Molecular Diffusion and Tensorial Slip at Surfaces with Periodic and Random Nanoscale Textures

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Movies, preprints @ http://www.egr.msu.edu/~priezjev

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

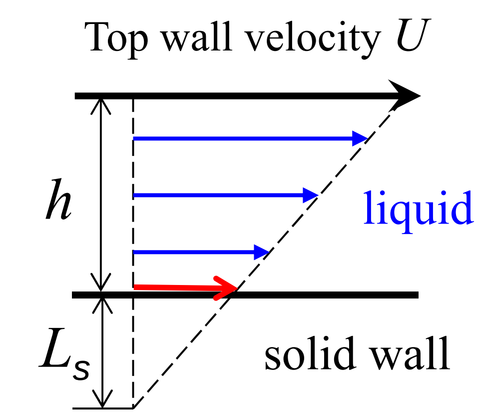
Motivation for investigation of slip phenomena at liquid/solid interfaces

- What is the proper boundary condition for liquid-on-solid flows in the presence of slip?

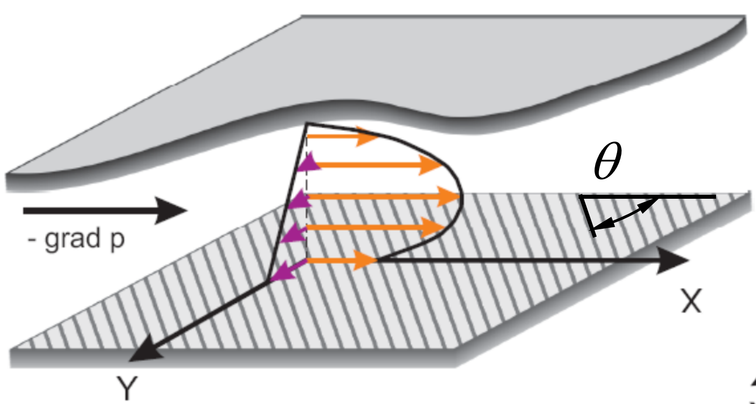
Still no fundamental understanding of slip or what is proper boundary condition for continuum modeling. Issue is very important in microfluidics and nanofluidics.

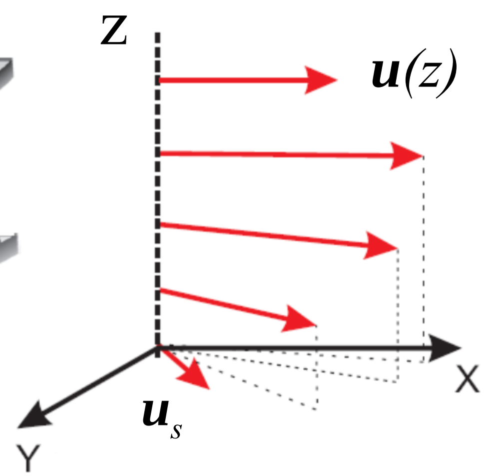
- Effective slip in flows over anisotropic textured surfaces

