Slip Behavior in Liquid Films: Influence of Patterned Surface Energy, Flow Orientation, and Deformable Gas-Liquid Interface

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Movies, preprints @
http://www.wright.edu/~nikolai.priezjev/

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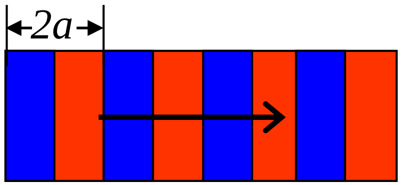
NSF, ACS, WSU

Outline of the talk

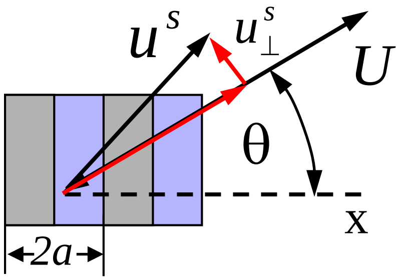
1. Brief introduction to modeling nanoflows over heterogeneous substrates

2. Details of molecular dynamics (MD) simulations (MD setup and parameter values, and movies)

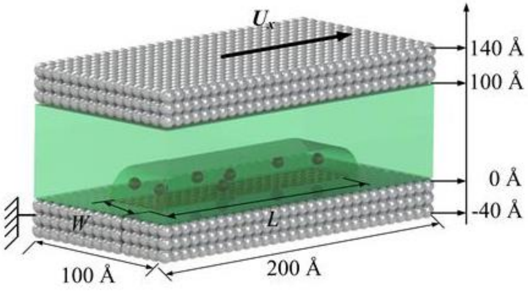
3. Transverse and longitudinal orientation of slip flows



4. Tensorial slip at surfaces with periodic and nanoscale textures



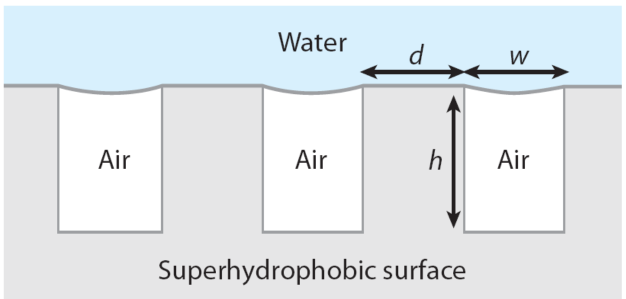
5. Liquid flows over a trapped nanobubble



6. Conclusions

Experimental measurements of the slip length L_s

- Typically slip length of water over hydrophobic surfaces is about 10 – 50 nm
- Possible presence of nanobubbles at hydrophobic surfaces: $L_s \sim 10\ \mu m$
- Factors that affect slip:
  1) Surface roughness
  2) Shear rate (= slope of the velocity profile)
  3) Poor interfacial wettability (weak surface energy)
  4) Nucleation of nanobubbles at hydrophobic surfaces
  5) Superhydrophobic surfaces ($L_s \sim 100\ \mu m$)



Rothstein, Review on slip flows over Superhydrophobic surfaces (2010).

Porous membranes?

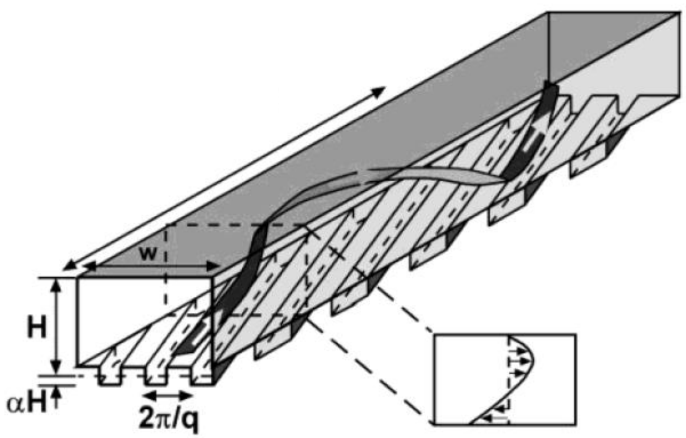
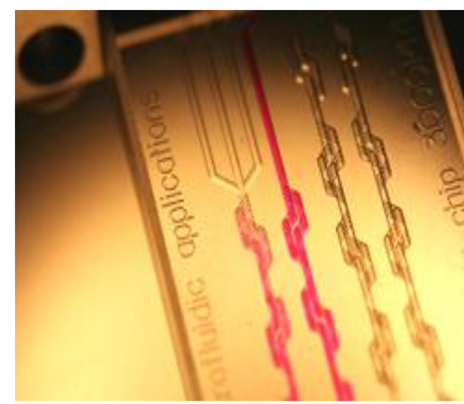


Figure 6. Schematic diagram of a microchannel with square grooves in the bottom wall. Below the channel to the right, the average flow profile in the cross section is drawn schematically. The ribbon indicates schematically a typical helical streamline in the channel.

Stroock, Dertinger, Whitesides, Ajdari, Patterning flows using grooved surfaces, Analytical Chemistry **74**, 5306 (2002).



A micromixer for rapid mixing of two or three fluid streams

Part I: Possibility of large slip lengths on patterned surfaces

(for simple liquids in the limit where L_S is shear rate independent)

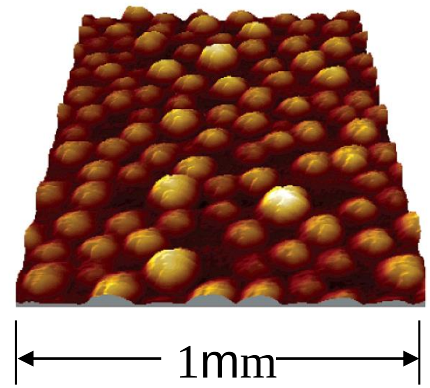
Do gas nanobubbles significantly enhance the slip length ?

Nanobubble formation in water on hydrophobic surfaces:

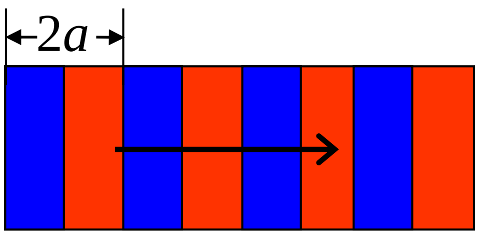
Lou et al., J. Vac. Sci. Tech. B **18**, 2573 (2000)
Ishida et al., Langmuir **16**, 6377 (2000)
Tyrrell and Attard, PRL **87**, 176104 (2001)
Steitz et al., Langmuir **19**, 2409 (2003)

Continuum models of slip for surfaces with mixed BCs

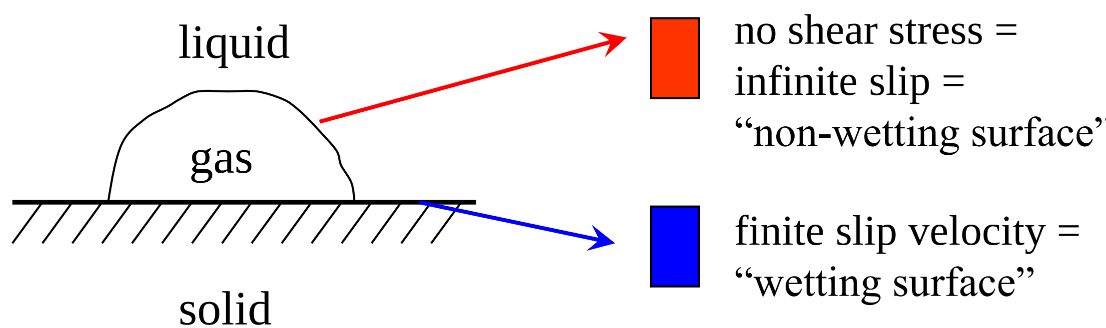
Philip, J. Appl. Math. Phys **23** (1972)
Lauga and Stone, JFM **489**, 55 (2003)
Cottin-Bizonne *et al.*, Euro.Phys. J. E **15**, 427 (2004)



Tapping mode AFM of water on hydrophobic wall Steitz *et al.*



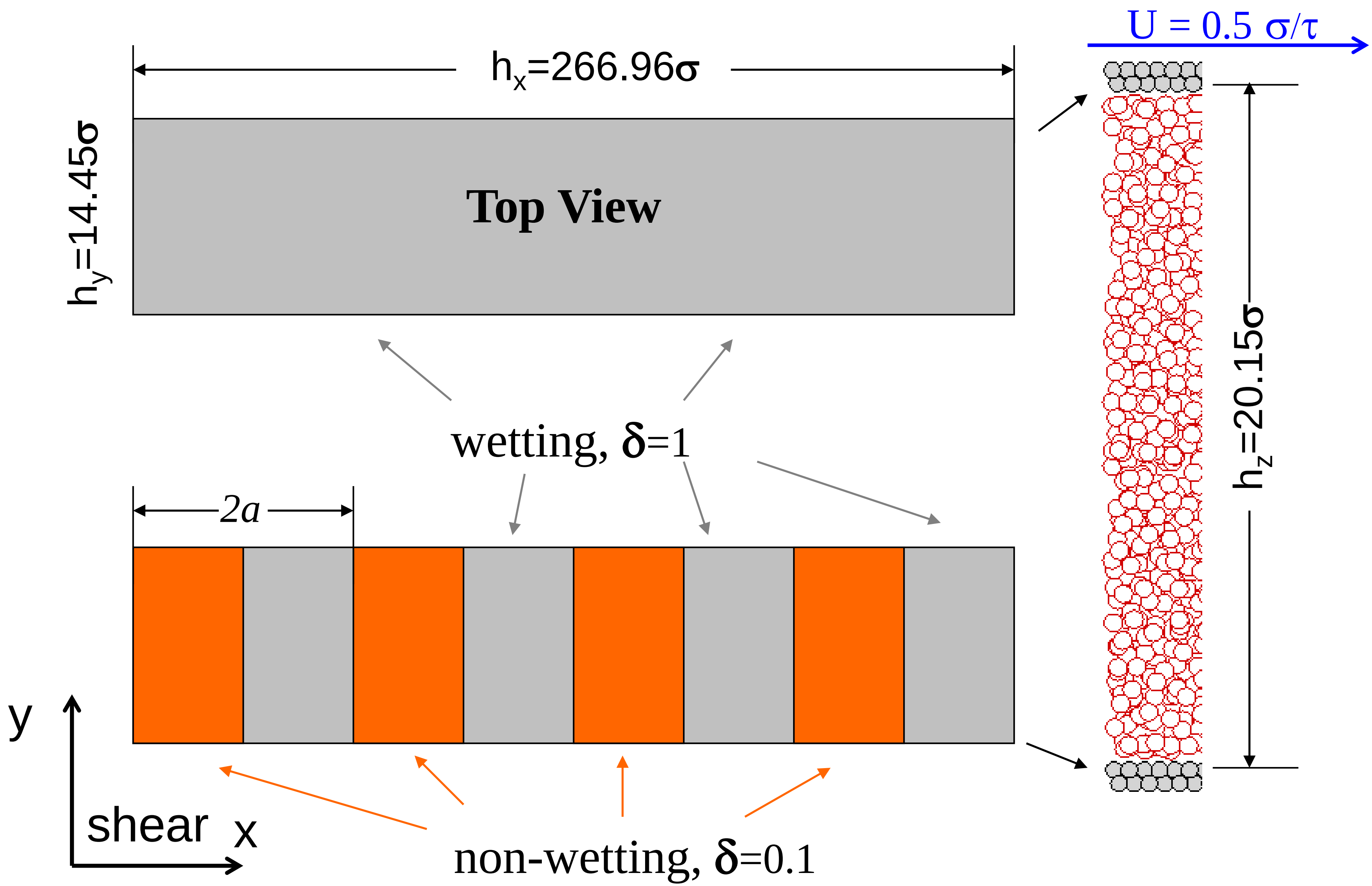
Transverse flow configuration



- Dependence of slip on period *a* and on orientation of shear flow ?
- Comparison of MD results with continuum predictions ?

