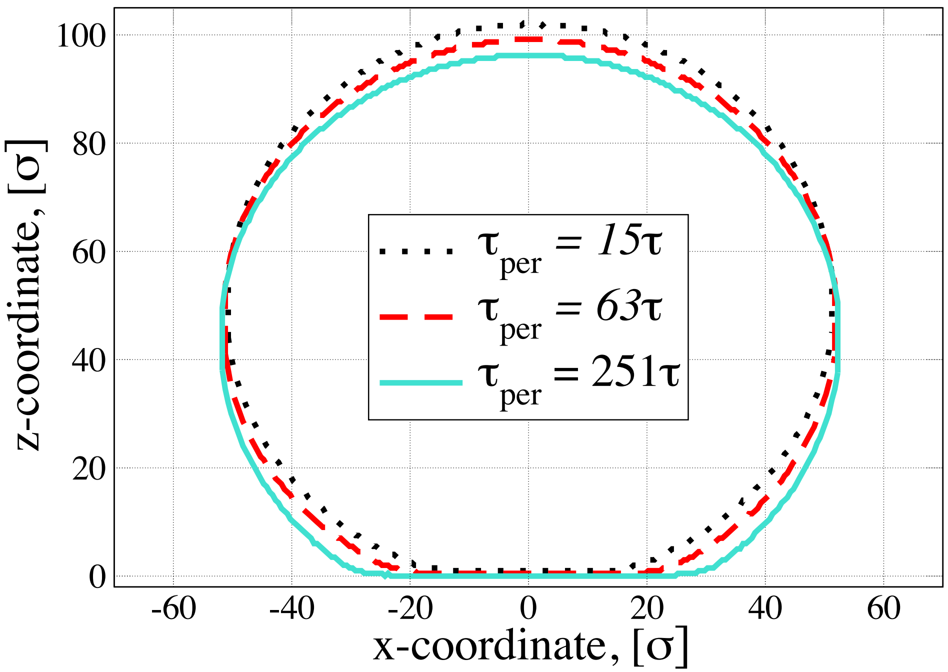




Tretyakov, Müller, Soft Matter **9**, 3613 (2013)

Directed motion on asymmetric, vibrating substrates





asymmetric substrate topology
\+ energy input by vertical vibration

➡

directed droplet motion

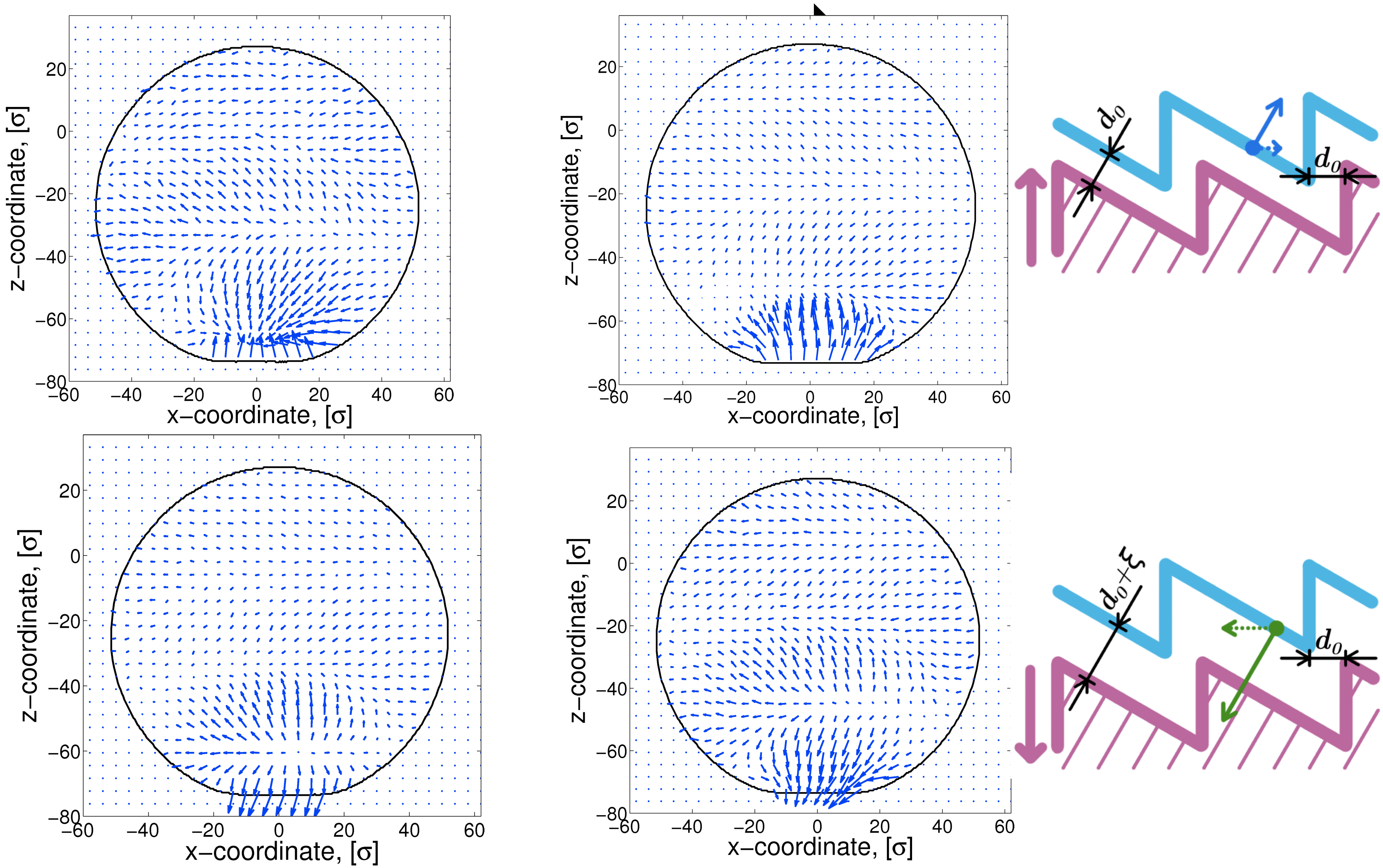
Questions:

- What is the driving mechanism?
- What is the character of motion: rolling *vs* sliding?
- What are the energy dissipation mechanisms?

(effective) contact angle depends on vibration period, τ

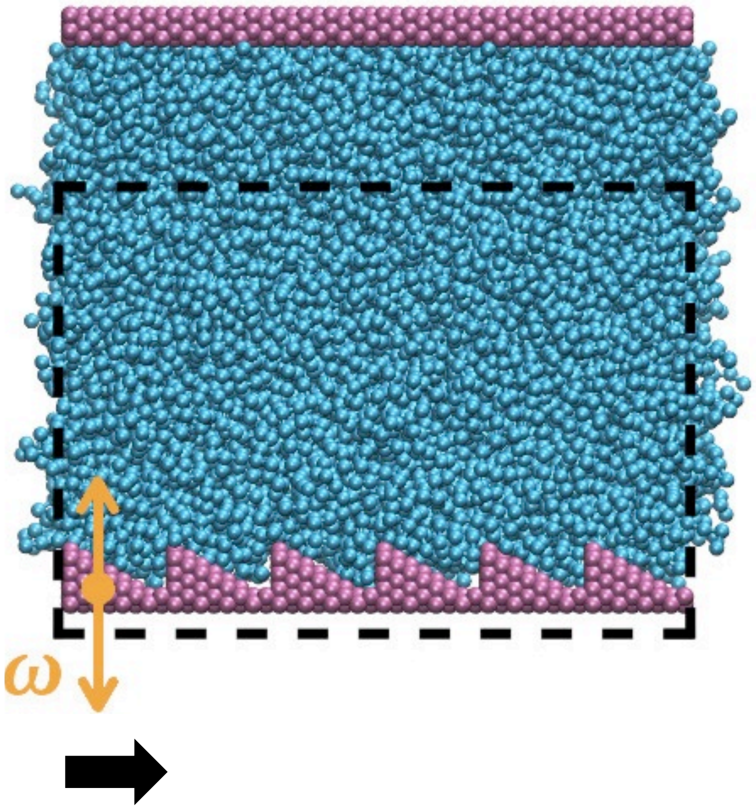
Tretyakov, Müller, Soft Matter submitted

