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Slip Flow Regimes and Induced Fluid Structure in Nanoscale Polymer Films: Recent Results from Molecular Dynamics Simulations

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Slip Flow Regimes and Induced Fluid Structure in Nanoscale Polymer Films: Recent Results from Molecular Dynamics Simulations

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Motivation: Nano- and Microfluidics

- Control and manipulation of fluids at submicron scales
- The behavior of fluids at the microscale is different from 'macrofluidic' behavior (low Re, high S/V ratio)
- Lab-on-a-chip devices allow automation of complex biological and chemical reactions (wikipedia)

“Microflows & Nanoflows” Karniadakis (2005)

Microchip system performs hundreds of parallel chemical reactions


A micromixer for rapid mixing of two or three fluid streams

*The Dolomite Center Ltd.*

Droplet actuation across junctions

Splitting of a droplet

Motivation for investigation of slip phenomena at liquid/solid interfaces

- What is the boundary condition for liquid-on-solid flows in the presence of slip?
  Still no fundamental understanding of slip or what is proper BC for continuum studies. Issue very important to micro- and nanofluidics. Contact line motion.

- Navier slip boundary condition assumes constant slip length. Recent MD simulations and experiments report rate-dependent slip length $L_s = L_s(\dot{\gamma})$. Shear rate threshold?

- Combined effect of surface roughness, wettability and rate-dependency on the slip length $L_s$: e.g., surface roughness reduces the degree of slip but shear rate might increase $L_s$

- Rate-dependence of the slip length in the shear flow of polymer melts past atomically smooth solid surfaces
  What molecular parameters (fluid structure, wall lattice type, wall-fluid interaction energy) determine the degree of slip?
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 ($= \text{slope of the velocity profile}$)
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).
Molecular dynamics simulations: polymer melt with chains $N=20$ beads

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: $\rho = 0.86–1.11 \, \sigma^{-3}$

FENE bead-spring model:

$$V_{FENE}(r) = \frac{1}{2} kr_o^2 \ln \left( 1 - \frac{r^2}{r_o^2} \right)$$


Top wall velocity $U$

$$\dot{\gamma} = \frac{\partial u}{\partial z}$$

$$\gamma \parallel \text{slip}$$

Solid wall

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

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

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

$f_i =$ Gaussian random force

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

Thermal FCC walls with density $\rho_w = 1.40 \, \sigma^{-3}$

Weak wall-fluid interactions: $\varepsilon_{wf} = 0.9 \, \varepsilon$

Fluid density and velocity profiles for selected values of top wall speed $U$

Density profiles near the lower wall:

- $\rho = 0.91 \sigma^{-3}$
  - $U = 0.05 \sigma/\tau$
  - $U = 1.0 \sigma/\tau$
  - $U = 5.0 \sigma/\tau$

**polymer coil N=20**

Liquid-solid interface

$\rho_c =$ contact density (max first fluid peak)

The amplitude of density oscillations $\rho_c$ is reduced at higher values of the top wall speed $U$ (by about 10%)

Velocity profiles are linear throughout:

The scaled slip velocity is smaller at the intermediate speed of the upper wall $U$!? 

Shear rate $\dot{\gamma} =$ slope of the velocity profiles

Shear rate dependence of the slip length $L_s$ and polymer viscosity $\mu$

Shear-thinning $\mu$ with the slope $-0.37$

$\sigma_{xz} = \dot{\gamma} \mu$

$\sigma_{xz} V = \sum_i m v^i_\alpha v^i_\beta + \sum_{i<j} r^i_\alpha F_\beta (r^{ij})$

Microscopic pressure-stress tensor

Slip length $L_s$ passes through a minimum as a function of shear rate and then increases rapidly at higher shear rates

A relation between the slip length $L_s$ and friction coefficient at the interface

Shear stress in steady flow:

In the bulk fluid $\sigma_{xz} = \mu \dot{\gamma}$
At the interface $\sigma_{xz} = k V_{\text{slip}}$

Friction coefficient:

$k = \mu / L_s$

Note the exception:
(higher viscosity boundary layer)
$L_s < 0$ but $k > 0$!

Shear rate threshold:

For simple fluids and weak surface energy: Thompson and Troian, Nature 389, 360 (1997)

$L_s (\dot{\gamma}) = L_s^0 \left(1 - \dot{\gamma} / \dot{\gamma}_c\right)^{-0.5}$

$k(V_s) = C_1 \left(\sqrt{C_2 + V_s^2} - V_s\right)$

Viscosity $\mu$ is rate-independent for simple fluids (N=1) where $C_1 = \mu / 2\dot{\gamma}_c (L_s^0)^2$, $C_2 = (2L_s^0 \dot{\gamma}_c)^2$.
Friction coefficient at the liquid-solid interface as a function of slip velocity

Friction coefficient: \( k = \frac{\mu}{L_s} \)

Master curve: \( \frac{k}{k^*} = [1 + (V_s/V_s^*)^2]^{-0.35} \)

Friction coefficient undergoes a gradual transition from a nearly constant value to the power law decay as function of \( V_s \)

\[ k(V_s) = C_1 \left( \sqrt{C_2 + V_s^2} - V_s \right) \] Thompson and Troian (1997)
Friction coeff. for simple fluids

\( \rho = \) polymer melt density

The transition point approximately corresponds to the location of the minimum in the shear-rate-dependence of \( L_s \)

