Shear rate threshold for the boundary slip in dense polymer films: A molecular dynamics study

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

Anoosheh Niavarani and NVP
Tuesday Nov. 24, 101F: 11.40 am

N. V. Priezjev, "Shear rate threshold for the boundary slip in dense polymer films", *Phys. Rev. E* **80**, 031608 (2009). Featured in V.J. Nano. Sci. Tech. and V.J. Bio. Phys. Res. (2009).

A. Niavarani and N.V. Priezjev, "Slip boundary conditions for shear flow of polymer melts past atomically flat surfaces", *Phys. Rev. E* **77**, 041606 (2008).

N. V. Priezjev, "Rate-dependent slip BC for simple fluids", *Phys. Rev. E* **75**, 051605 (2007).

Motivation for investigation of the slip phenomena at liquid/solid interfaces

- What is *THE* boundary condition 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 very important to micro- and nanofluidics.
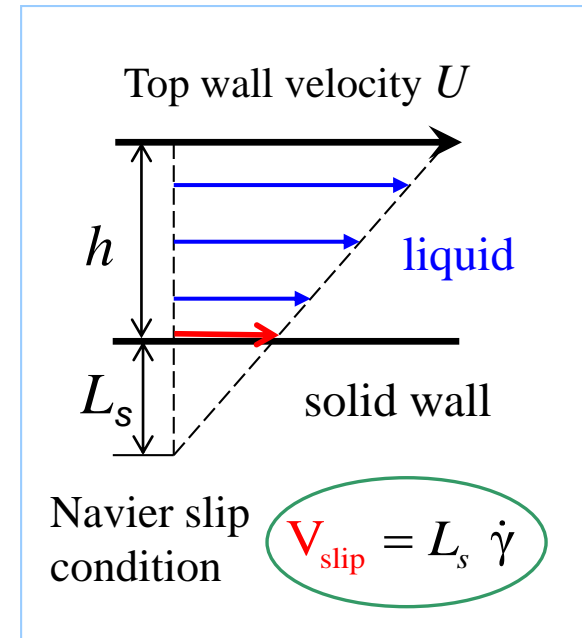
- Navier slip boundary condition (1827) assumes constant slip length. Recent MD simulations and experiments report rate-dependence $L_s = L_s(\dot{\gamma})$. Shear rate threshold?

- Combined effect of surface roughness, wettability and rate-dependency on the slip length L_s:

Slip length as a function of surface roughness and shear rate:
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Slip length as a function of polymer density and shear rate:

What molecular parameters (structure factor, contact density, temperature, fluid structure) determine the degree of slip?

Top wall velocity U

h liquid

L_s solid wall

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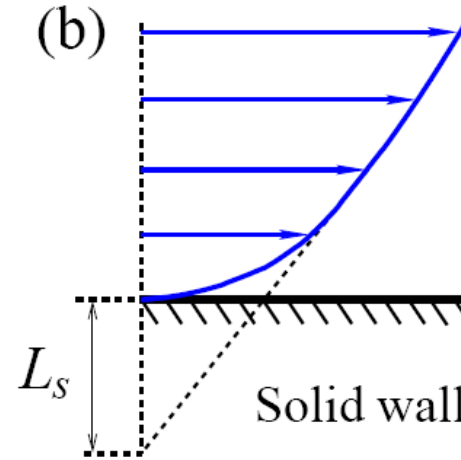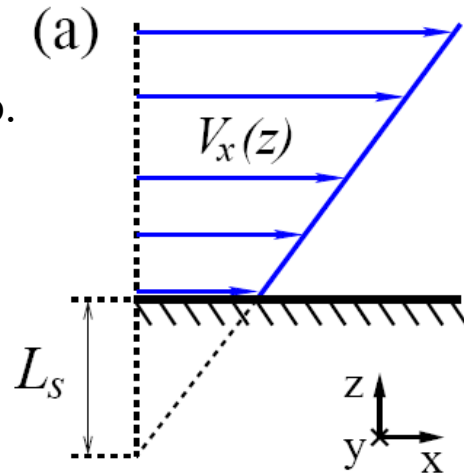
Molecular dynamics simulations

x
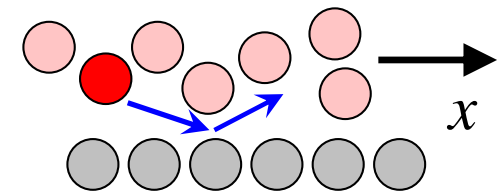
Thermal atoms of FCC wall

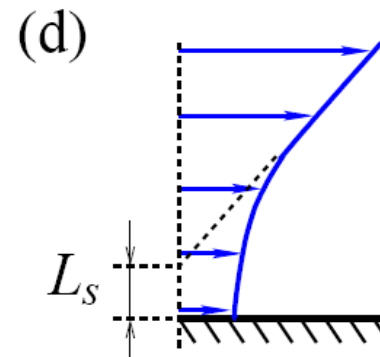# Velocity profiles and slip length in steady-state shear flow over a solid wall

Liner velocity profile = 'true' slip. Navier relation:

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

(a) $V_x(z)$

L_s

z
y x

(b)

L_s

Solid wall

Apparent slip is associated with lower viscosity interfacial layer.

Curvature of the velocity profile is due to higher viscosity boundary layer. Negative L_s !