N.V. Priezjev, A.A. Darhuber, S.M. Troian, “Slip behavior in liquid films on surfaces of patterned wettability: Comparison between continuum and molecular dynamics simulations”, *Phys. Rev. E* **71**, 041608 (2005).

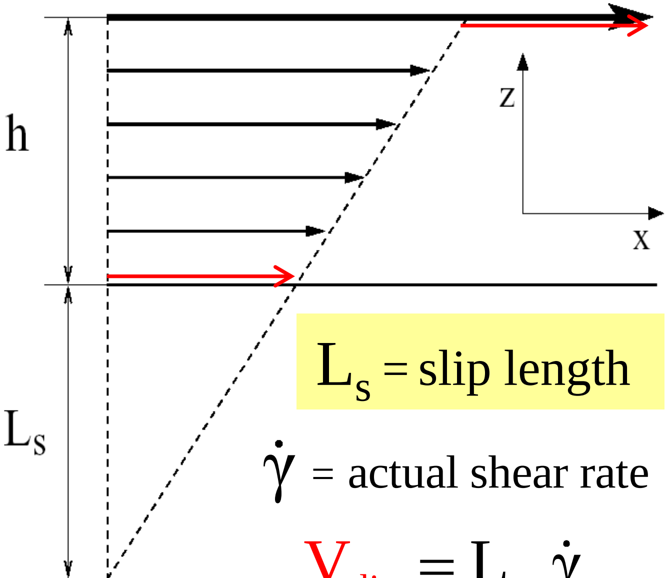
Details of molecular dynamics simulations



Total wetting/nonwetting area is the same; different spatial distribution

Details of molecular dynamics simulations

U velocity of the upper wall



L_s = slip length

$\dot{\gamma}$ = actual shear rate

$V_{slip} = L_s\ \dot{\gamma}$

Interaction potentials:

$$V_{LJ}(r) = 4\,\varepsilon_{wf}\left[\left(\frac{r}{\sigma}\right)^{-12} - \delta\left(\frac{r}{\sigma}\right)^{-6}\right]$$

$\delta = 1$ - wetting

$\delta = 0.1$ - non-wetting

$r_{cut\text{-}off} = 2.5\sigma$

$\varepsilon_{wf} = 0.8\varepsilon$ wall-fluid interaction

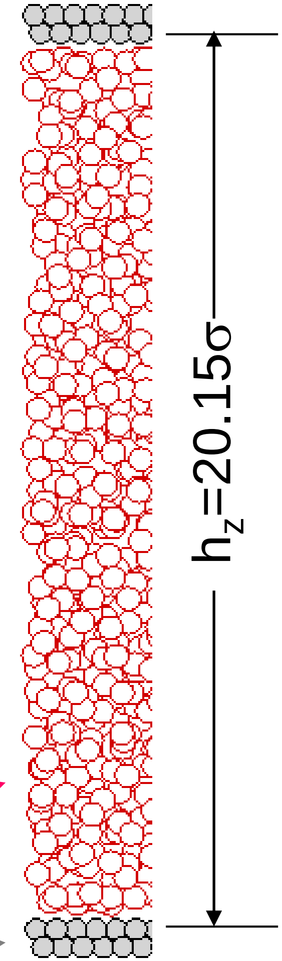
$\rho = 0.81\sigma^{-3}$ fluid density

$\rho_w = 4\rho$ wall density

30720 fluid atoms

24576 wall atoms

$$\mathrm{Re} = \frac{\rho U h}{\eta} \sim O(10)$$



Langevin thermostat: $T=1.1\varepsilon/k_B$

$$m\ddot{y}_i + m\Gamma\dot{y}_i = -\sum_{i\neq j}\frac{\partial V_{ij}}{\partial y_i} + f_i$$

$\Gamma = \tau^{-1}$ friction coefficient

f_i = Gaussian random force

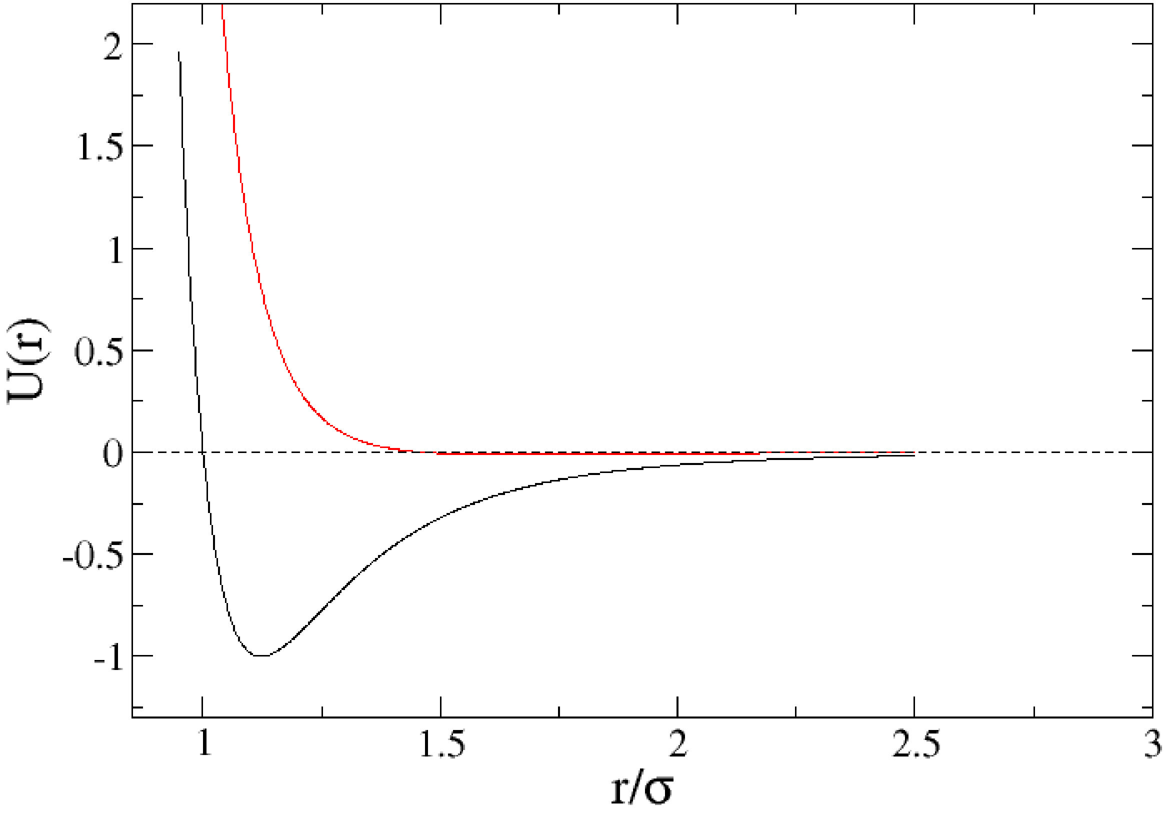
Properties of the Lennard-Jones (LJ) potential

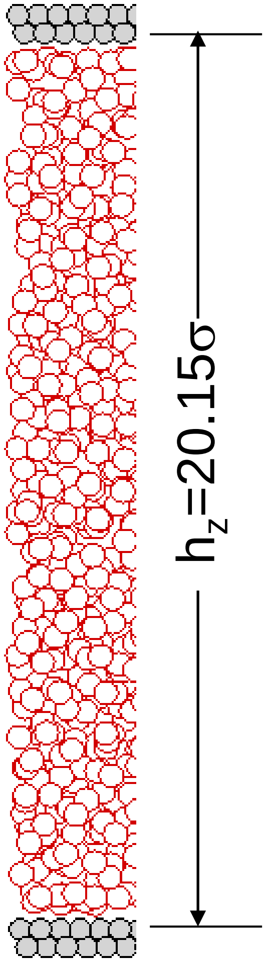
$$V_{LJ}(r) = 4\,\varepsilon_{\mathrm{wf}}\left[\left(\frac{r}{\sigma}\right)^{-12} - \delta\left(\frac{r}{\sigma}\right)^{-6}\right]$$