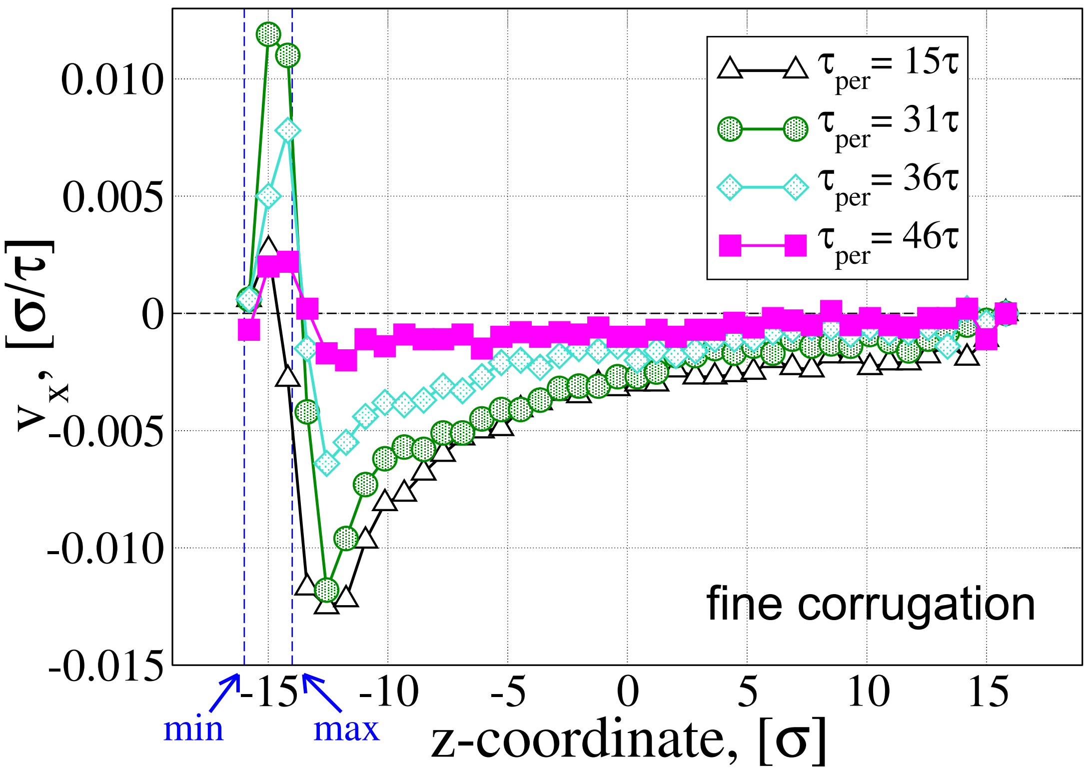
Contact area driving



Tretyakov, Müller, Soft Matter submitted

Contact area driving



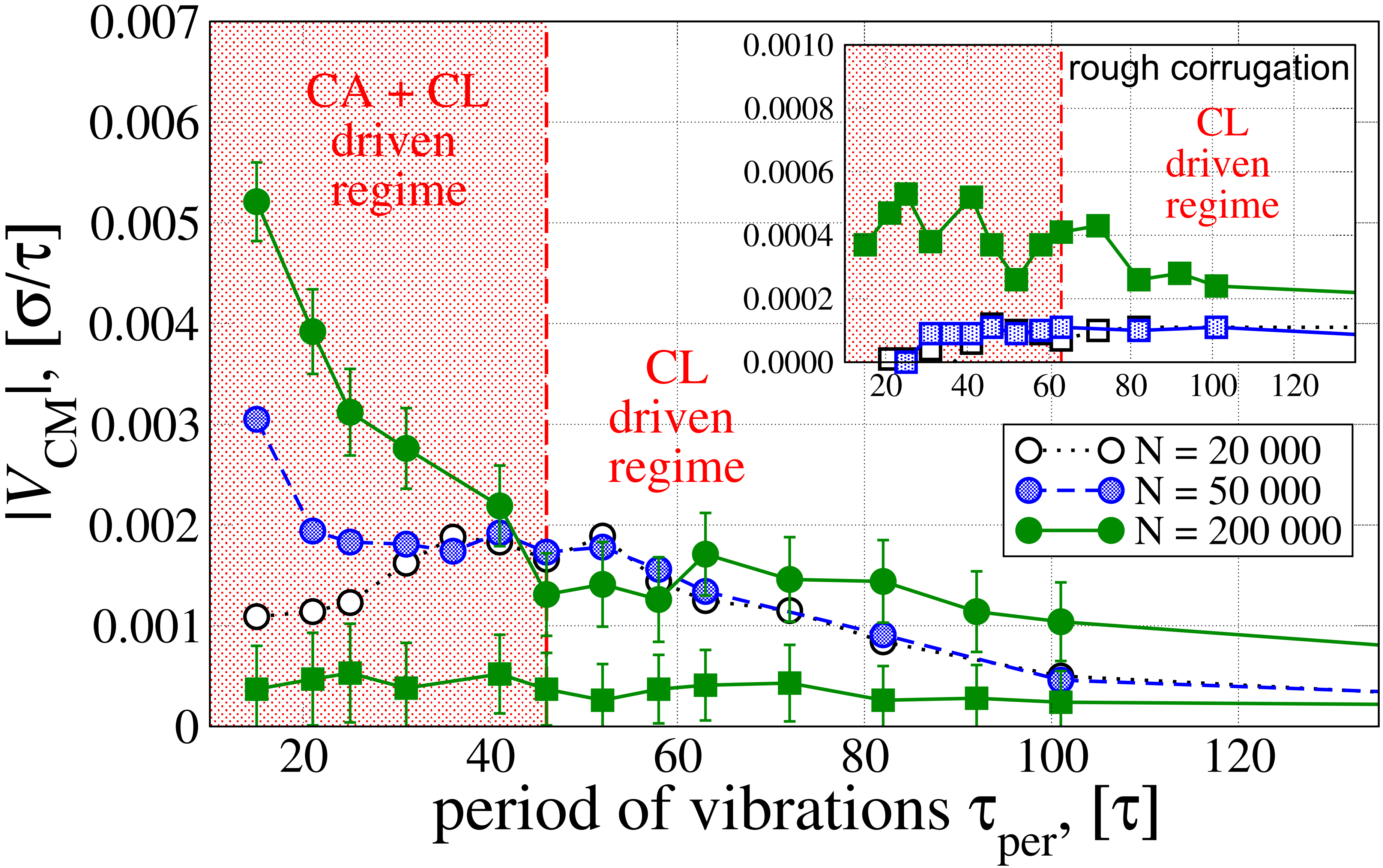


contact area driving leads to a surface flow in –x direction (left)
mechanism is effective for small vibration periods but is negligible for τ_{per}>46τ
for larger τ_{per} the directed motion is driven by contact line hysteresis

this simulation set-up is also used to obtain the friction coefficient, λ=η/δ, which is independent from the direction (see dissipation mechanisms)