(c)

L_s Fluid

(d)

L_s
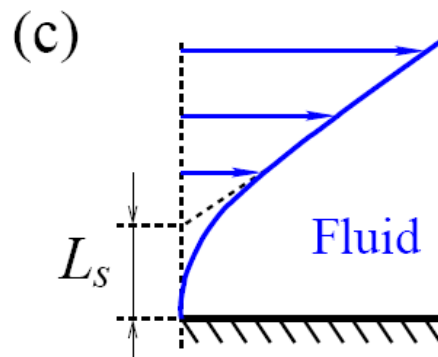
A combination of a 'true' slip and the curvature of the velocity profile.

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: $\rho = 0.86\text{--}1.11\,\sigma^{-3}$

FENE bead-spring model:
$$V_{FENE}(r) = \frac{1}{2}kr_o^2\ln\left(1 - \frac{r^2}{r_o^2}\right)$$
$$k = 30\varepsilon\sigma^{-2} \text{ and } r_o = 1.5\sigma$$

Kremer and Grest, *J. Chem. Phys.* **92**, 5057 (1990)

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

Weak wall-fluid interactions: $\varepsilon_{wf} = 0.9\,\varepsilon$
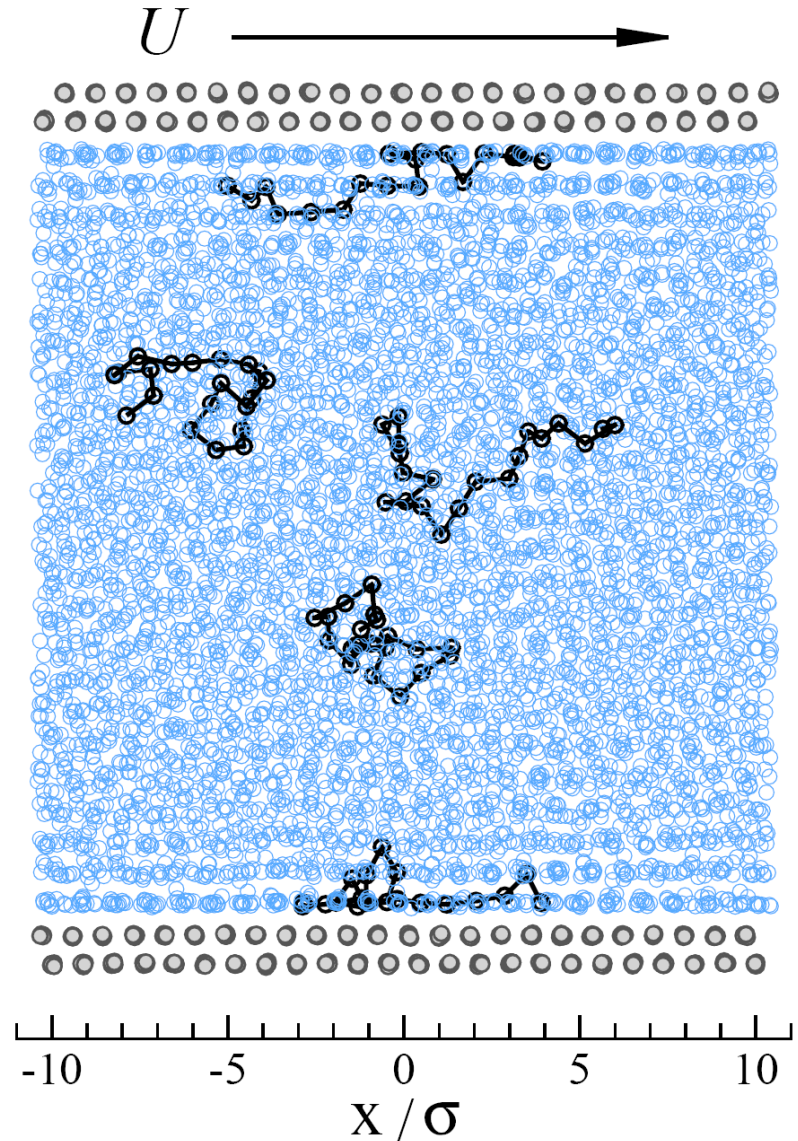
$$m\ddot{y}_i + m\Gamma\dot{y}_i = -\sum_{i\neq j}\frac{\partial V_{ij}}{\partial y_i} + f_i$$
$\Gamma = \tau^{-1}$ friction coefficient
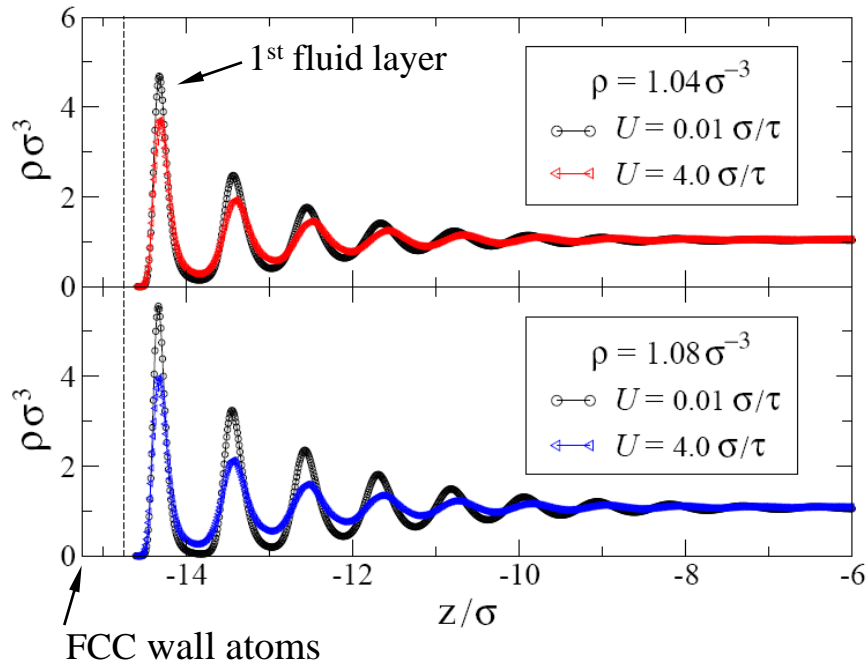f_i = Gaussian random force
Langevin thermostat: T=1.1ε/k$_B$
Thompson and Robbins, *PRA* (1990)