$\delta = 1$ - wetting

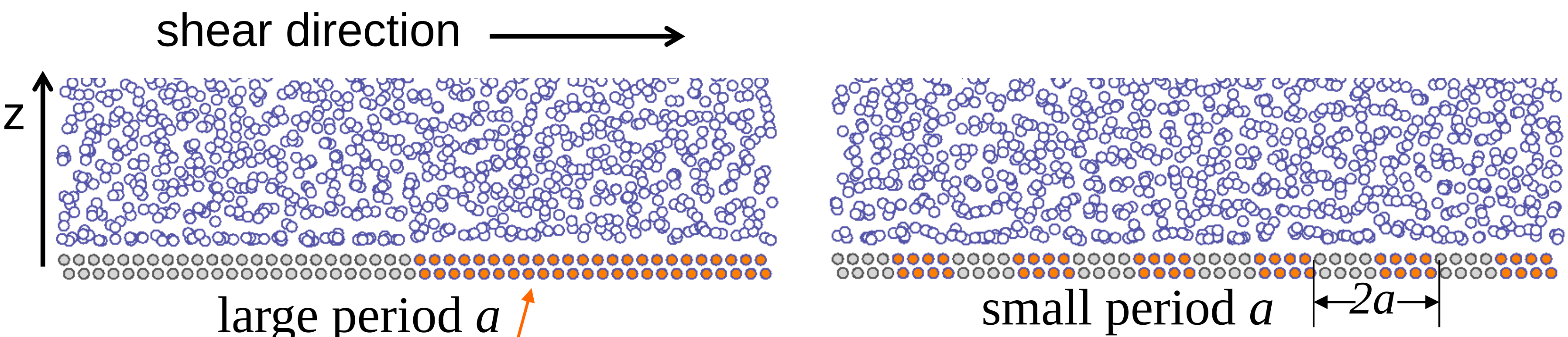
$\delta = 0.1$ - non-wetting

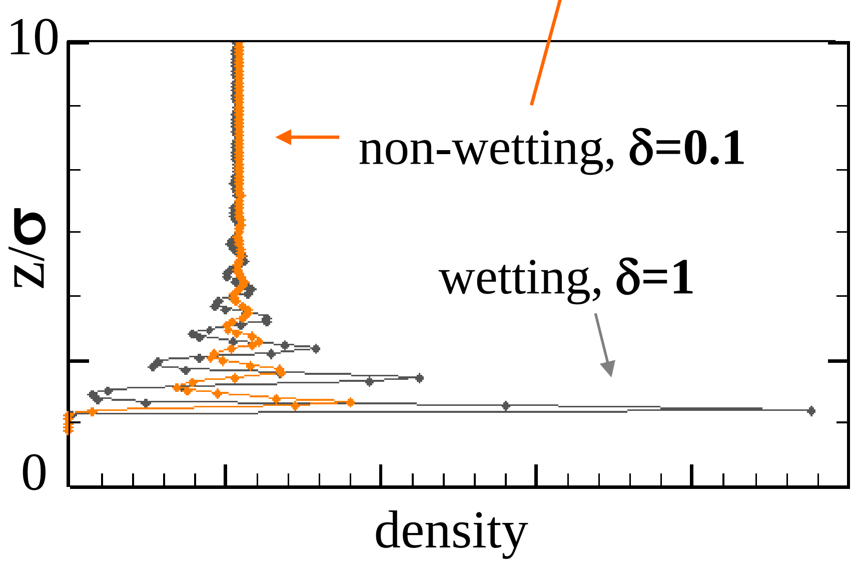
$r_{\text{cut-off}} = 2.5\sigma$

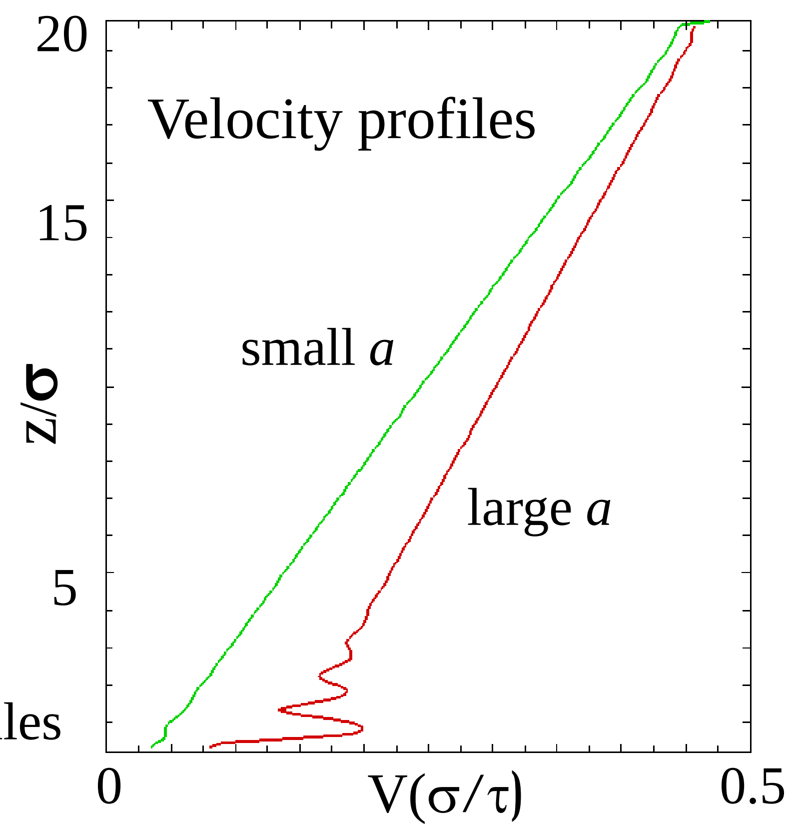




Density and velocity profiles near the stationary lower wall

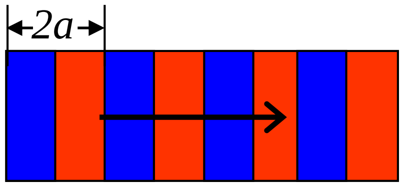






- More slip for larger period *a*
- Layering in density and velocity profiles

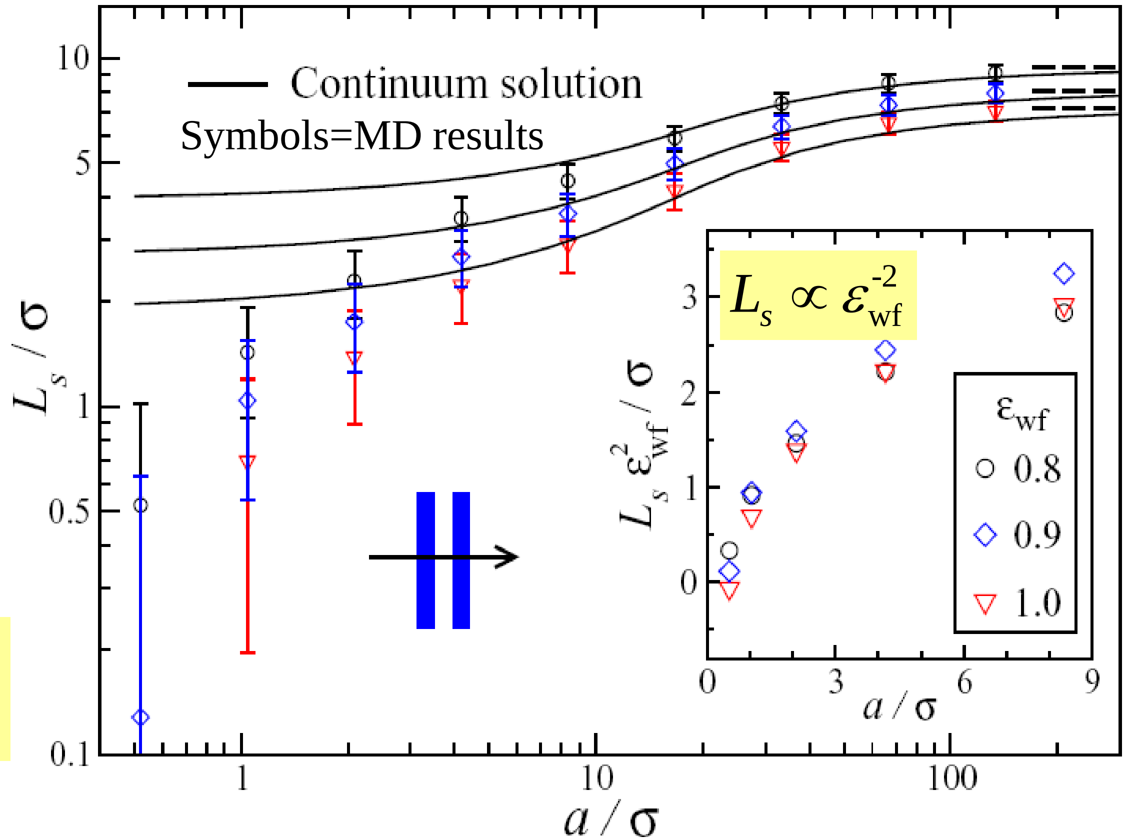
Transverse flow configuration: Slip length dependence on period *a*



no shear stress =
infinite slip =
"non-wetting surface"

finite slip velocity =
"wetting surface"

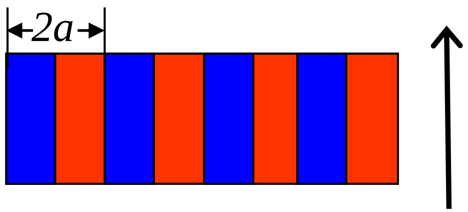
Effective slip length L_s
increases with the period *a*



- For $a \geq 30\boldsymbol{\sigma}$ MD recovers continuum results (similar to rough surface!)
- At small period $a \sim \boldsymbol{\sigma}$, deviations caused by effective surface roughness
- At small period $a \sim \boldsymbol{\sigma}$, L_s smaller than slip length on wettable stripes

Priezjev, Darhuber and Troian, *Phys. Rev. E* **71**, 041608 (2005).

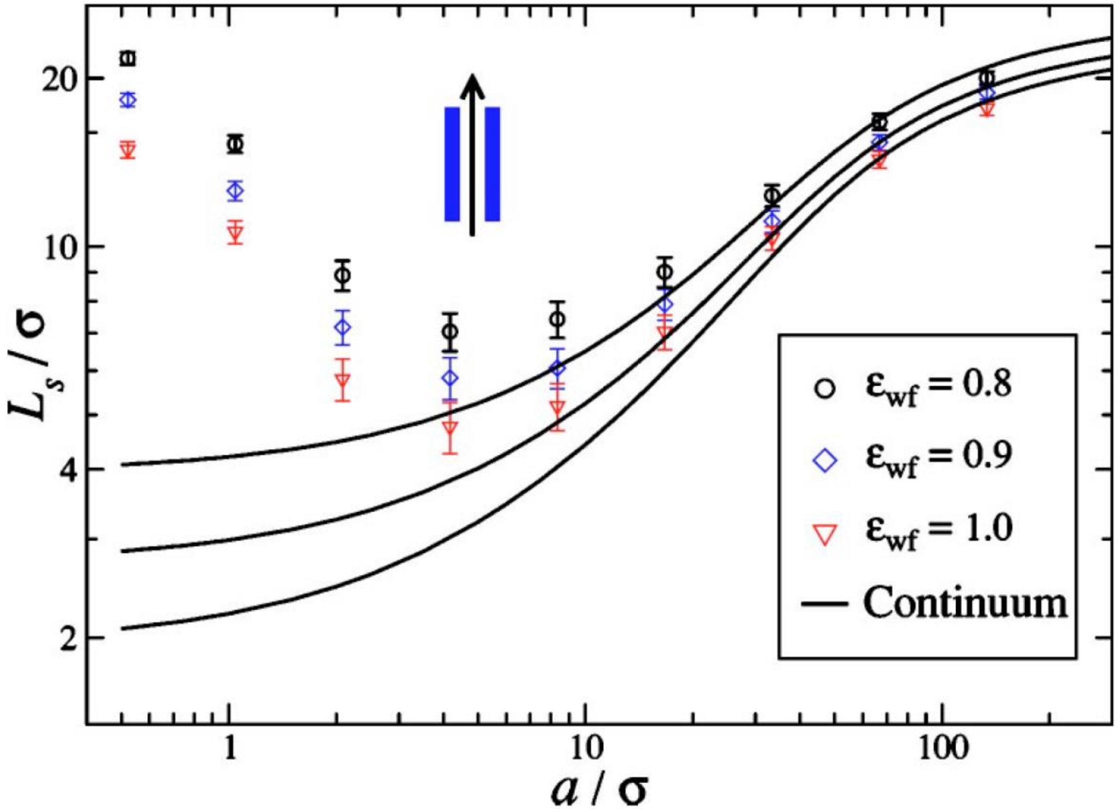
Longitudinal orientation: Effective slip length dependence on period *a*



- Slip length $L_s(a)$ increases with the period for $a \geq 20\boldsymbol{\sigma}$

- Agreement with continuum calculations for $a \geq 30\boldsymbol{\sigma}$

- At small period $a \sim \boldsymbol{\sigma}$, deviations explained by $L_S \sim 1/S(q)$, less order in the first fluid layer near the wall



No fitting parameters!

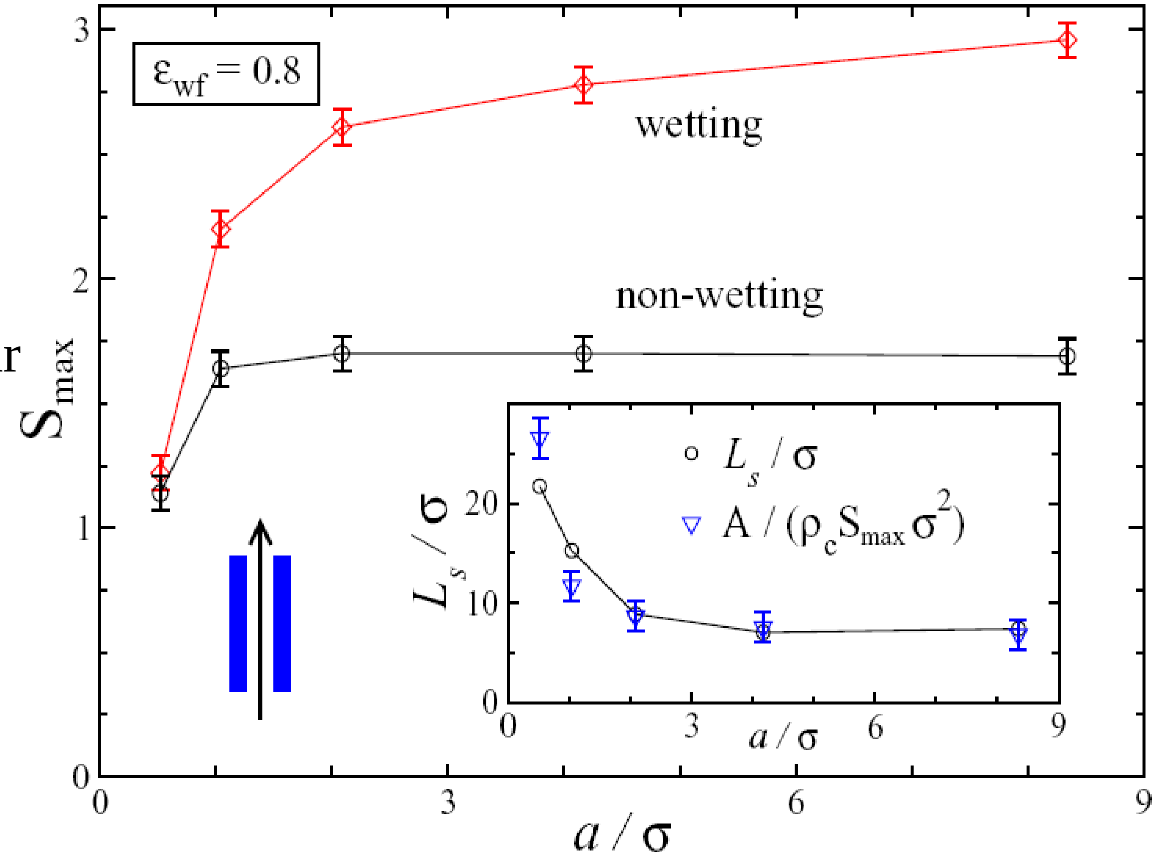
N.V. Priezjev, A.A. Darhuber, S.M. Troian, "Slip behavior in liquid films on surfaces of patterned wettability: Comparison between continuum and molecular dynamics simulations", *Phys. Rev. E* **71**, 041608 (2005).