Tretyakov, Müller, Soft Matter submitted

velocity: dependence on τ and N



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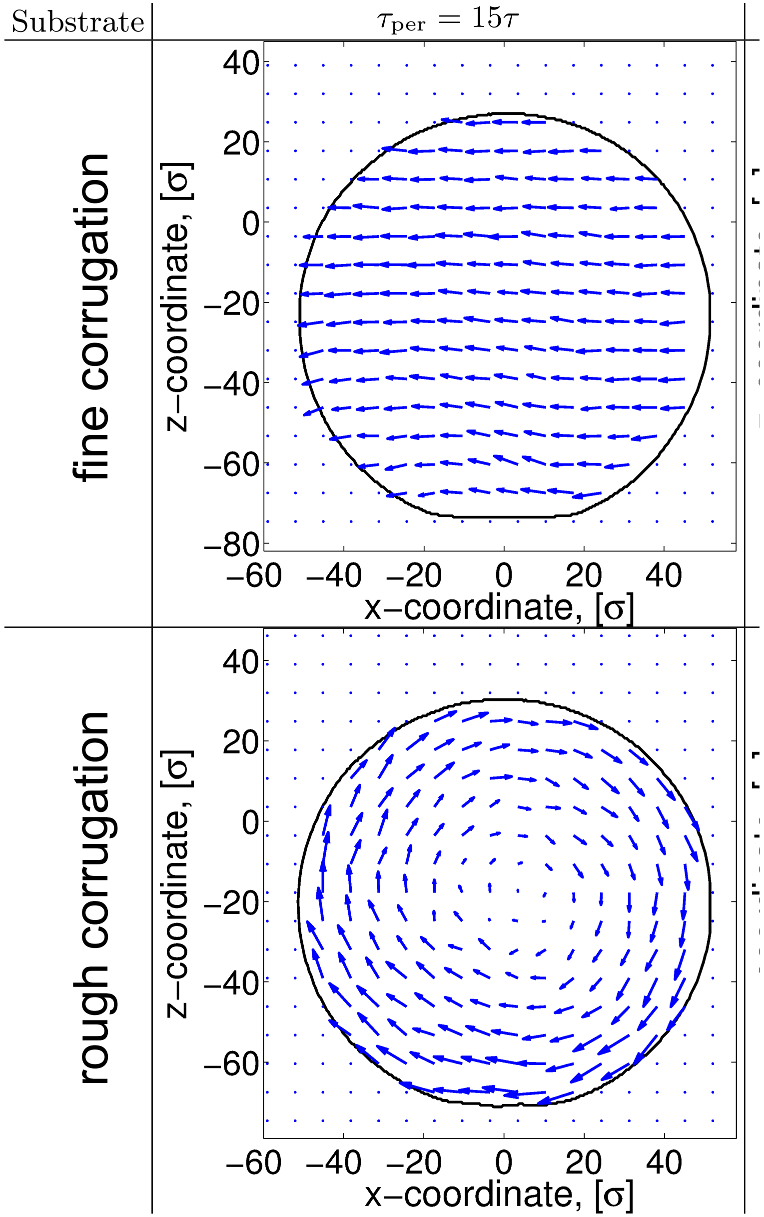
Character of motion



time-averaged velocity fields of flow inside the droplets

fine corrugation: sliding motion

rough corrugation: rolling motion,

direction of rolling is opposite to that of a rigid cylinder because the driving is localized at substrate

➡ both flow patterns give rise to rather small viscous dissipation

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Dissipation mechanisms

	small period	large period
input power $$P_{\text{in}} = \frac{1}{\tau_{\text{per}}} \left\langle \int_0^{\tau_{\text{per}}} v_z^{\text{s}}(t)\,\mathbf{F}^{\text{s}}(t)\cdot\mathbf{n}_z\,\text{d}t \right\rangle$$	large	small
viscous dissipation ~V $$T\Sigma_{\text{V}} = \frac{1}{2}\eta \int_V \left(\frac{\partial v_k}{\partial x_i} + \frac{\partial v_i}{\partial x_k} - \frac{2}{3}\delta_{ik}\frac{\partial v_l}{\partial x_l}\right)^2 dV.$$	constant (in absolute value)	constant (increasing fraction of input power, up to 80%)
friction at substrate ~A $$T\Sigma_{\text{CA}} = \frac{\lambda_{\text{av}}}{\tau_{\text{per}}}\left\langle \int_0^{\tau_{\text{per}}} L_y \int \left(v(x,t)\vert_{z_b}\right)^2 \,\text{d}x\text{d}t\right\rangle$$	constant	constant (up to 15% of input power)
sound waves ~A $$T\Sigma_{\text{SW}} = \zeta \int_V (\text{div}\,\mathbf{v})^2\, dV.$$	~5% of input power	~5% of input power
contact line and thermostat	large	small (even relative to input power)

Tretyakov, Müller, Soft Matter submitted

Summary and conclusion

- **static properties:** *surface tension and interface potential*

  measurement of the anisotropy of the pressure in the canonical ensemble yields the Legendre transform of the interface potential

  using the measured interface potential continuum theory (ie interface Hamiltonian) can describe deviations from cap-shapes drop profile at the three-phase contact line (except for liquid-like layering effects)

  simulations can provide input for effective interface Hamiltonians

- **dynamic properties**: *friction/slip length and hydrodynamic boundary position*

  two parameters – slip length and interface position – describe hydrodynamic boundary condition

  Navier-slip condition may need generalization (layer model, gradient terms)

  microscopic flow at surface may differ from hydrodynamic prediction

  - flow inversion inside a brush
  - crossover between macroscopic topography and roughness
  - dissipation mechanisms (friction, sound waves, contact-line contribution)

thanks to **Fabien Leonforte, Claudio Pastorino, Cem Servantie, and Nikita Tretyakov**

KITP Santa Barbara, March 19, 2014