U

X / σ

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Density profiles near the lower wall:

Normalized velocity profiles:
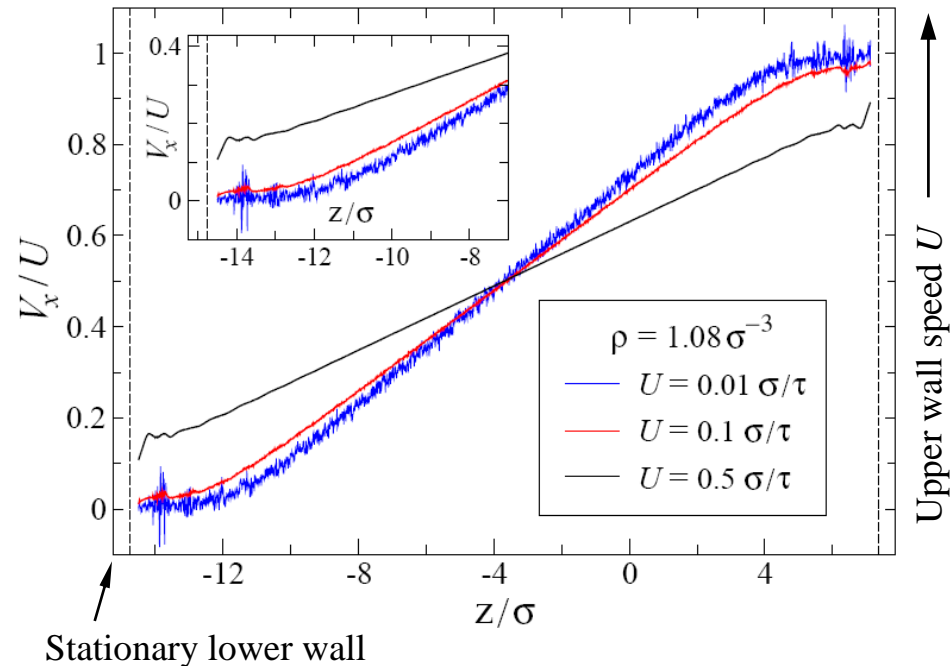

ρ_c = contact density (max first fluid peak)

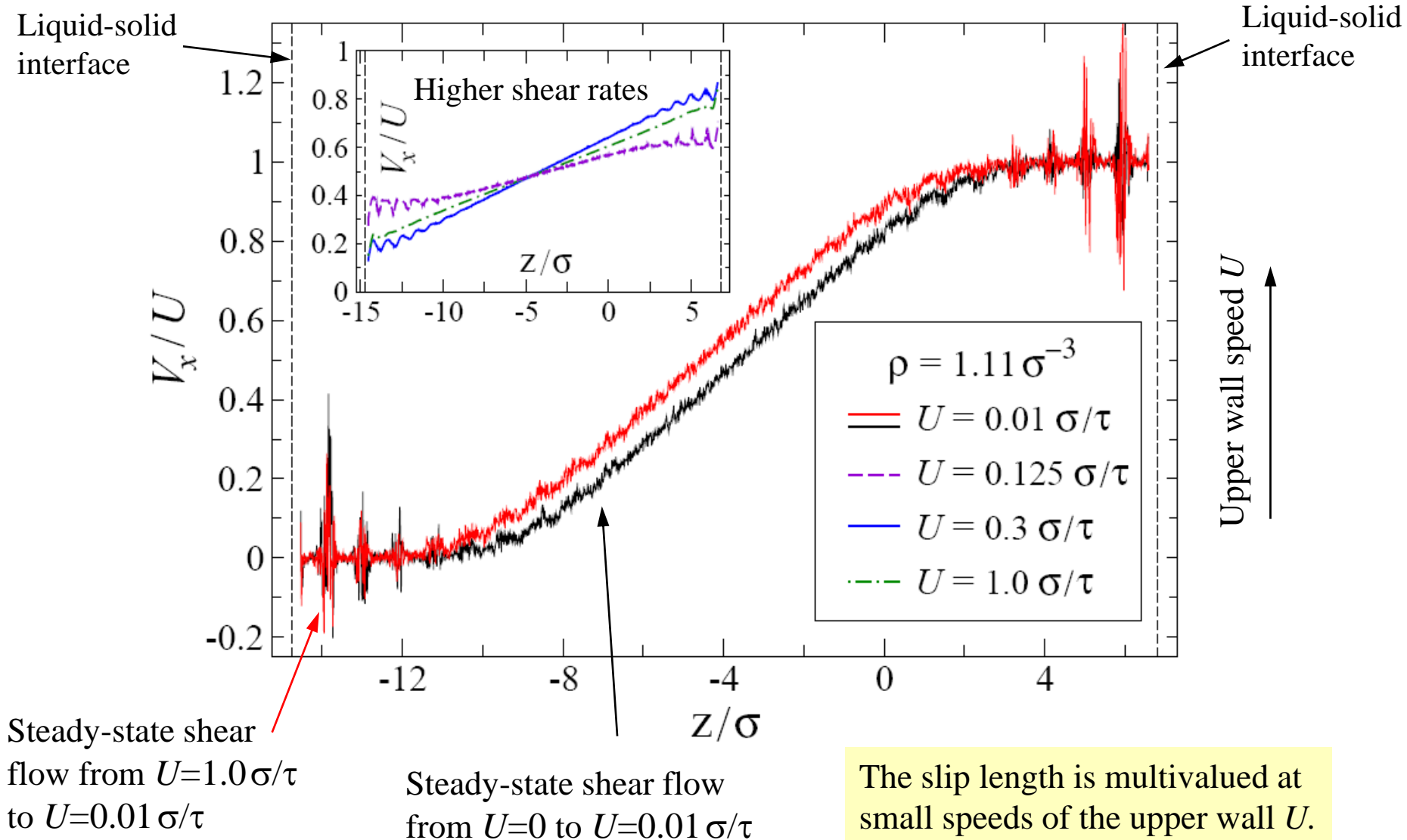Pronounced density oscillations near the solid walls at low shear rates and high polymer melt densities.