Longitudinal orientation: S(q) dependence on period *a*

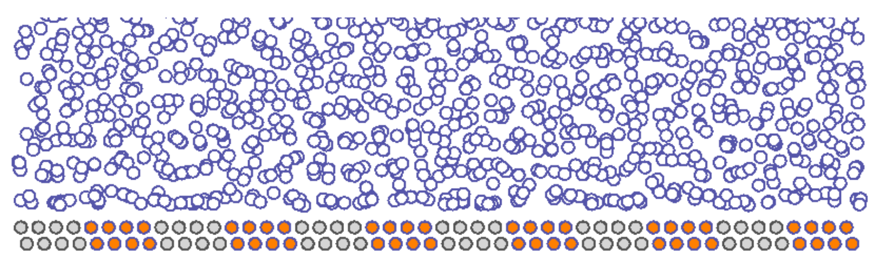
Structure factor:

$$S(q) = \left| \sum_j \exp(iqx_j) \right|^2$$

- Reduction of molecular ordering above the wetting regions for small period *a*.
- Inverse value of the structure factor peak correlates well with the slip length.



Thompson & Robbins, PRA, 1990.
Barrat & Boucquet, PRL, 1999.

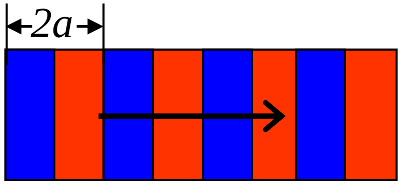


Important conclusions:

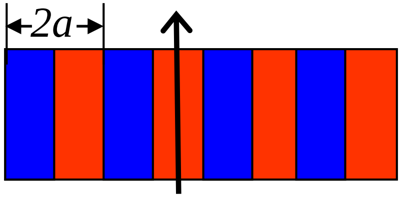
- Slip length $L_s(a)$ increases with the period for $a \geq 20\boldsymbol{\sigma}$

- Excellent agreement between MD and hydrodynamic predictions for periods $a \geq 30\boldsymbol{\sigma}$, with no adjustable parameters.

- For the flow perpendicular to the stripes:
  At small period $a \sim \boldsymbol{\sigma}$, deviations from hydrodynamics caused by effective roughness of the surface potential.



- For the flow parallel to the stripes:
  At small period $a \sim \boldsymbol{\sigma}$, deviations explained by $L_S \sim 1/S(q)$, less order in the first fluid layer near the wall.

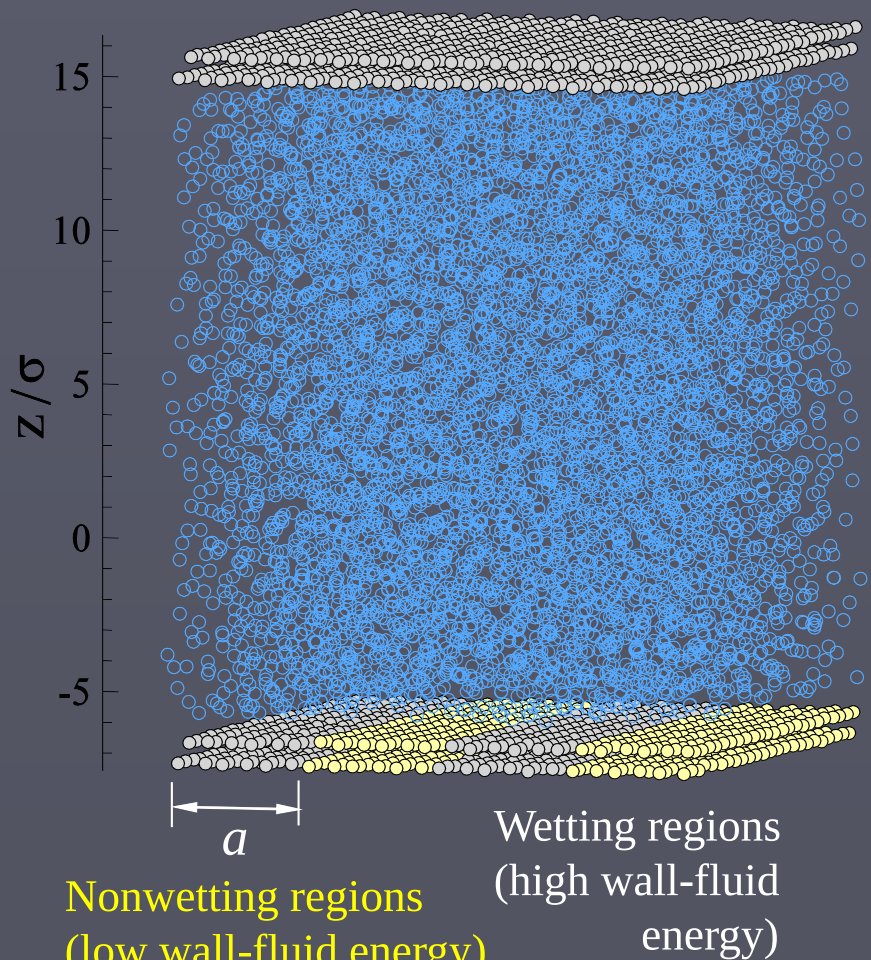


N.V. Priezjev, A.A. Darhuber, S.M. Troian, "Slip behavior in liquid films on surfaces of patterned wettability: Comparison between continuum and molecular dynamics simulations", *Phys. Rev. E* **71**, 041608 (2005).

Influence of Confinement on Flow, Diffusion, and Boundary Conditions in Nano Channels: A Combined Quantum Dot Imaging and Molecular Dynamics Simulations Approach

Nikolai Priezjev and Manoochehr Koochesfahani, Michigan State University (NSF-1033662)

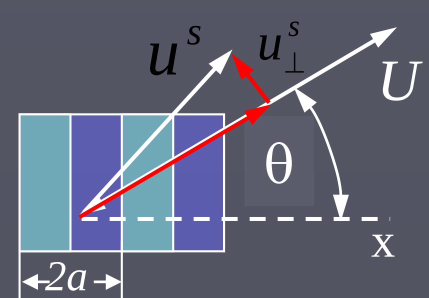
N. V. Priezjev, "Molecular diffusion and slip boundary conditions at smooth surfaces with periodic and random nanoscale textures", *Journal of Chemical Physics* **135**, 204704 (2011).



Microscopic justification of the tensor formulation of the effective slip boundary conditions: interfacial diffusion coefficient D_θ correlates well with the effective slip length $L_s(\theta)$ as a function of the shear flow direction U.

Shear flow over an array of parallel stripes:

$$L_s(\theta) = b_\perp \cos^2\theta + b_\parallel \sin^2\theta$$



$$\langle \boldsymbol{u}_s \rangle = \boldsymbol{L}_{eff} \cdot \left\langle \left(\frac{\partial \boldsymbol{u}}{\partial z} \right)_s \right\rangle$$

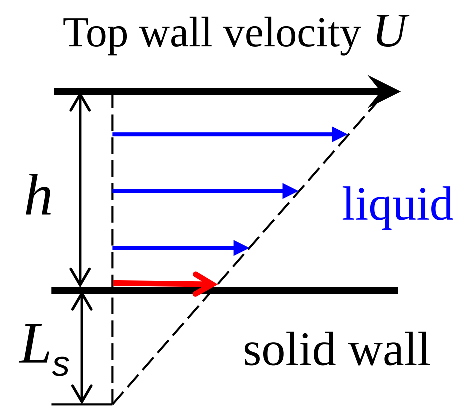
Motivation for investigation of slip phenomena at liquid/solid interfaces

- What is the boundary condition (BC) for liquid on solid flow in the presence of slip?

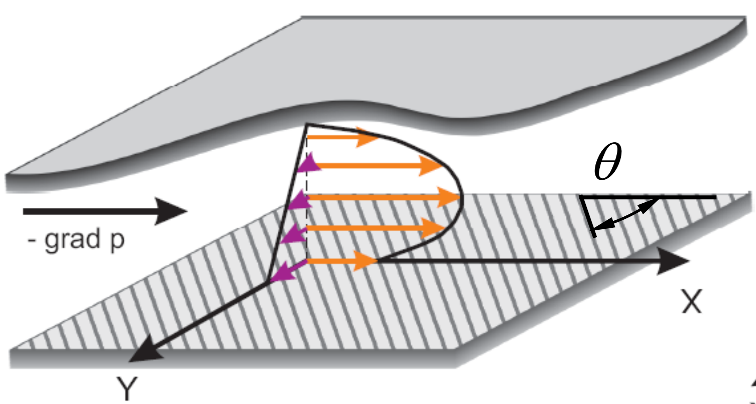
  Still no fundamental understanding of slip or what is proper BC for continuum studies. Issue is very important in micro- and nanofluidics. Contact line motion.

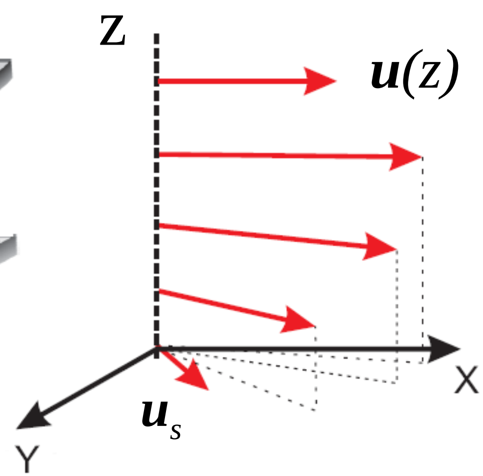
- Effective slip in flows over anisotropic textured surfaces

  O. Vinogradova and A. Belyaev, "Wetting, roughness and flow boundary conditions", *J. Phys.: Condens. Matter* **23**, 184104 (2011).



