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

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

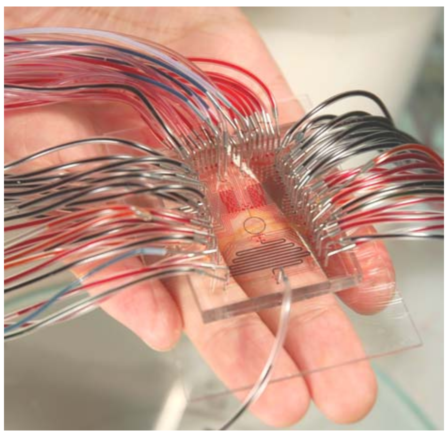
Acknowledgement:
NSF, ACS, MSU

N. V. Priezjev, “Fluid structure and boundary slippage in nanoscale liquid films”, Chapter 16 “Detection of Pathogens in Water Using Micro and Nano-Technology”, IWA Publishing (2012).

Motivation: Nano- and Microfluidics

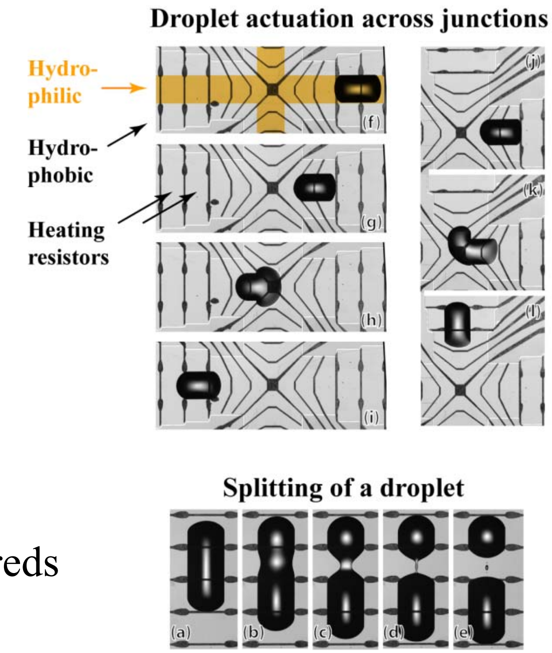
- Control and manipulation of fluids at submicron scales
- The behavior of fluids at the microscale is different from 'macrofluidic' behavior (low Re, high S/V ratio)
- Lab-on-a-chip devices allow automation of complex biological and chemical reactions (wikipedia)

“Microflows & Nanoflows” Karniadakis (2005)

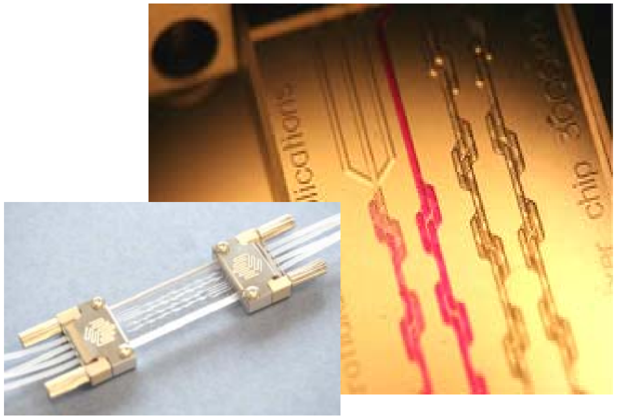


Microchip system performs hundreds of parallel chemical reactions

Lab. Chip. **9**, 2281-2285 (2009)



Appl. Phys. Lett. 82, 657 (2003)



A micromixer for rapid mixing of two or three fluid streams

The Dolomite Center Ltd.

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?

  Thompson and Troian, *Nature* **389**, 360 (1997)

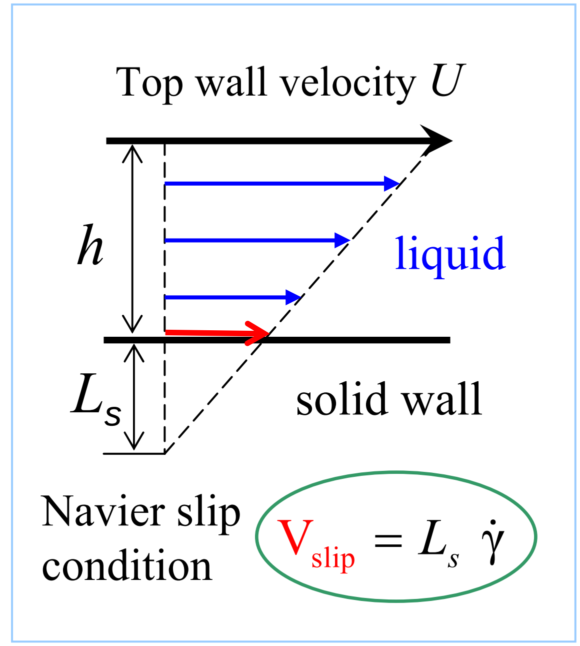
- Combined effect of surface roughness, wettability and rate-dependency on the slip length L_S: e.g., surface roughness reduces the degree of slip but shear rate might increase L_S