Immobile viscous layer near the walls at small values of the upper wall speed U.

Shear rate = slope of the velocity profiles in the central bulk region.

(History-dependent) averaged velocity profiles at high melt density

Liquid-solid interface

Liquid-solid interface

Upper wall speed U

Higher shear rates

$\rho = 1.11\,\sigma^{-3}$

$U = 0.01\,\sigma/\tau$
$U = 0.125\,\sigma/\tau$
$U = 0.3\,\sigma/\tau$
$U = 1.0\,\sigma/\tau$

Steady-state shear flow from $U=1.0\,\sigma/\tau$ to $U=0.01\,\sigma/\tau$

Steady-state shear flow from $U=0$ to $U=0.01\,\sigma/\tau$

The slip length is multivalued at small speeds of the upper wall U.

Shear-thinning polymer melt viscosity •••
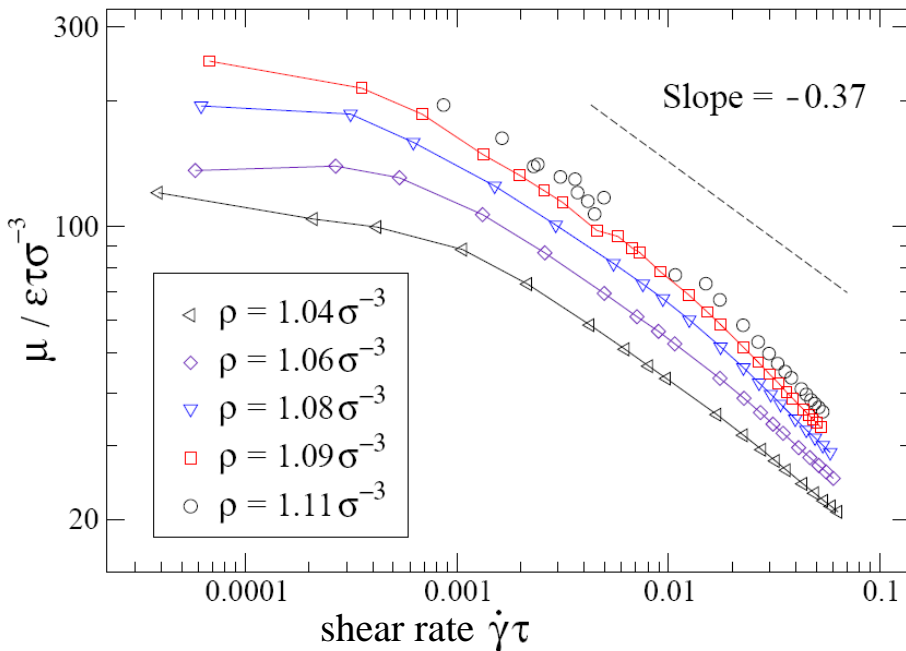
ρ = polymer density
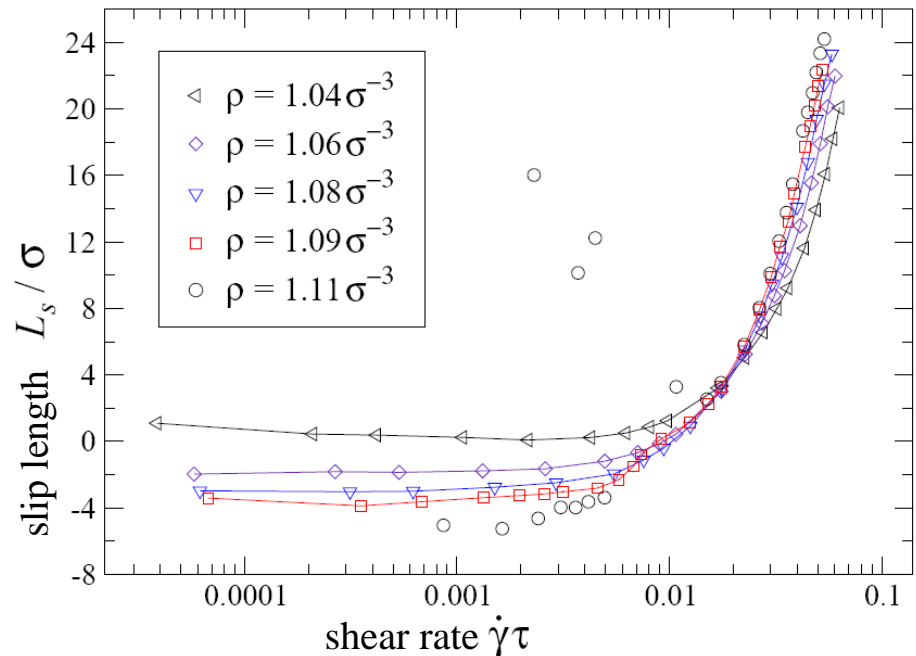
Shear stress: $\sigma_{xz} = \dot{\gamma}\,\mu$