Navier slip condition $V_{slip} = L_s \, \dot{\gamma}$





$$\langle \boldsymbol{u}_s \rangle = \boldsymbol{L}_{eff} \cdot \left\langle \left(\frac{\partial \boldsymbol{u}}{\partial z} \right)_s \right\rangle$$

Flow over parallel stripes:

$$L_s(\theta) = b_\perp \cos^2\theta + b_\parallel \sin^2\theta$$

$$L_s(\theta = 0^\circ) = b_\perp \qquad L_s(\theta = 90^\circ) = b_\parallel$$

Details of molecular dynamics simulations

Lennard-Jones potential: $V_{LJ}(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right]$

Fluid monomer density: $\rho = 0.81\,\sigma^{-3}$

Thermal FCC walls with density $\rho_w = 2.3\,\sigma^{-3}$

Wall-fluid interaction: $\varepsilon_{wf} = \varepsilon$ and $\sigma_{wf} = \sigma$

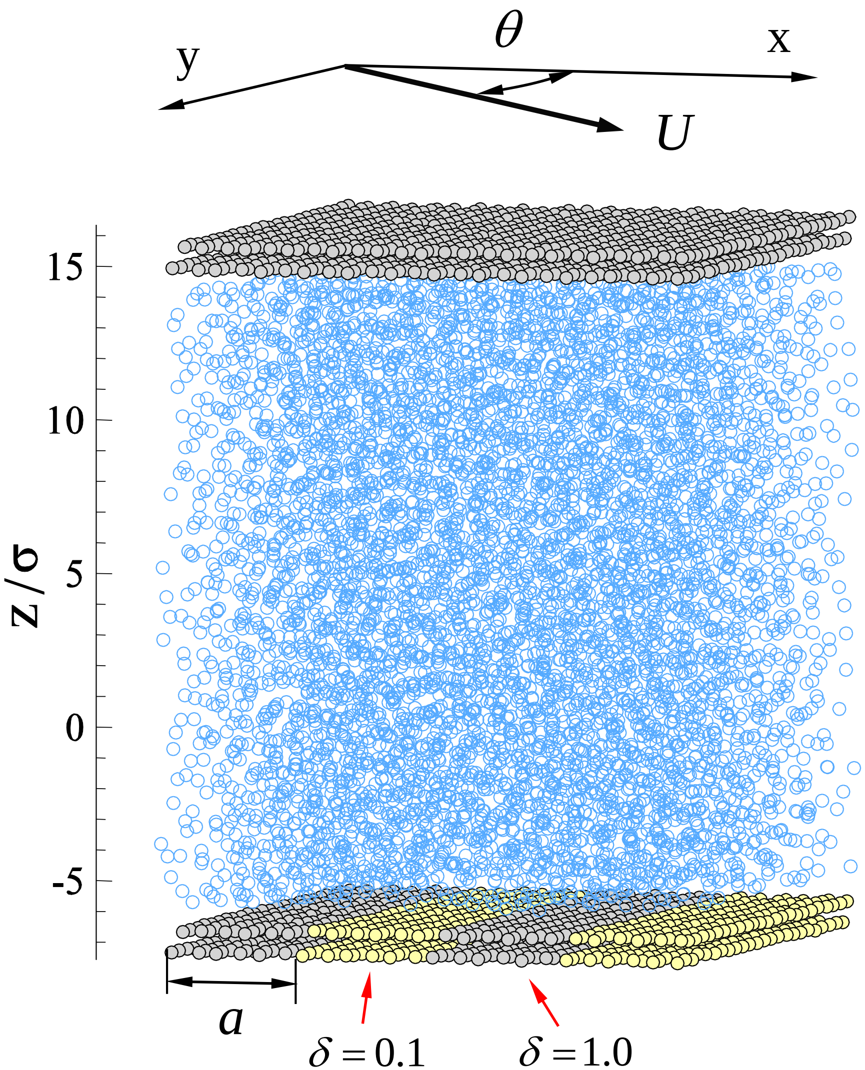
$$V_{LJ}(r) = 4\,\varepsilon_{wf}\left[\left(\frac{r}{\sigma}\right)^{-12} - \delta\left(\frac{r}{\sigma}\right)^{-6}\right]$$

Nonwetting regions, large slip length: $\delta = 0.1$

Wetting regions, small slip length: $\delta = 1.0$

- Thermostat to thermal walls only!
  Langevin thermostat applied to fluid introduces a bias in flow profiles near patterned walls for $0 < \theta < 90°$

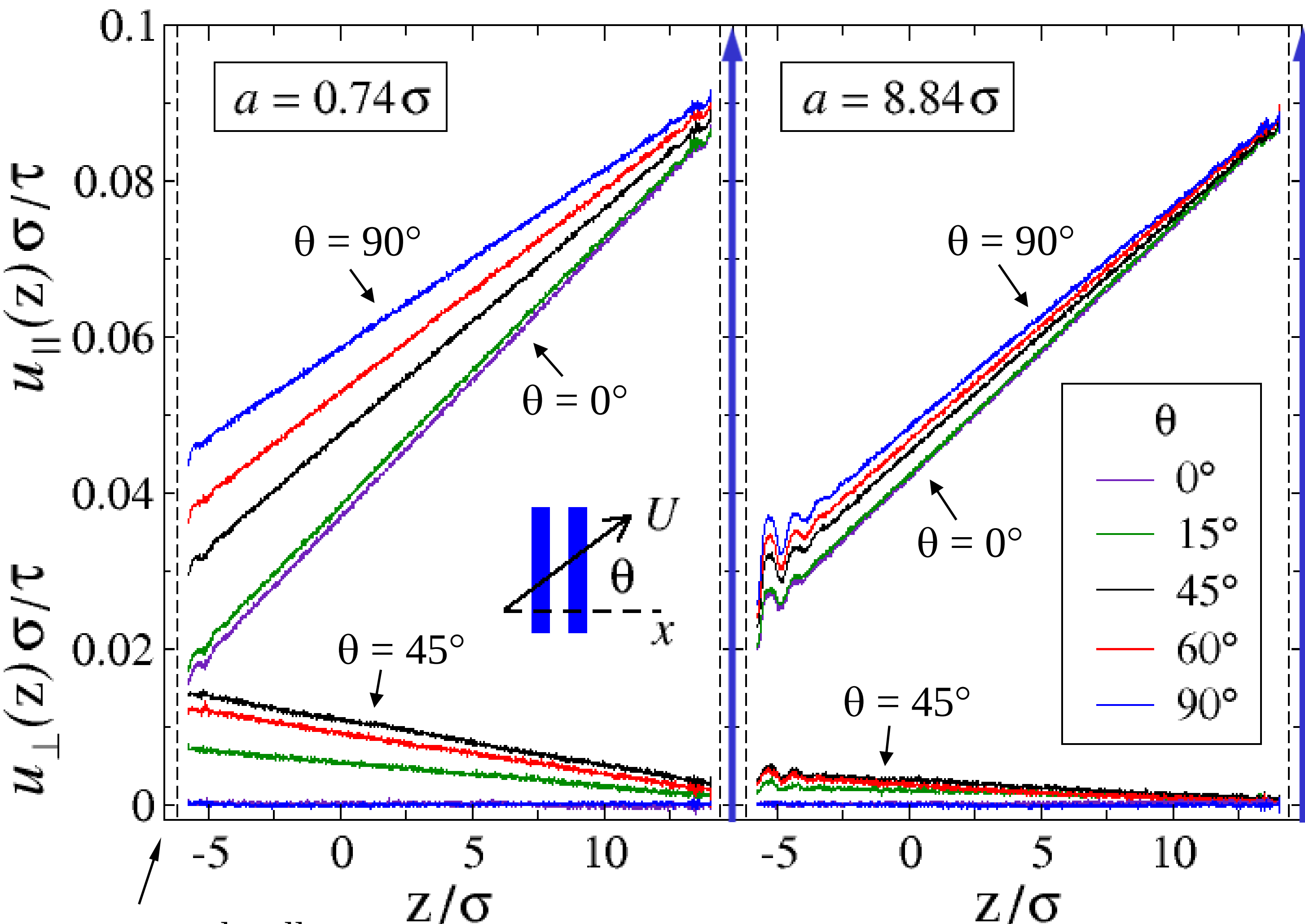
  Friction term: $-m\Gamma\dot{x}$ $\quad T=1.1\varepsilon/k_B$



Nonwetting regions (low wall-fluid energy) $b_n = 156\,\sigma$

Wetting regions (high wall-fluid energy) $b_w = 3.6\,\sigma$

Part I: Flow over periodic stripes; longitudinal and transverse velocity profiles



Lower patterned wall

Upper wall $U = 0.1\sigma/\tau$

a = stripe period

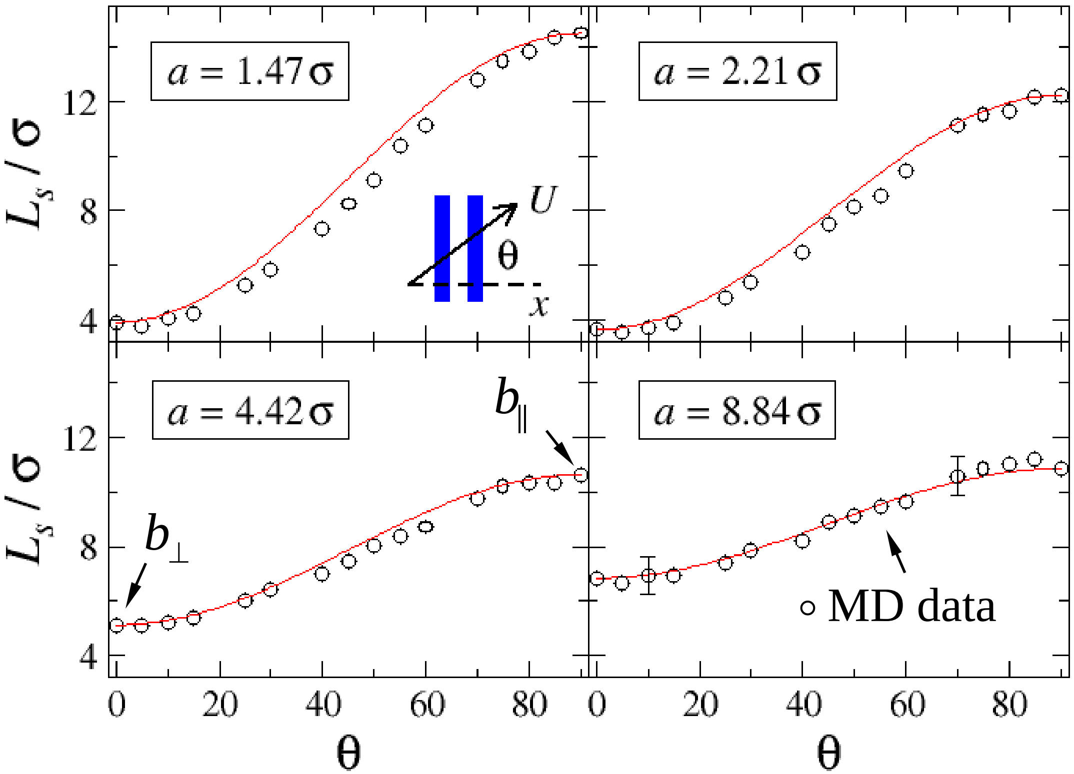
U = upper wall speed

Longitudinal component: $u_{||}(z) \parallel U$

Transverse component: $u_{\perp}(z) \perp U$

Transverse flow $u_{\perp}(z)$ is maximum when θ = 45°

Slip length as a function of angle θ between flow orientation U and stripes

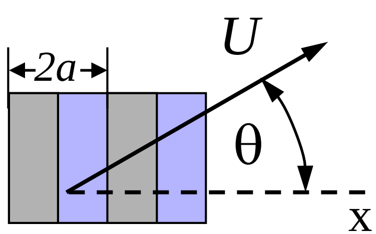


- For stripe widths $a \geq 30\,\sigma$ MD recovers continuum results for flows either $\parallel$ or $\perp$ to stripes. Priezjev, Darhuber and Troian, *Phys. Rev. E* **71**, 041608 (2005).
- $L_s = b_\perp \cos^2\theta + b_\parallel \sin^2\theta$ Eq.(1)

  continuum prediction (red curves). Bazant and Vinogradova, *J. Fluid Mech.* **613**, 125 (2008).

- For stripe widths $a/\sigma = O(10)$ MD reproduces slip lengths for anisotropic flows over an array of parallel stripes, see Eq.(1).

Flat FCC stationary lower wall plane: *U*=upper wall speed.

