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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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**

\[ \langle u_s \rangle = L_{eff} \cdot \left( \frac{\partial u}{\partial z} \right)_s \]

Flow over parallel stripes:
\[ L_s(\theta) = b_\perp \cos^2 \theta + b_\parallel \sin^2 \theta \]

\[ L_s(\theta = 0^\circ) = b_\perp \quad L_s(\theta = 90^\circ) = b_\parallel \]
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 \( 0 < \theta < 90^\circ \)

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

Transverse flow \( u_\perp(z) \) is maximum when \( \theta = 45^\circ \)

\( a = \) stripe period

\( U = \) upper wall speed

Longitudinal component: \( u_\parallel(z) \parallel U \)

Transverse component: \( u_\perp(z) \perp U \)

Lower patterned wall

Upper wall \( U = 0.1\sigma/\tau \)
Slip length as a function of angle $\theta$ 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.

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

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

Wetting region (high wall-fluid energy, small slip)
Ratio of transverse and longitudinal components of slip velocity $u^s$ versus $\theta$

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 $D_\theta$ and slip length $L_s$.

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

$U = 0$

$\theta = 90^\circ$

Flow over parallel stripes:

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

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

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)

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

\[ \phi = \text{areal fraction of wetting (}\delta = 1.0\text{) lower wall atoms} \]

\[ 1 - \phi = \text{fraction of nonwetting (}\delta = 0.1\text{) lower wall atoms} \]

Wall-fluid interaction:

\[ V_{LJ}(r) = 4\varepsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \delta \left( \frac{r}{\sigma} \right)^{-6} \right] \]
A correlation between interfacial diffusion coefficient $D_{xy}$ and slip length $L_s$

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

\[ r_{xy}^2 = 4D_{xy} t \]

$\phi = \text{areal fraction of wetting (}\delta = 1.0\text{) wall atoms}$

$1 - \phi = \text{fraction of nonwetting (}\delta = 0.1\text{) wall atoms}$
Important conclusions

\[ \langle u_s \rangle = L_{\text{eff}} \cdot \left\langle \frac{\partial u}{\partial z} \right\rangle \]

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

- Good agreement between MD and hydrodynamic results for anisotropic flows over periodically textured surfaces provided length scales \( \approx O(10 \text{ molecular diameters}) \).

- Microscopic justification of the tensor formulation of the effective slip boundary conditions: interfacial diffusion coefficient \( D_{\theta} \) 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.