$$\sigma_{xz}V = \sum_i m v_\alpha^i v_\beta^i + \sum_i \sum_{j>i} r_\alpha^{ij} F_\beta(r^{ij})$$
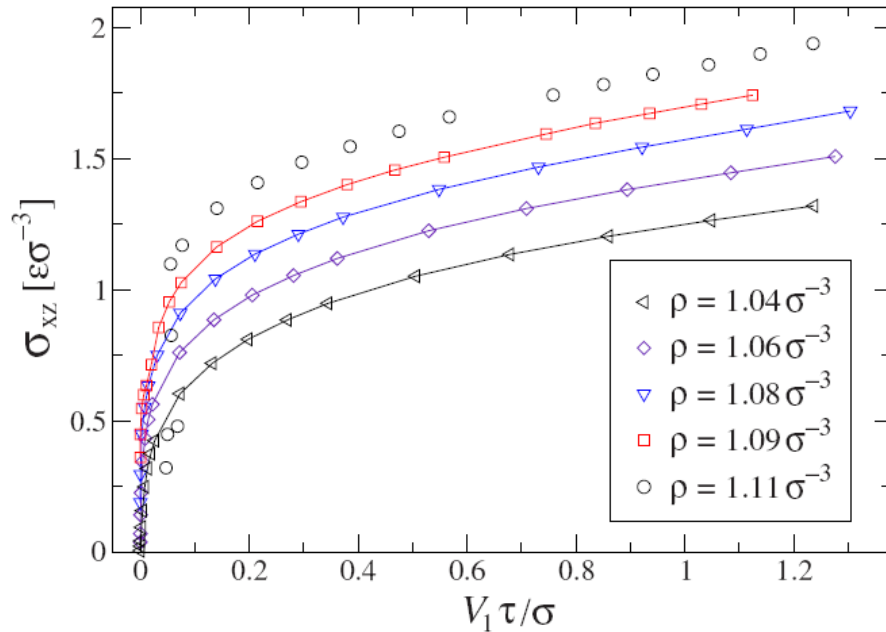
Microscopic pressure-stress tensor

Slip length is negative at low shear rates
($L_s \approx$ thickness of the viscous interfacial layer)
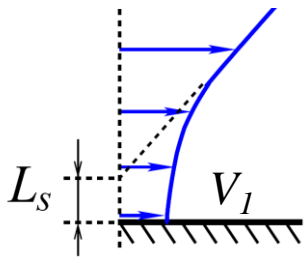and L_s increases rapidly at higher shear rates.

Slip length is multivalued at high melt density.

Friction coefficient at the melt/solid interface as a function of slip velocity

Bulk shear stress = wall shear stress σ_{xz}

Friction coefficient $\quad k = \sigma_{xz}/V_1$
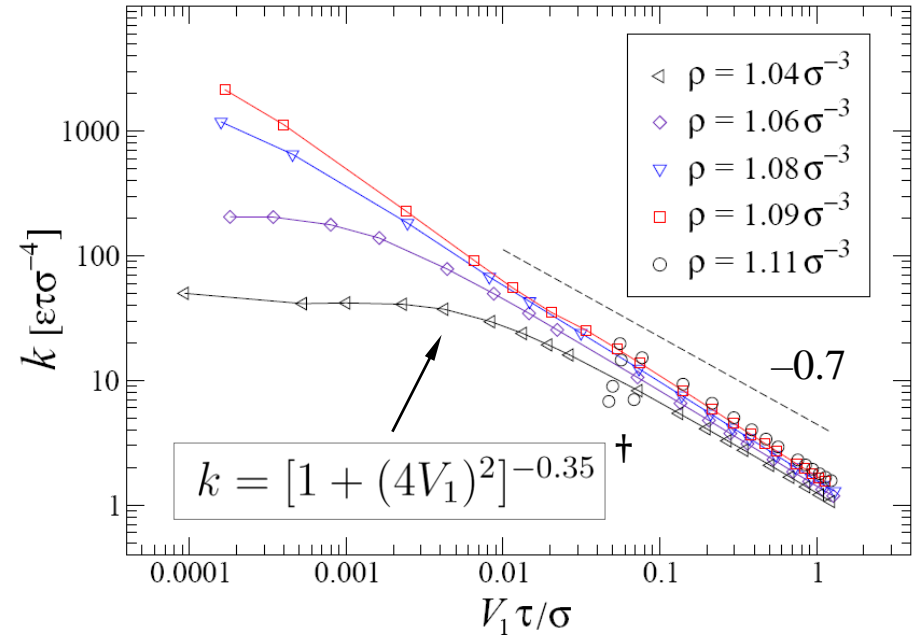
V_1 = velocity of the first fluid layer. Navier definition $V_s = L_s \dot{\gamma}$ does not apply! ($L_s < 0$ but $V_s > 0$!)