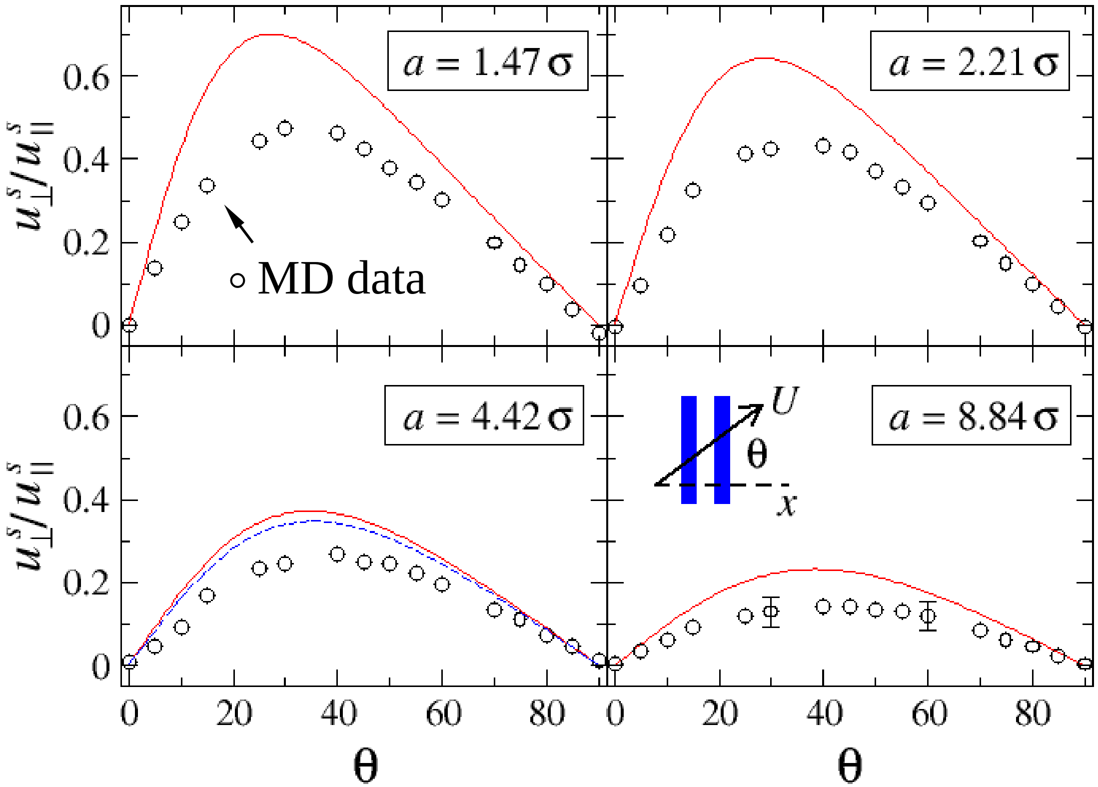


Non-wetting region (low wall-fluid energy, large slip length)

Wetting region (high wall-fluid energy, small slip)

$$L_s(\theta = 0^\circ) = b_\perp \qquad L_s(\theta = 90^\circ) = b_\parallel$$

Ratio of transverse and longitudinal components of slip velocity u^s versus θ



Continuum prediction (red curves)

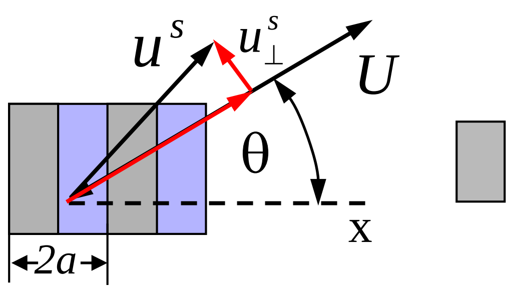
$$\frac{u^s_\perp}{u^s_\parallel} = \frac{(b_\parallel - b_\perp)\sin\theta\cos\theta}{b_\perp\cos^2\theta + b_\parallel\sin^2\theta}$$

$$L_s(\theta = 0^\circ) = b_\perp$$

$$L_s(\theta = 90^\circ) = b_\parallel$$

- For stripe widths $a/\sigma = O(10)$ MD qualitatively reproduces the ratio of transverse and longitudinal components of the apparent slip velocity u^s

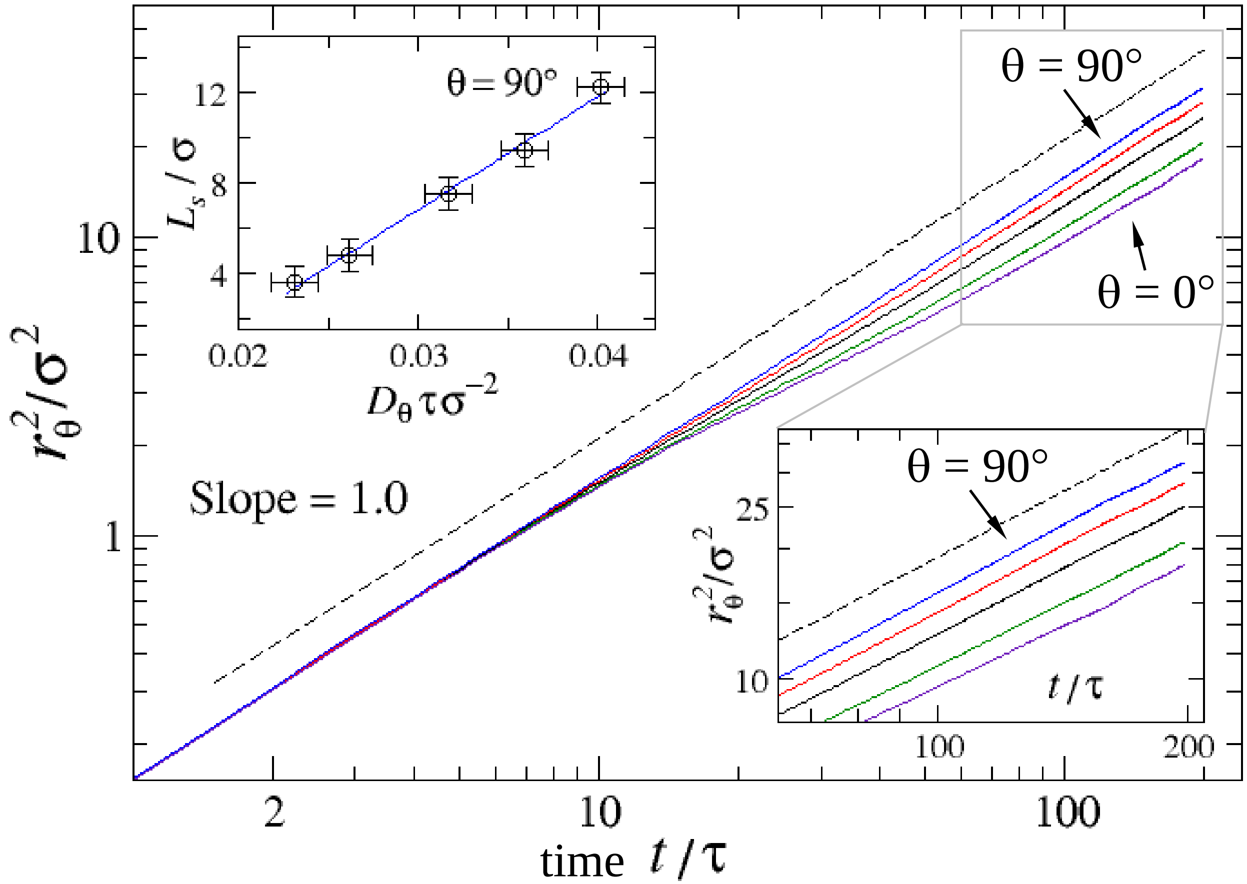
Flat FCC stationary lower wall plane:
U=upper wall speed
u^s = slip velocity

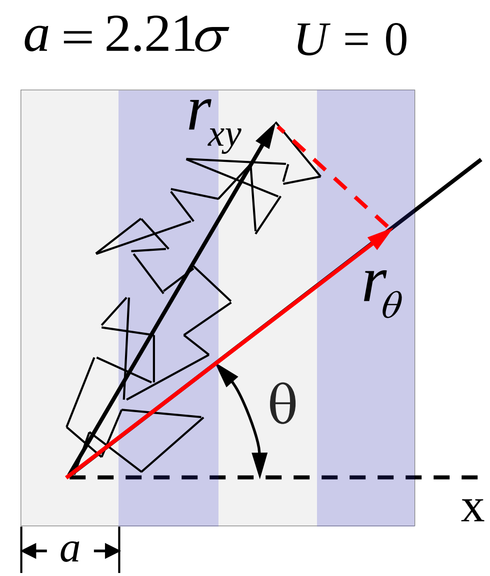


Non-wetting region (low wall-fluid energy, large slip length)

Wetting region (high wall-fluid energy, small slip)

A correlation between interfacial diffusion coefficient D_θ and slip length L_s





$$r_\theta^2 = 4 D_\theta t$$

$$\langle \boldsymbol{u}_s \rangle = \boldsymbol{L}_{eff} \cdot \left\langle \left(\frac{\partial \boldsymbol{u}}{\partial z} \right)_s \right\rangle$$

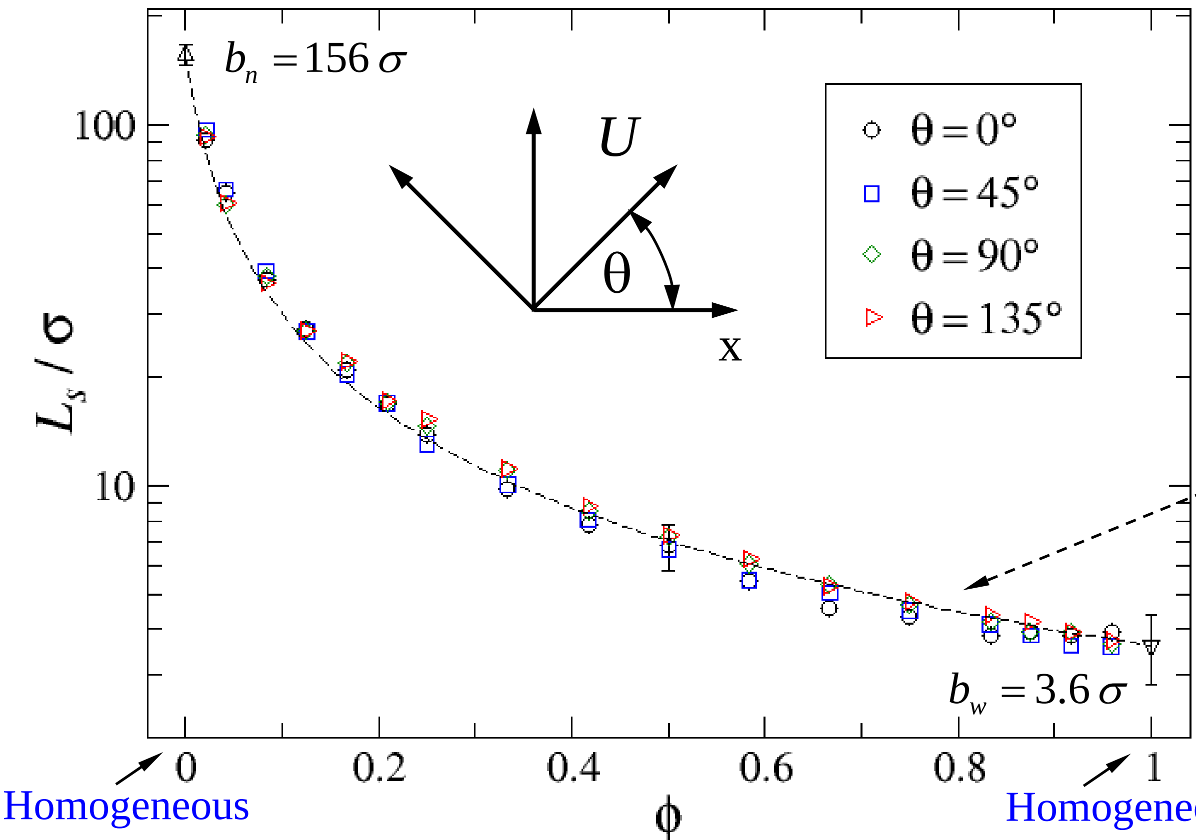
Flow over parallel stripes:

$$L_s(\theta) = b_\perp \cos^2\theta + b_\parallel \sin^2\theta$$

Bazant and Vinogradova, *J. Fluid Mech.* **613**, 125 (2008).