Friction coefficient at the liquid-solid interface as a function of slip velocity

Friction coefficient: 
\[ k = \frac{\mu}{L_s} \]

20 liquid-solid systems

Dashed curve = best fit: 
\[ \frac{k}{k^*} = \left[ 1 + \left( \frac{V_s}{V_s^*} \right)^2 \right]^{-0.35} \]


Parameters varied: wall type FCC and BCC, lattice orientation, wall density, thermal or frozen walls, fluid density, wall-fluid interaction energy, fluid structure: polymers \( N=10, N=20 \) and simple fluids \( N=1 \).
Diffusion of fluid monomers in the first fluid layer at equilibrium (i.e. $U=0$)

Side view: polymer melt near solid wall

Top view: (111) plane of FCC wall lattice

Mean square displacement in the first layer

The diffusion time $t_d$ was estimated from the mean square displacement of fluid monomers in the first layer at the distance between nearest minima of the periodic surface potential $d_{nn}$.

A correlation between the diffusion time $t_d$ and the characteristic slip time $t_s^*$

Characteristic slip time:

$$t_s^* = \frac{d_{nn}}{V_s^*}$$

$$k / k^* = [1 + (V_s / V_s^*)^2]^{-0.35}$$

The linear-response regime holds when the slip velocity of the first layer is smaller than the diffusion velocity of fluid monomers in contact with flat crystalline surfaces.

Analysis of the fluid structure in the first layer near the solid wall

Structure factor in the first fluid layer:

\[ S(k) = \frac{1}{N_l} \left| \sum e^{i \mathbf{k} \cdot \mathbf{r}_j} \right|^2 \]

Sharp peaks in the structure factor (due to periodic surface potential) are reduced at higher slip velocities \( V_s \) or lower wall-fluid interaction energies \( \varepsilon_{wf} \).

Review of current slip models

Bocquet & Barrat (1999) Kubo relation

\[ \frac{1}{k} = \frac{L_s^0}{\mu} \propto \frac{D_{q||}}{S(q||)\rho_c \varepsilon_{wf}^2} \]

simple fluids

\( (N=1) \)

\( S(q||) = \) in-plane structure factor

\( D_{q||} = \) in-plane diffusion coefficient

\( q|| = \) reciprocal lattice vector

in the shear flow direction

\( \rho_c = \) contact density

All parameters evaluated in first fluid layer from equilibrium simulations

low shear rates

Thompson & Robbins (1990) simple fluids

\( (N=1) \)

\[ \frac{L_s}{\sigma} \]

\[ S_1(G_1)/S_1(0) \]

Slip length \( L_s \) does not depend on shear rate (or the upper wall speed \( U \))

Thompson & Robbins (1990) simple fluids

\( (N=1) \)

\[ \text{Varied: } \rho_{\text{wall}}, \varepsilon_{\text{wf}} \]

Priezjev & Troian (2004) polymers \( N \leq 16 \)


For chain length \( N > 10 \)

\[ L_s^0(N) \propto \mu(N) \]

Smith et al. (1996) Friction on monolayers

\[ \tau = \frac{S_1(0)}{S_1(G_1)} t_{ph} \]

Slip time \( \tau \)

phonon lifetime

in-plane structure factor

Analysis of the fluid structure in the first layer near the solid wall

Density profiles near the lower wall:

![Graph showing density profiles with polymer coil N=20](image)

Liquid-solid interface

\[ \rho_c = \text{contact density (max first fluid peak)} \]

The amplitude of density oscillations \( \rho_c \) is reduced at higher values of the top wall speed \( U \) (by about 10%)  


Structure factor in the first fluid layer:

\[
S(k) = \frac{1}{N} \left| \sum e^{i \mathbf{k} \cdot \mathbf{r}_j} \right|^2
\]

Sharp peaks in the structure factor (due to periodic surface potential) are reduced at higher slip velocities \( V_s \)
Correlation between slip and fluid structure in the first layer near the solid wall

Parameters varied: wall type FCC and BCC, lattice orientation, wall density, thermal or frozen walls, fluid density, wall-fluid interaction energy, fluid structure: polymers $N=10$, $N=20$ and simple fluids $N=1$. 

Friction coefficient: 
$$ k = \frac{\mu}{L_s} $$

$S(0) [S(G_1) \rho c \sigma^3]^{-1}$

$$ k / k^* = [1 + (V_s / V_s^*)^2]^{-0.35} $$
Important conclusions

• Molecular dynamics simulations show that the slip length $L_s$ in sheared polymer films passes through a minimum as a function of shear rate and then increases rapidly at higher shear rates. Shear rate threshold is reported in dense polymer films.

• Friction coefficient at the polymer-solid interface $k$ undergoes a transition from a constant value to the power law decay as a function of the slip velocity.

$$\frac{k}{k^*} = [1 + \left(\frac{V_s}{V_{s^*}}\right)^2]^{-0.35}$$

• For linear velocity profiles, the friction coefficient $k$ is determined by the product of the surface-induced peak in the structure factor $S(G_1)$ and the contact density $\rho_c$ in the first fluid layer near the solid wall.

$$k^* = k \left[\frac{S(0)}{S(G_1)\rho_c}\right]$$

• The linear-response regime holds when the slip velocity of the first layer is smaller than the diffusion velocity of fluid monomers in contact with flat crystalline surfaces.

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