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 $\sigma_{wf} = \sigma$

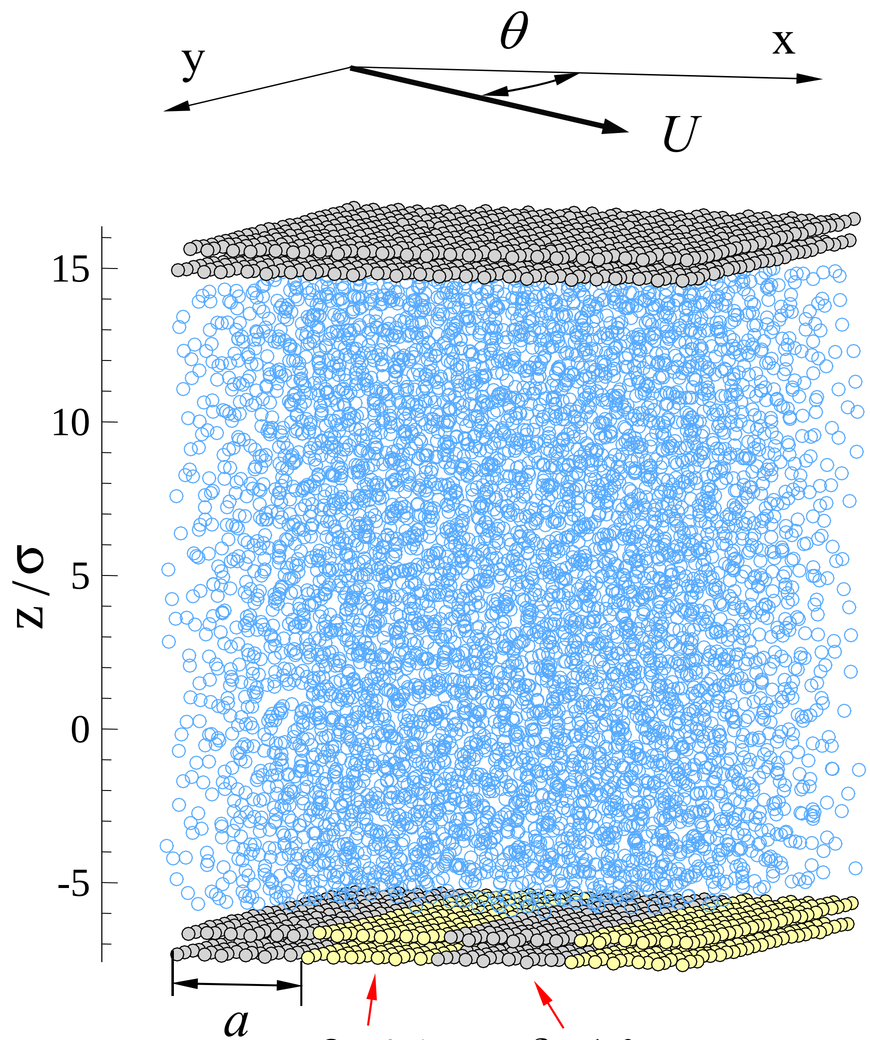
$$V_{LJ}(r) = 4\,\varepsilon_{wf}\left[\left(\frac{r}{\sigma}\right)^{-12} - \delta\left(\frac{r}{\sigma}\right)^{-6}\right]$$