Microscopic justification of the tensor formulation of the effective slip boundary conditions: interfacial diffusion coefficient D_θ correlates well with the effective slip length as a function of the shear flow direction *U*.

Part II: Slip flow over flat surfaces with random nanoscale textures



Homogeneous nonwetting wall

Homogeneous wetting wall

Additive friction from wetting and nonwetting areas:

$$\frac{\mu}{L_s(\phi)} = \frac{\mu\,\phi}{b_w} + \frac{\mu\,(1-\phi)}{b_n}$$

$$L_s(\phi) = \frac{b_w\, b_n}{\phi\, b_n + (1-\phi)\, b_w}$$

(dashed curve)

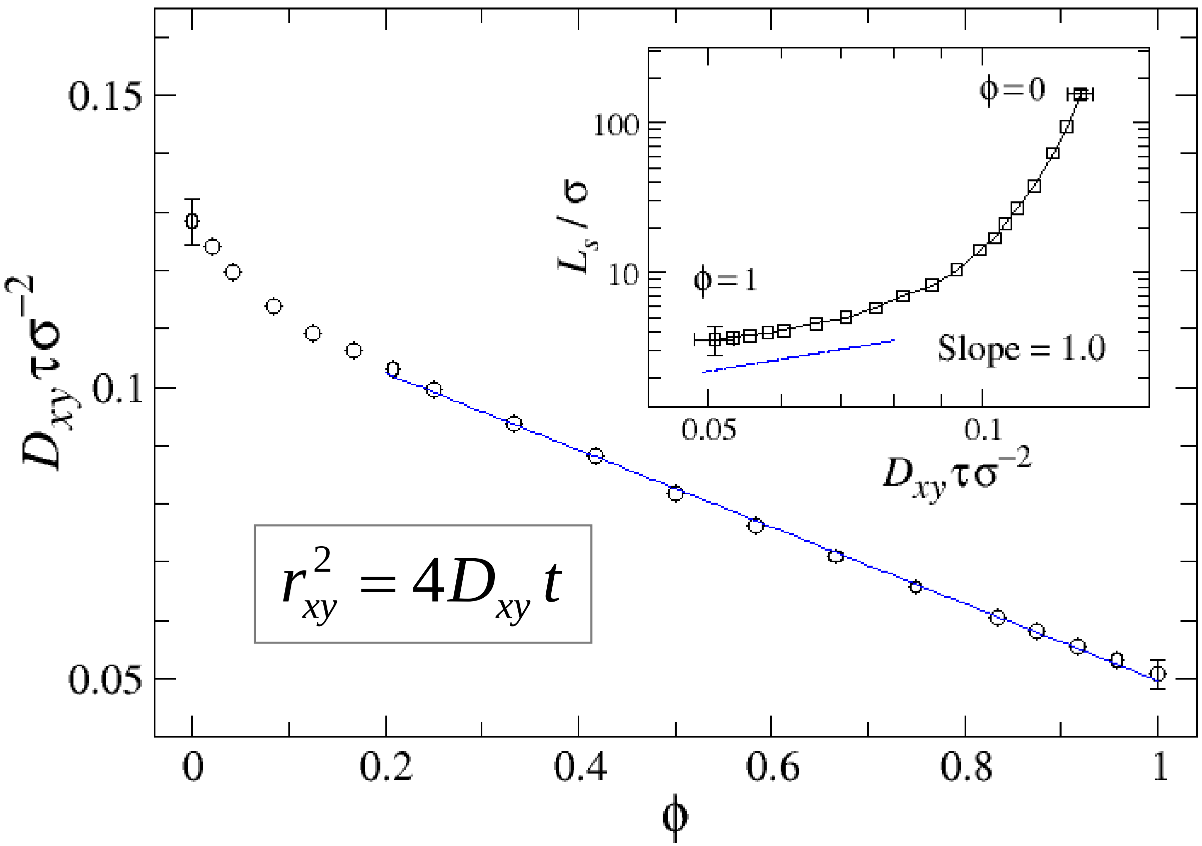
ϕ = areal fraction of wetting ($\delta = 1.0$) lower wall atoms

1 - ϕ = fraction of nonwetting ($\delta = 0.1$) lower wall atoms

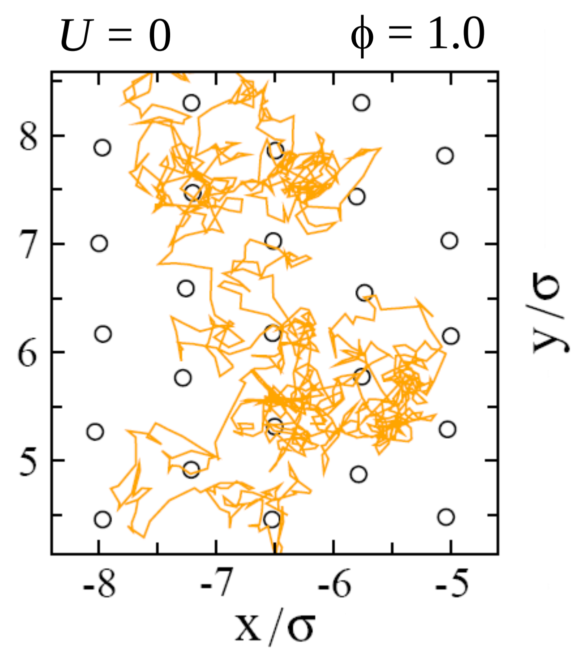
Wall-fluid interaction: $V_{LJ}(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \delta\left(\frac{r}{\sigma}\right)^{-6}\right]$

- Slip length is isotropic (finite size effects).
- The variation of L_s is determined by the total area of wetting regions.

A correlation between interfacial diffusion coefficient D_{xy} and slip length L_s



$$r_{xy}^2 = 4D_{xy}t$$



Trajectory for ≈ 100τ

ϕ = areal fraction of wetting (δ = 1.0) wall atoms

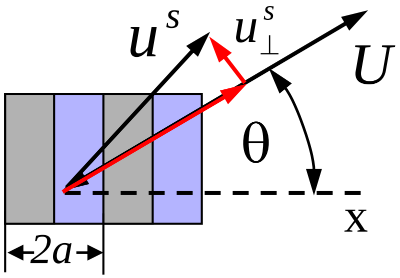
1 - ϕ = fraction of nonwetting (δ = 0.1) wall atoms

- When ϕ > 0.6, the slip length L_s is proportional to the interfacial diffusion coefficient of fluid monomers in contact with wall.

N. V. Priezjev, "Molecular diffusion and slip boundary conditions at smooth surfaces with periodic and random nanoscale textures", *J. Chem. Phys.* **135**, 204704 (2011).

Important conclusions:

$$\langle \boldsymbol{u}_s \rangle = \boldsymbol{L}_{eff} \cdot \left\langle \left(\frac{\partial \boldsymbol{u}}{\partial z} \right)_s \right\rangle \qquad L_s(\theta) = b_{\perp} \cos^2\theta + b_{\parallel} \sin^2\theta$$



- Good agreement between MD and hydrodynamic results for anisotropic flows over periodically textured surfaces *provided* length scales ≈ *O*(10 molecular diameters).

- Microscopic justification of the tensor formulation of the effective slip boundary conditions: interfacial diffusion coefficient D_θ correlates well with the effective slip length as a function of the shear flow direction.

- In case of random surface textures, the effective slip length is determined by the total area of wetting regions. When $\phi > 0.6$, L_s is linearly proportional to the interfacial diffusion coefficient of fluid monomers in contact with periodic surface potential.

N. V. Priezjev, “Molecular diffusion and slip boundary conditions at smooth surfaces with periodic and random nanoscale textures”, *J. Chem. Phys.* **135**, 204704 (2011).

A comparative analysis of the effective and local slip lengths for liquid flows over a trapped nanobubble

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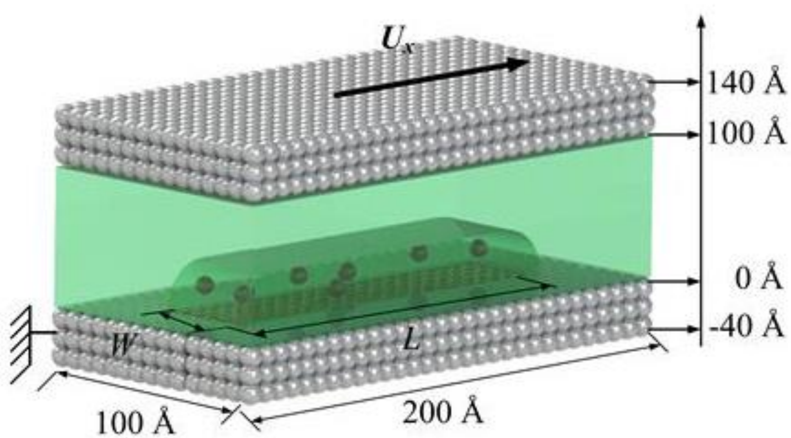