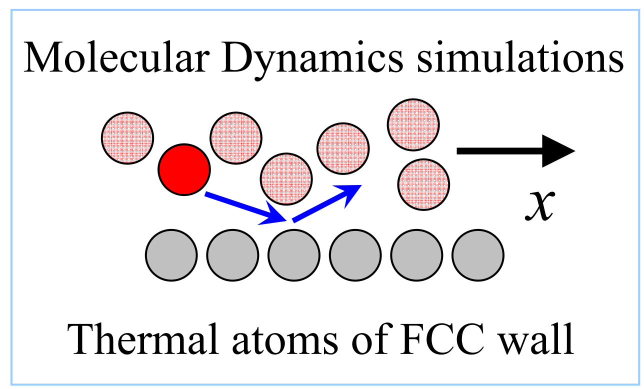
  Niavarani and Priezjev, *Phys. Rev. E* **81**, 011606 (2010)

- 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?

  Thompson and Robbins, *Phys. Rev. A* **41**, 6830 (1990)
  Barrat and Bocquet, *Faraday Disc.* **112**, 109 (1999)
  Priezjev, *Phys. Rev. E* **82**, 051603 (2010), *MFNF* (2013)

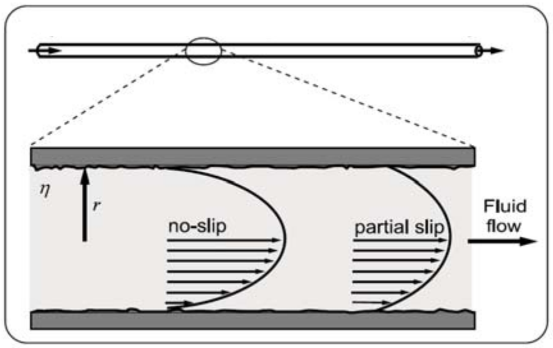




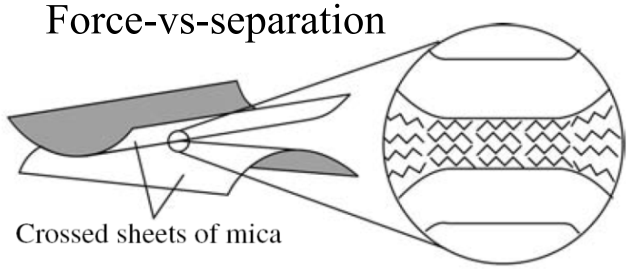
Experimental measurements of the slip length L_s

- Typically slip length of water over hydrophobic surfaces is about 10 – 50 nm
- Possible presence of nanobubbles at hydrophobic surfaces: $L_s \sim 10$ μm

Flow rate versus pressure

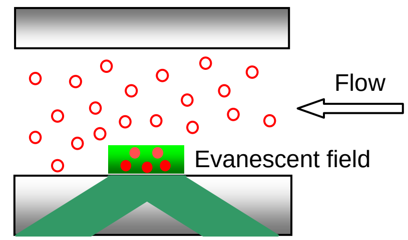


Surface Force Apparatus



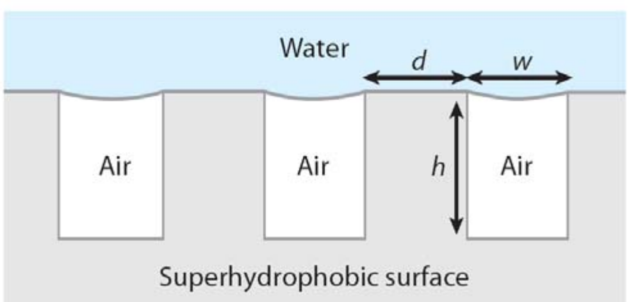
SFA: J. Israelachvili (UCSB)

Particle Image Velocimetry (PIV)



Quantum Dots: M. Koochesfahani

- 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 ($L_s \sim 100$ μm)

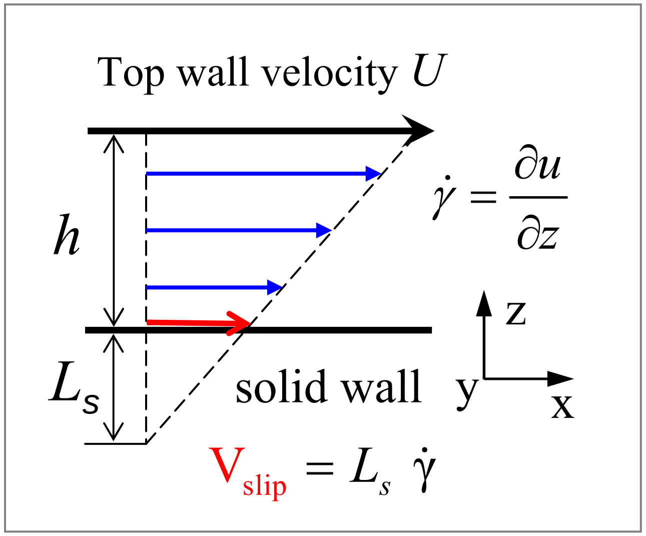


Rothstein, Review on slip flows over Superhydrophobic surfaces (2010).