<u>Nonwetting regions, large slip length:</u> $\delta = 0.1$

<u>Wetting regions, small slip length:</u> $\delta = 1.0$

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

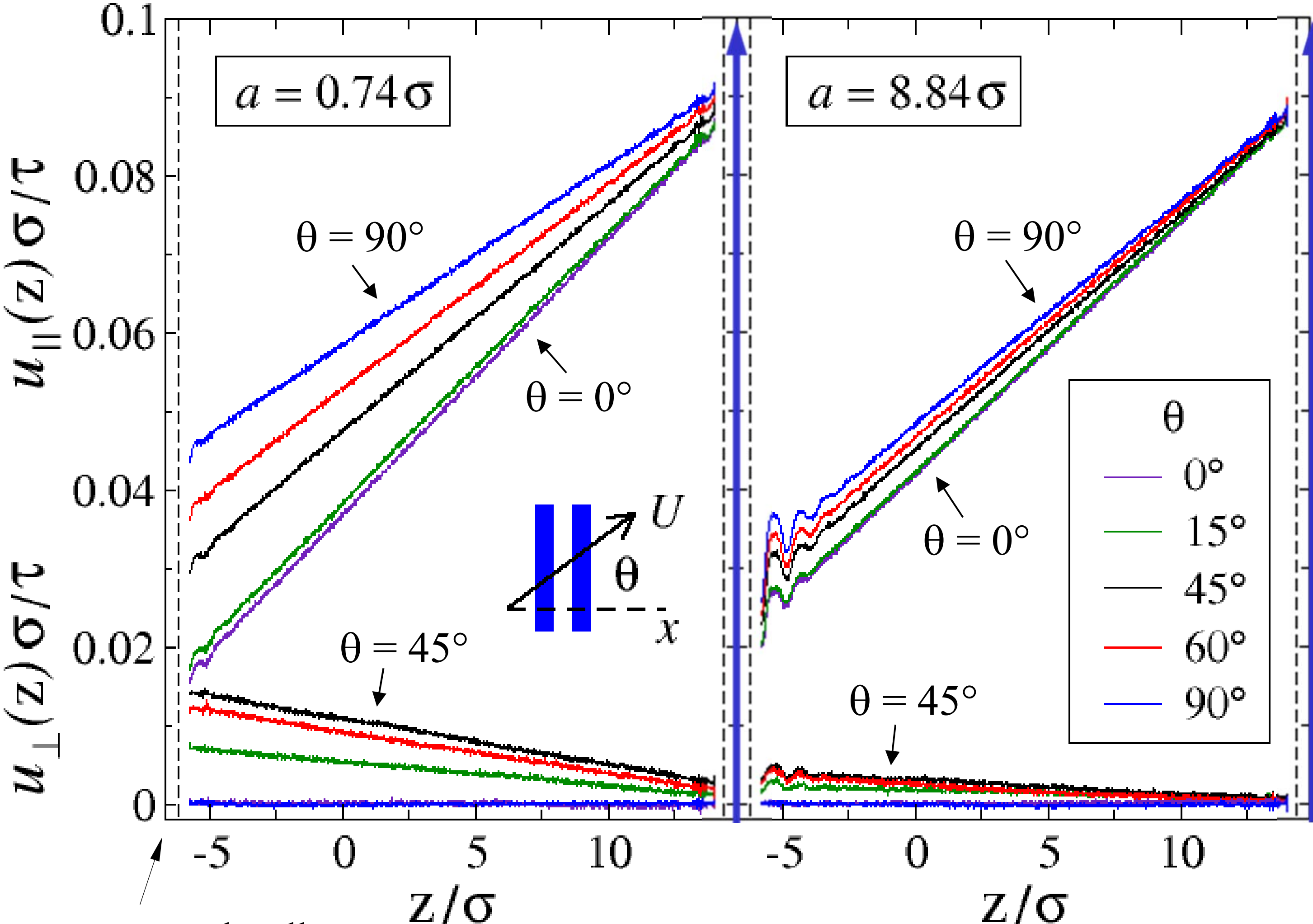


$\delta = 0.1$ $\quad$ $\delta = 1.0$

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