At lower melt densities: friction coefficient undergoes a transition from a nearly constant value to the power law decay as a function of slip velocity V_1.

[†] Lower density polymer melts: Niavarani and Priezjev, *Phys. Rev. E* **77**, 041606 (2008).

$k = [1 + (4V_1)^2]^{-0.35}$ [†]

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

Structure factor in the first fluid layer:

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

S(k)

S(k)

$V_1 = 0.012\,\sigma/\tau$

$V_1 = 0.95\,\sigma/\tau$
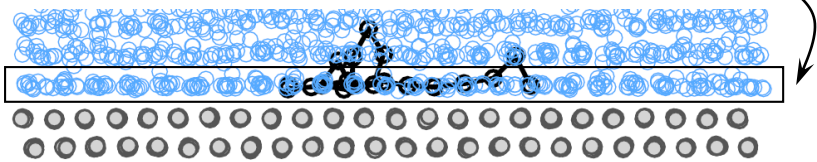
Sharp peaks in the structure factor (due to periodic surface potential) are reduced at higher slip velocities V_1.
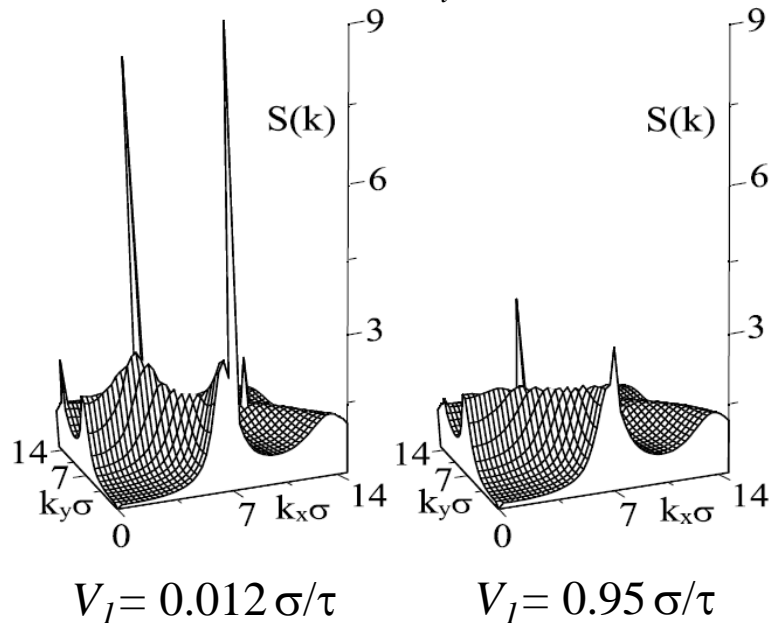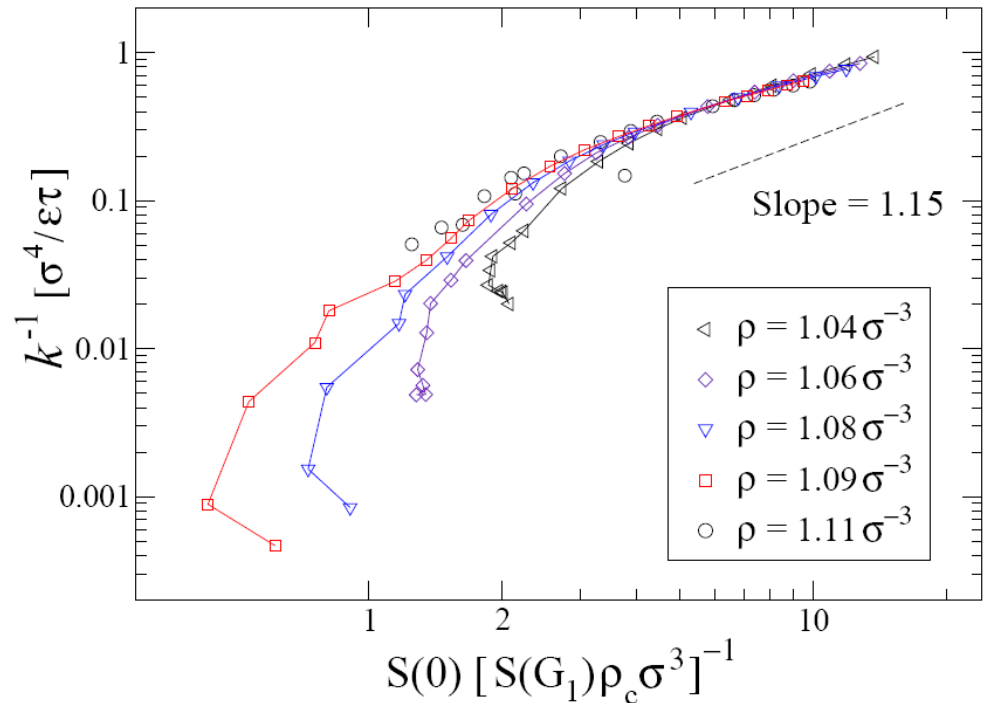
At large V_1: friction coefficient $k = \sigma_{xz}/V_1$ is determined by the product of the $S(\mathbf{G}_1)$ and the contact density ρ_c in the first layer.