Details of molecular dynamics simulations

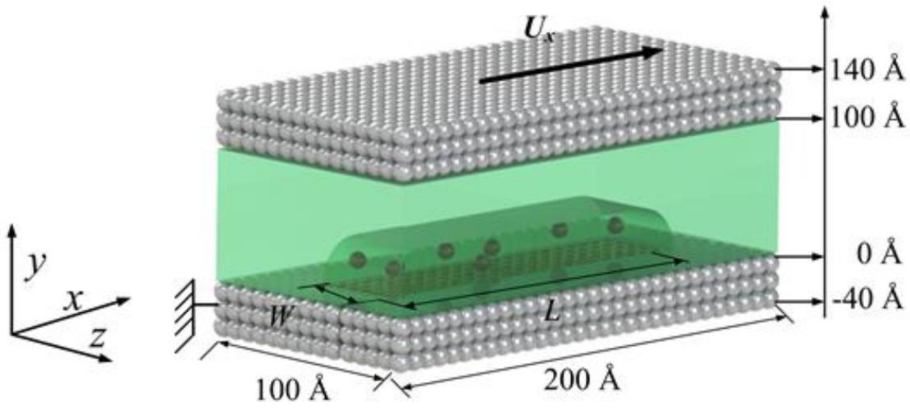
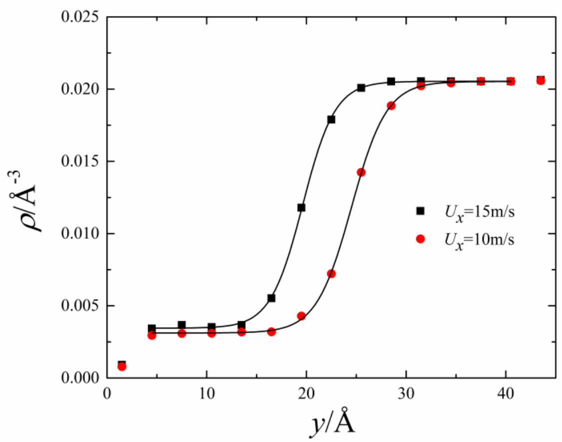
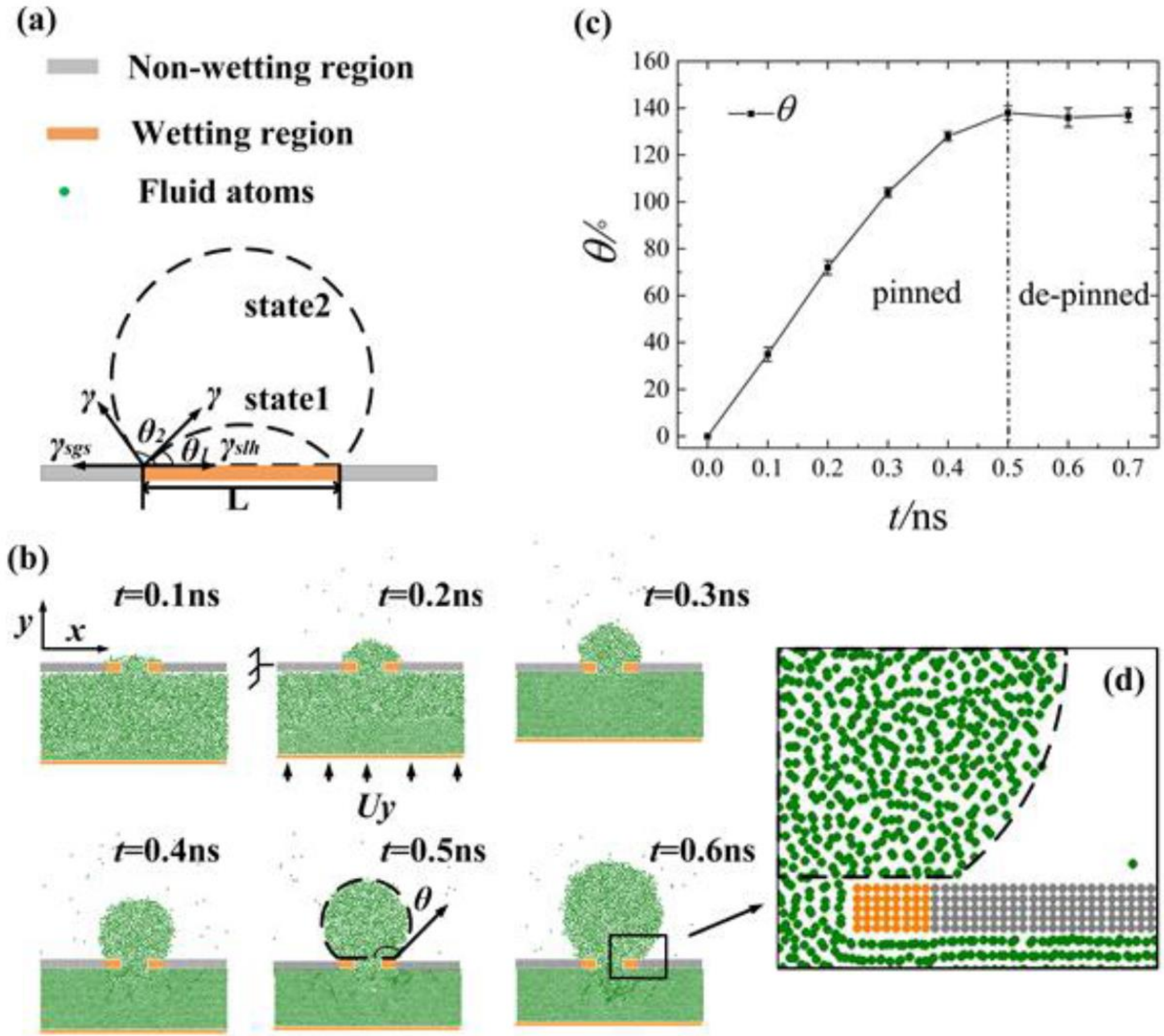


Fig.1 Illustration of the simulation domain. The symbols (●), (●), (●) and (■) denote the wetting solid, non-wetting solid, gas atoms and liquid phase, respectively. The liquid consists of 13750 atoms, each wall contains 15225 atoms, and the gas phase is formed by 78 atoms. The reference plane at y = 0, the channel height, and the wall thickness are indicated on the vertical axis (y).

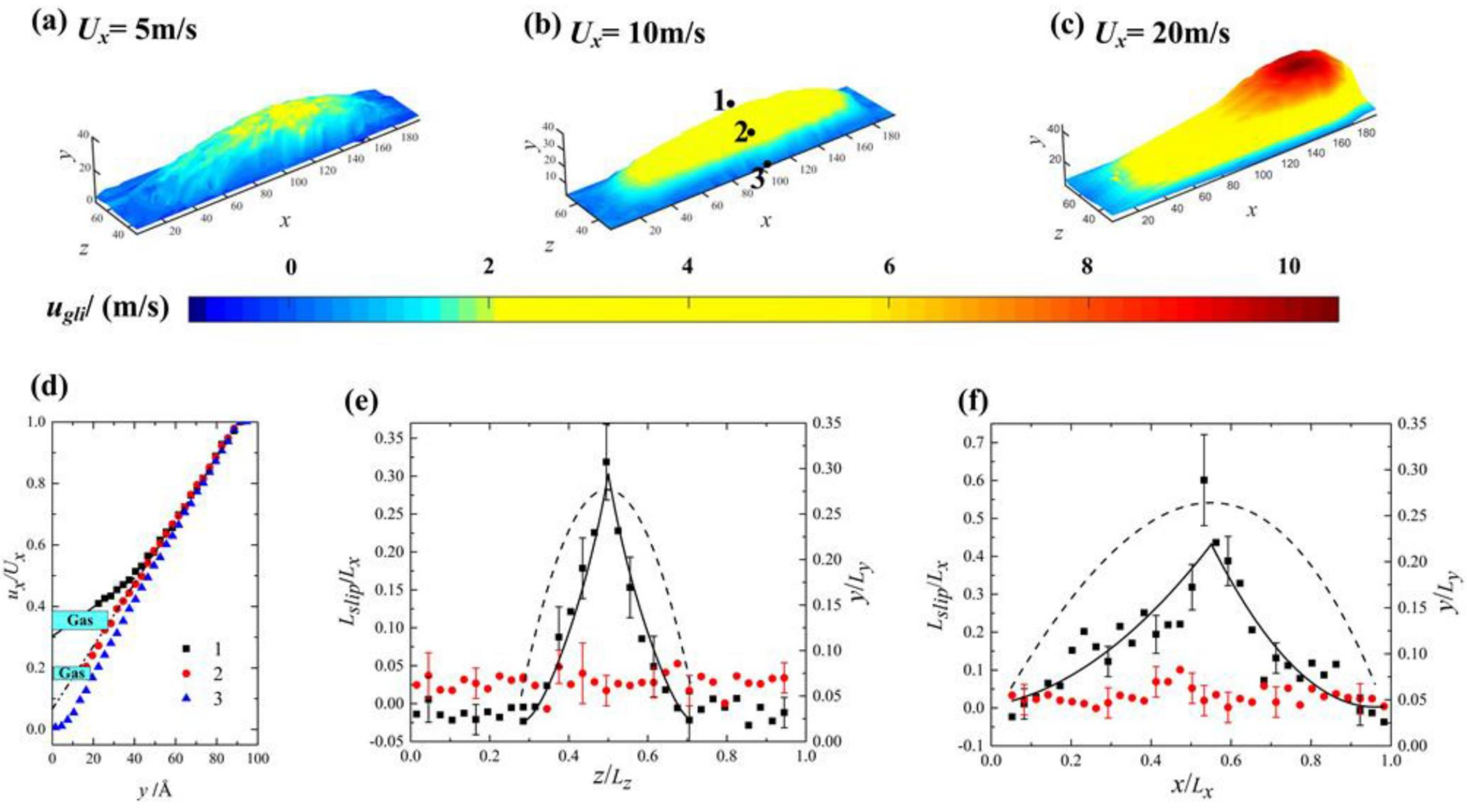
$$E_{ij}=\begin{cases} 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right], & r<r_c \\ 0, & r\geqslant r_c \end{cases}$$



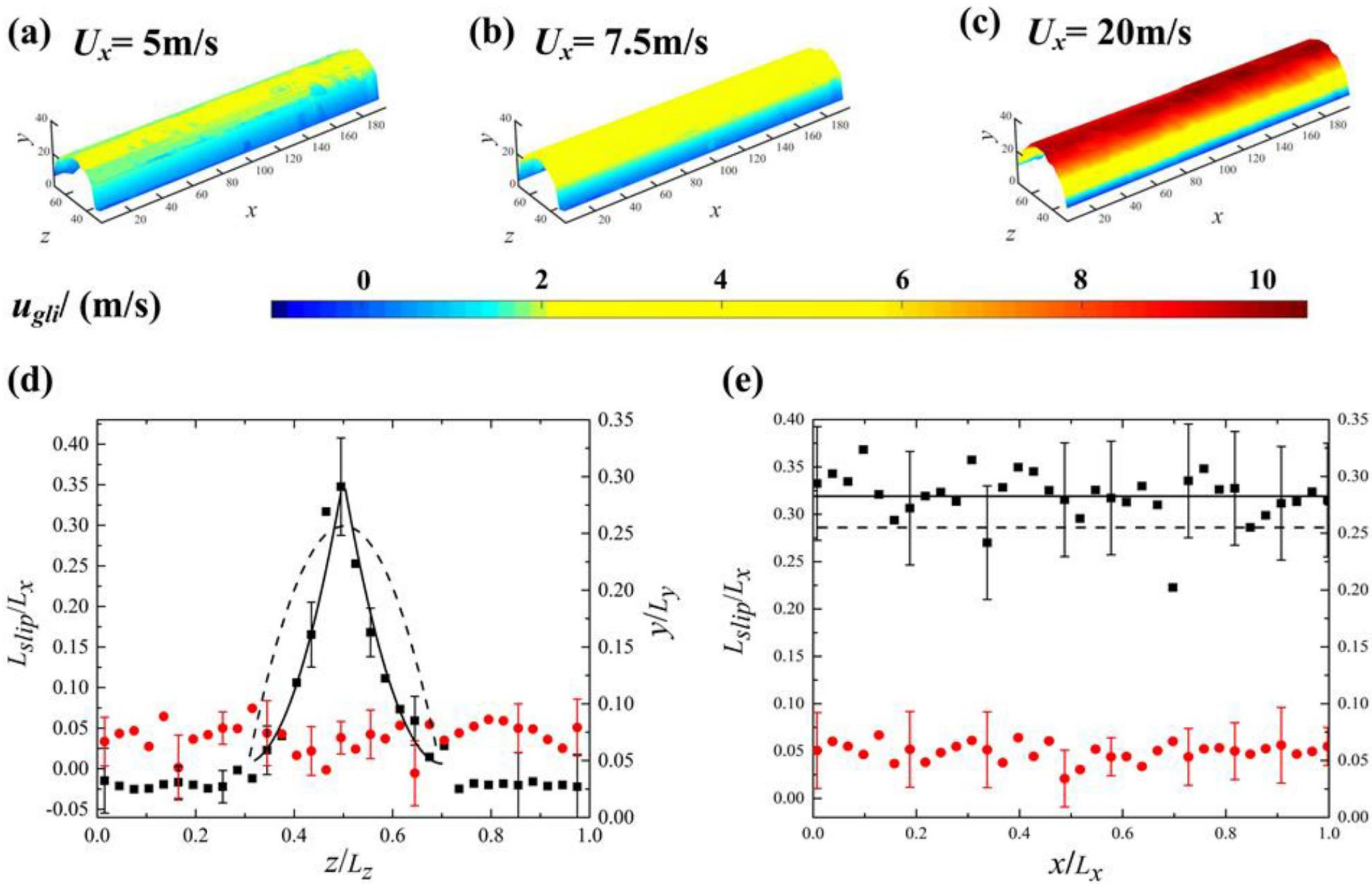
The pinning mechanism of the three-phase contact line



The slip velocities and slip lengths for flows over surface-attached nanobubble



The slip velocities and slip lengths for flows over surface-attached nanobubble



Conclusions:

- We investigated the behavior of the local and effective slip lengths that describe shear flows over nanobubbles attached to smooth solid surfaces using molecular dynamics simulations.
- Contact line at the gas-liquid interface can be pinned by the wettability step on a smooth substrate and the contact angle hysteresis depends strongly on the wettability contrast.
- The local slip length is finite at the gas-liquid interface and its spatial distribution becomes asymmetric due to deformation of the nanobubble under high shear.