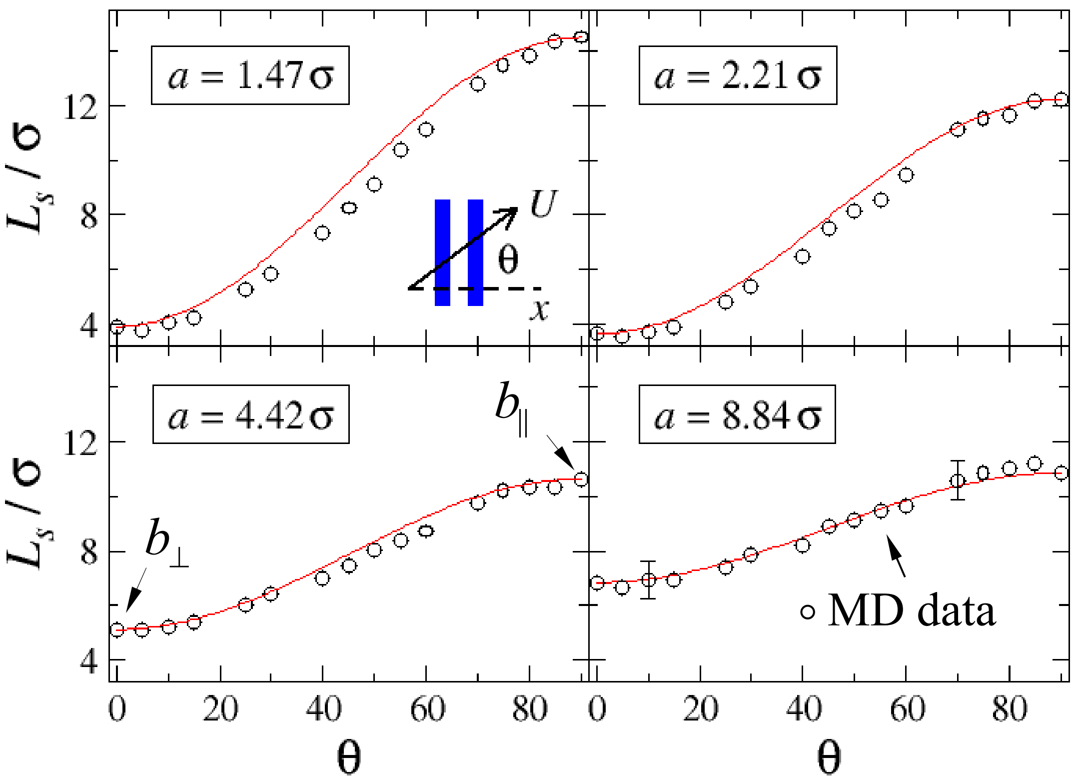
U = upper wall speed

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

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

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

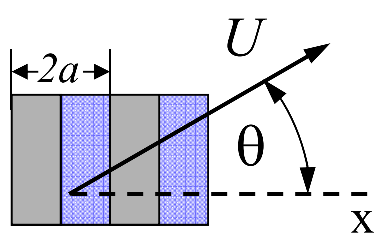
Slip length as a function of angle θ between flow orientation U and stripes