$k^{-1}\,[\sigma^4/\varepsilon\tau]$

Slope = 1.15

$\triangleleft \quad \rho = 1.04\,\sigma^{-3}$
$\diamond \quad \rho = 1.06\,\sigma^{-3}$
$\triangledown \quad \rho = 1.08\,\sigma^{-3}$
$\square \quad \rho = 1.09\,\sigma^{-3}$
$\circ \quad \rho = 1.11\,\sigma^{-3}$

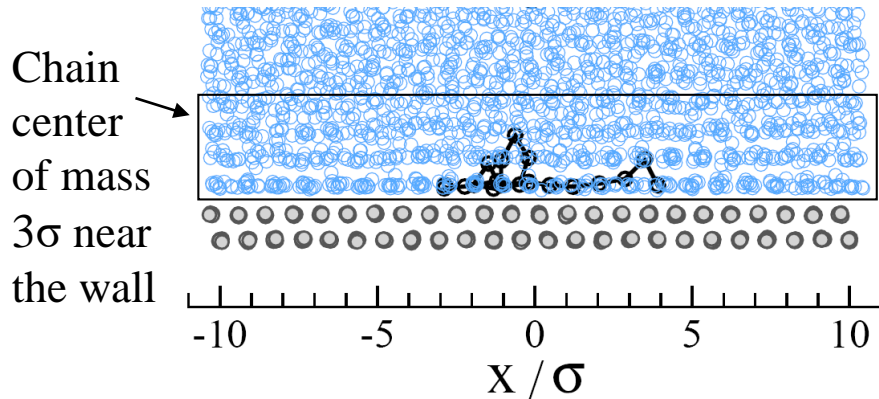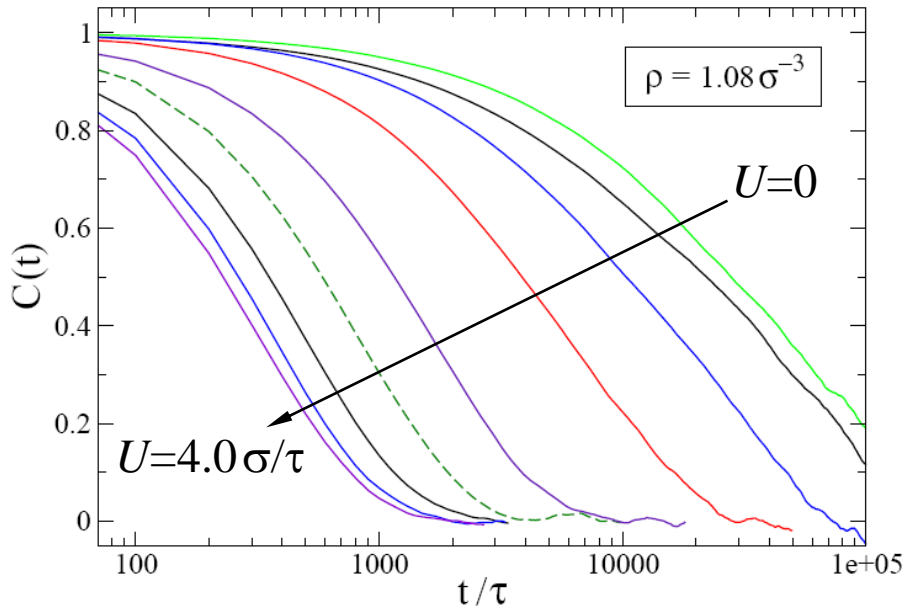$S(0)\,[\,S(\mathbf{G}_1)\rho_c\sigma^3\,]^{-1}$

$\mathbf{G}_1 = (7.23\,\sigma^{-1}, 0)$ is the first reciprocal lattice vector

Simple fluids: NVP, *Phys. Rev. E* **75**, 051605 (2007) and polymer melts: Niavarani *Phys. Rev. E* **77**, 041606 (2008)

Decay of the time-autocorrelation function of the 1st normal mode in shear flow

$$C(t) = \langle Y(t) \cdot Y(0) \rangle / \langle Y(0) \cdot Y(0) \rangle$$

$$Y(t) = N^{-1} \sum_{i=1}^{N} y_i(t) \cdot \cos[\pi(i-1)/(N-1)]$$

First normal mode for $N = 20$ polymer chain
y = vorticity direction ($\curlyvee$ to shear flow plane)