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

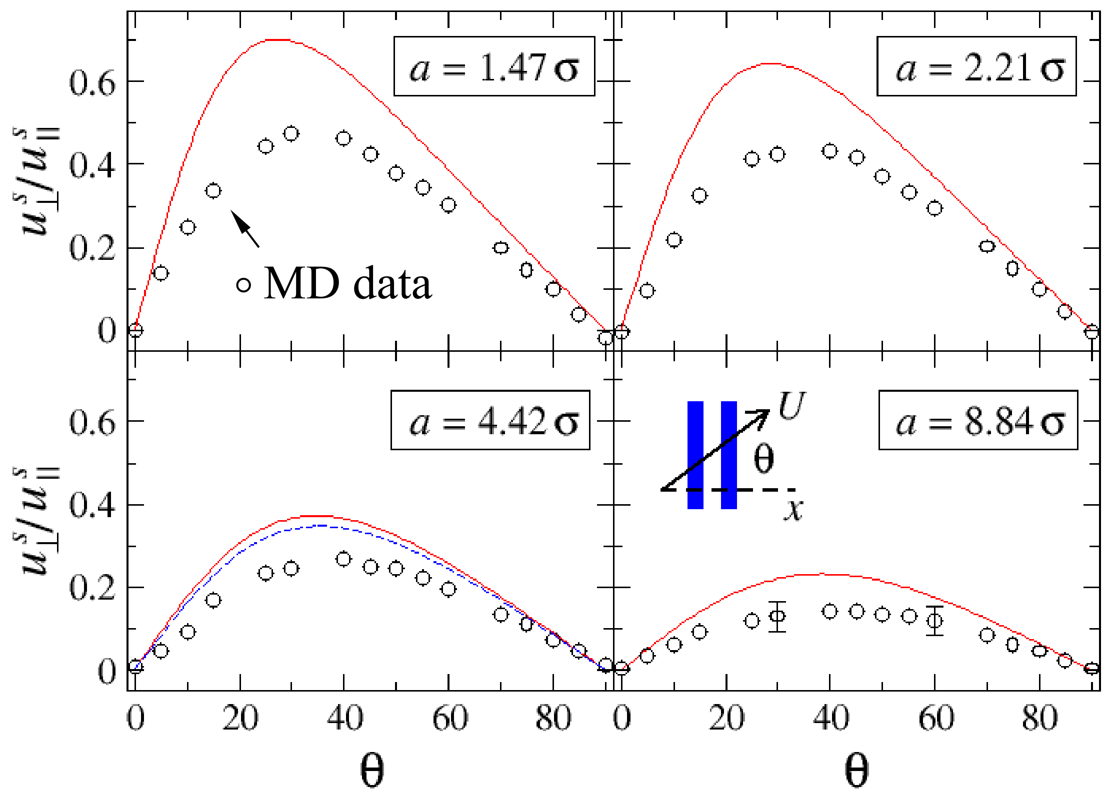


Non-wetting region (low wall-fluid energy, large slip length)

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

$$L_s(\theta = 0^\circ) = b_\perp \qquad L_s(\theta = 90^\circ) = b_{||}$$

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



Continuum prediction (red curves)

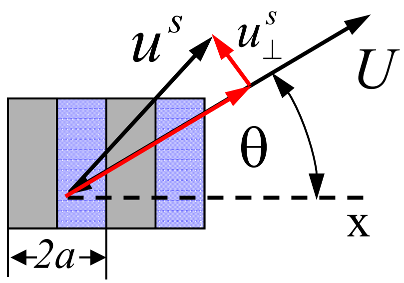
$$\frac{u^s_\perp}{u^s_\parallel} = \frac{(b_\parallel - b_\perp)\sin\theta\cos\theta}{b_\perp\cos^2\theta + b_\parallel\sin^2\theta}$$

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

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

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

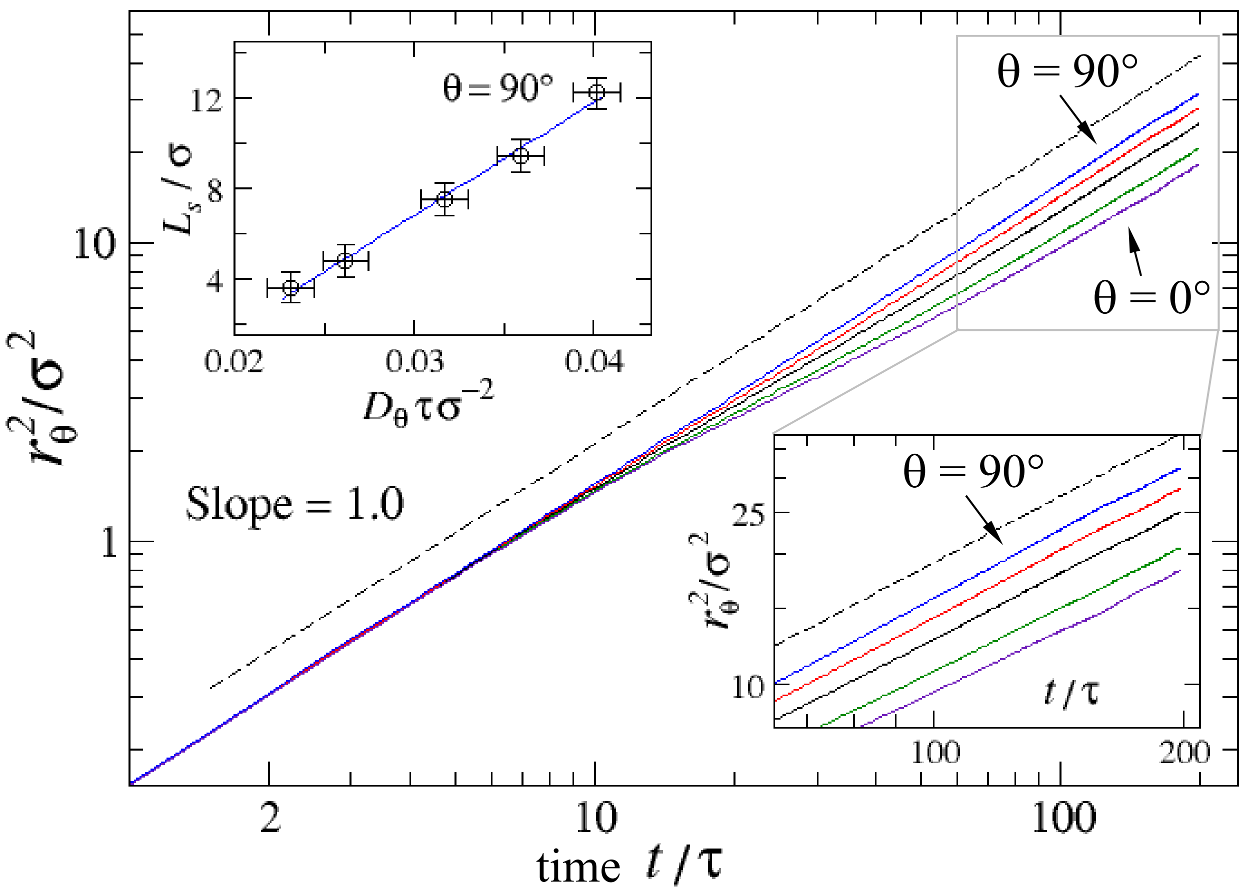
Flat FCC stationary lower wall plane:
U=upper wall speed
u^s = slip velocity