$\rho = 1.08 \, \sigma^{-3}$

$U=0$

$U=4.0 \, \sigma/\tau$

C(t)

t/τ

$$C(t) = \exp[-(t/\tau_1)^{\beta}]$$

Polymer density: $\rho = 1.08 \, \sigma^{-3}$

τ / τ_y^*

L_s / σ

shear stress $\sigma_{xz} \, [\varepsilon\sigma^{-3}]$

Chain center of mass 3σ near the wall

X / σ
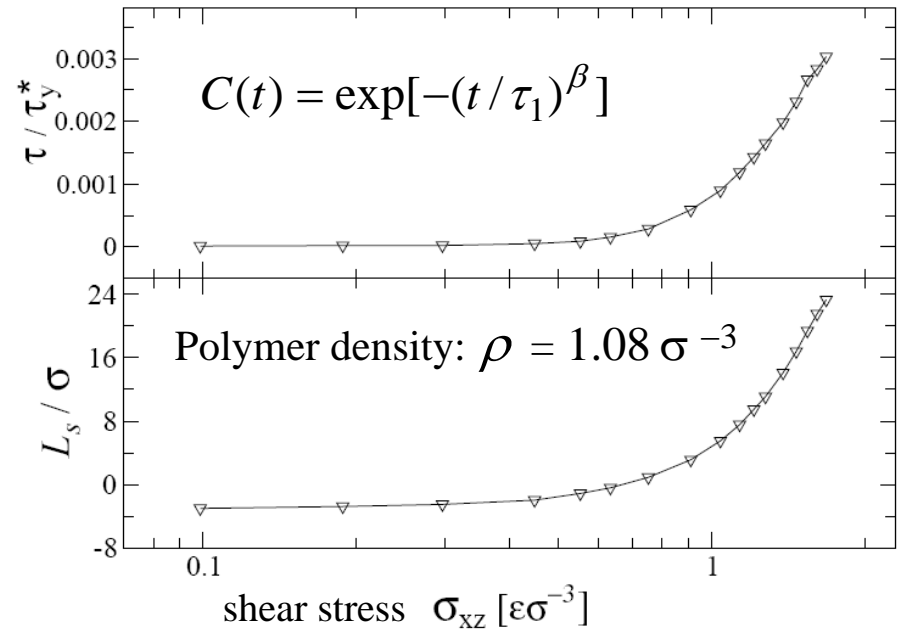
Rate-dependent slip length L_s correlates well with the relaxation time of polymer chains in the viscous interfacial layer.

Important conclusions

- Molecular dynamics simulations show that the slip length L_s in dense polymer films is negative at low shear rates (due to the viscous interfacial layer) and L_s increases rapidly at higher shear rates (when the viscosity of the layer is reduced).

- Friction coefficient at the melt/solid interface k undergoes a transition from a nearly constant value to the power law decay as a function of the slip velocity. [†]

$$k = [1 + (4V_1)^2]^{-0.35}$$

- At *large slip velocities* the friction coefficient k is determined by the product of the value of surface-induced peak in the structure factor $S(\mathbf{G}_1)$ and the contact density of the first fluid layer near the solid wall.

$$k = k \, [S(0)/S(\mathbf{G}_1)\rho_c]$$

- Rate-dependent slip length L_s correlates well with the relaxation time of the polymer chains in the viscous interfacial layer.

N. V. Priezjev, "Shear rate threshold for the boundary slip in dense polymer films", *Phys. Rev. E* **80**, 031608 (2009). Featured in V.J. Nano. Sci. Tech. and V.J. Bio. Phys. Res. (2009).

[†] A. Niavarani and N.V. Priezjev, "Slip boundary conditions for shear flow of polymer melts past atomically flat surfaces", *Phys. Rev. E* **77**, 041606 (2008).

Experimental measurements of slip length

Reference	Slip length	Method	Liquid	Surface	Size	Shear rate	Roughness
Schnell (1956)	1 – 10 μm	Flow rate	Water	Glass + DDS	<800μm	$10^{2\sim3}$ sec^{-1}	——
Churaev, Sobolev Somov (1984)	30 –70 nm	Flow rate– press. drop	Water and mercury	Quartz	< 7.2μm	$10^{1\sim4}$ sec^{-1}	——
Watanabe, Uda- gawa (1999)	~ 100 μm	Flow rate– press. drop	Water, Glycerin	Acrylic resin, hydrophobic	6-12mm	——	——
Migler, Hervet & Leger (1993)	0.1–300μm	EWIF	PDMS	Quartz + OTS	——	0.1 –1 sec^{-1}	2 – 3 Å
Horn, Vinograd ova *et al.* (00)	30 – 50 nm	SFA + drainage	Boger fluid	Mica	50-900nm	——	——
Zhu & Granick PRL (2001)	0 – 2 μm	SFA + drainage	Tetradecane and water	Mica + OTE	~100 nm	$10^{1\sim5}$ sec^{-1}	~ 1 Å
Zhu & Granick PRL (2002)	0 – 40 nm	SFA + drainage	Tetradecane and water	Mica + OTE	~100 nm	$10^{1\sim5}$ sec^{-1}	0.2 – 6 nm
Tretheway and Meinhart (2002)	~ 1 μm	μ–PIV	Water	Glass + OTS hydrophobic	30μm	10^{2} sec^{-1}	2 – 3 Å
Choi, Westen & Breuer (2003)	~ 30 nm	Flow rate– press. drop	Water	Glass + OTS hydrophobic	21μm	10^{5} sec^{-1}	2 – 3 Å
Charlaix group PRL (2005)	~ 20 nm	SFA + drainage	Dodecane and water	Glass + OTS hydrophobic	<200 nm	$< 5\cdot10^{3}$ sec^{-1}	~ 1 nm