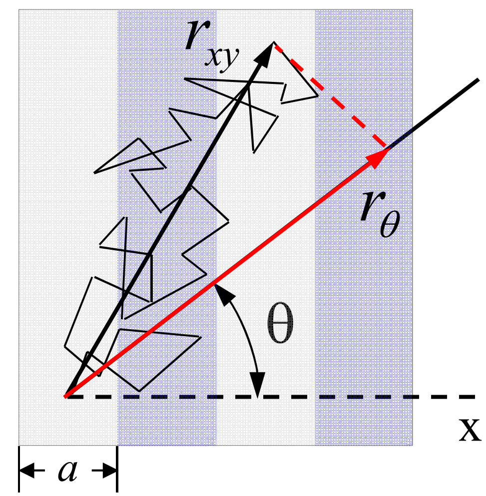
Non-wetting region (low wall-fluid energy, large slip length)

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

A correlation between interfacial diffusion coefficient D_θ and slip length L_s



$a = 2.21\sigma \qquad U = 0$



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

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

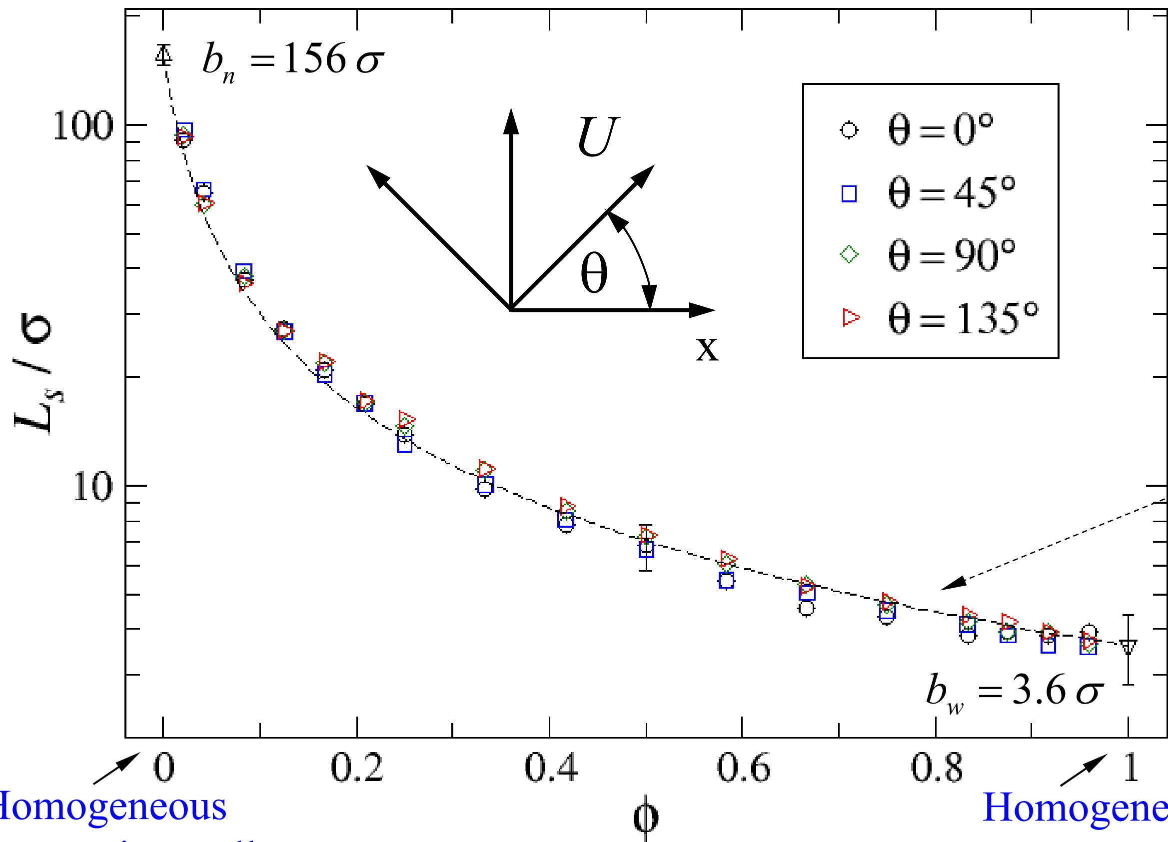
Microscopic justification of the tensor formulation of the effective slip boundary conditions: interfacial diffusion coefficient D_θ correlates well with the effective slip length as a function of the shear flow direction U.

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).

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)

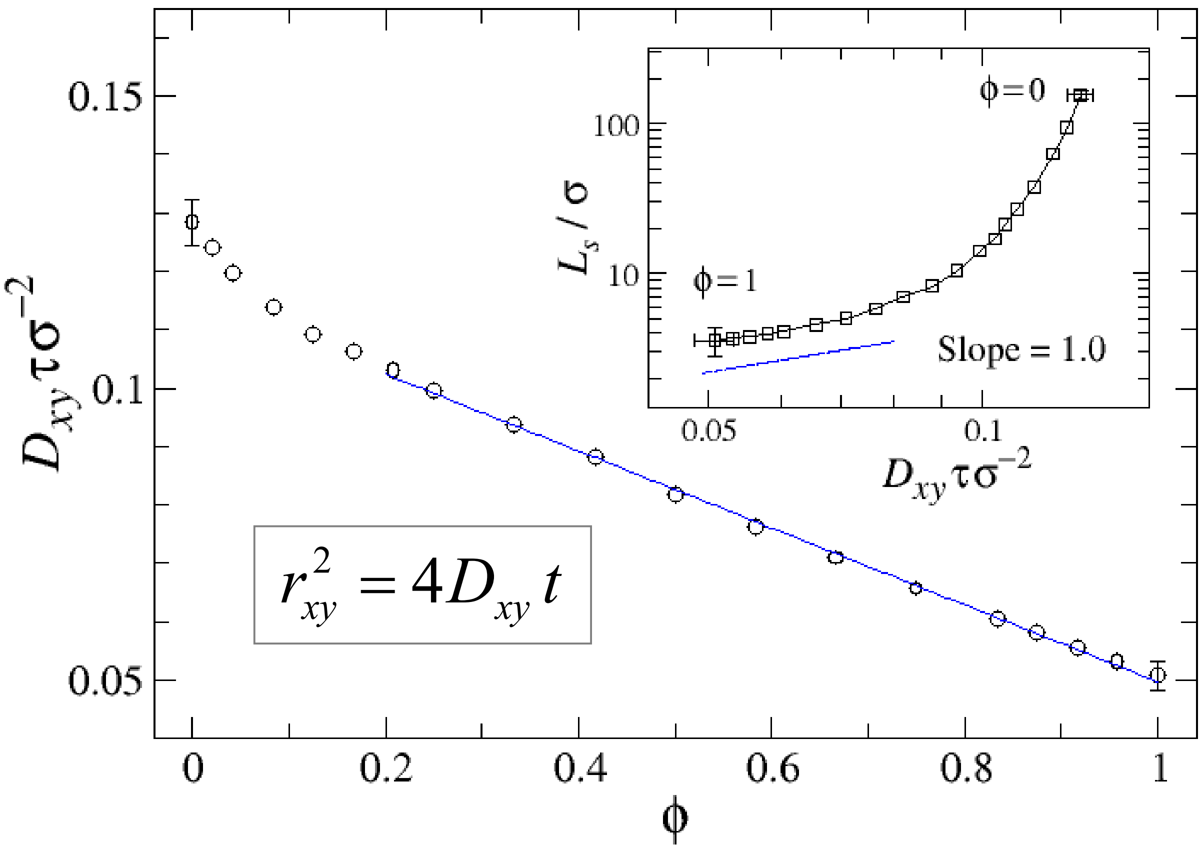
ϕ = areal fraction of wetting ($\delta = 1.0$) lower wall atoms

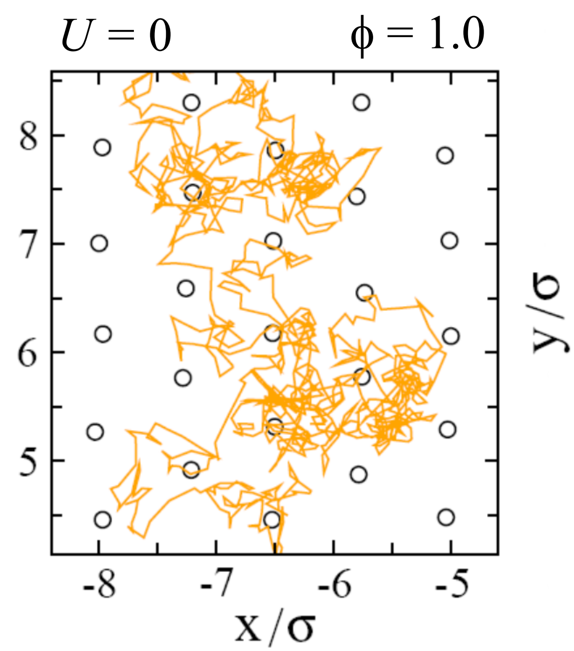
1 - ϕ = fraction of nonwetting ($\delta = 0.1$) lower wall atoms

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





Trajectory for ≈ 100τ

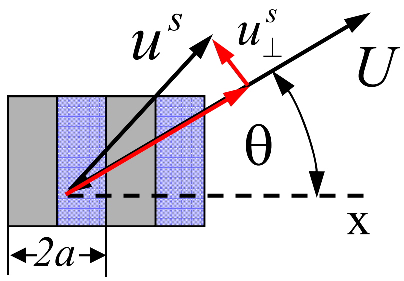
ϕ = areal fraction of wetting ($\delta = 1.0$) wall atoms

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

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

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).