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



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

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

f_i = Gaussian random force

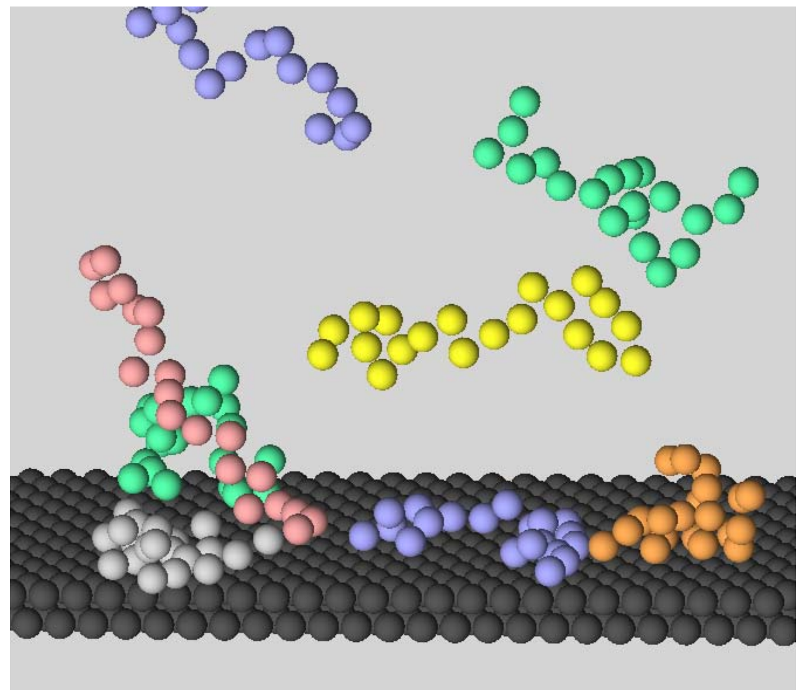
Langevin thermostat: $T = 1.1\varepsilon/k_B$

Thompson and Robbins, *Phys. Rev. A* **41**, 6830 (1990)

FENE bead-spring model: $V_{FENE}(r) = \frac{1}{2} k r_o^2 \ln\left(1 - \frac{r^2}{r_o^2}\right)$

$k = 30\varepsilon\sigma^{-2}$ and $r_o = 1.5\sigma$

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

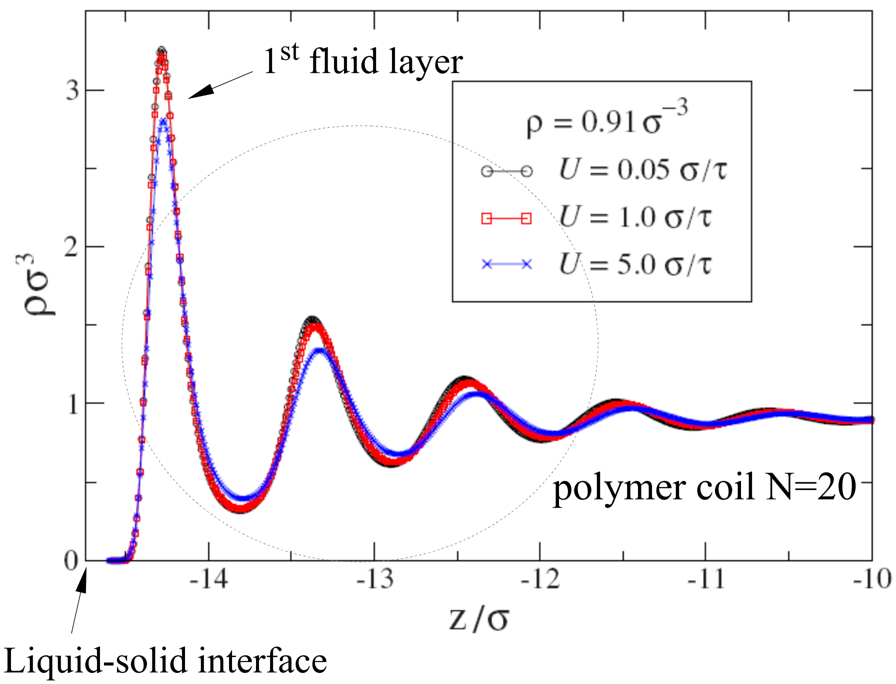


Thermal FCC walls with density $\rho_w = 1.40\ \sigma^{-3}$

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

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

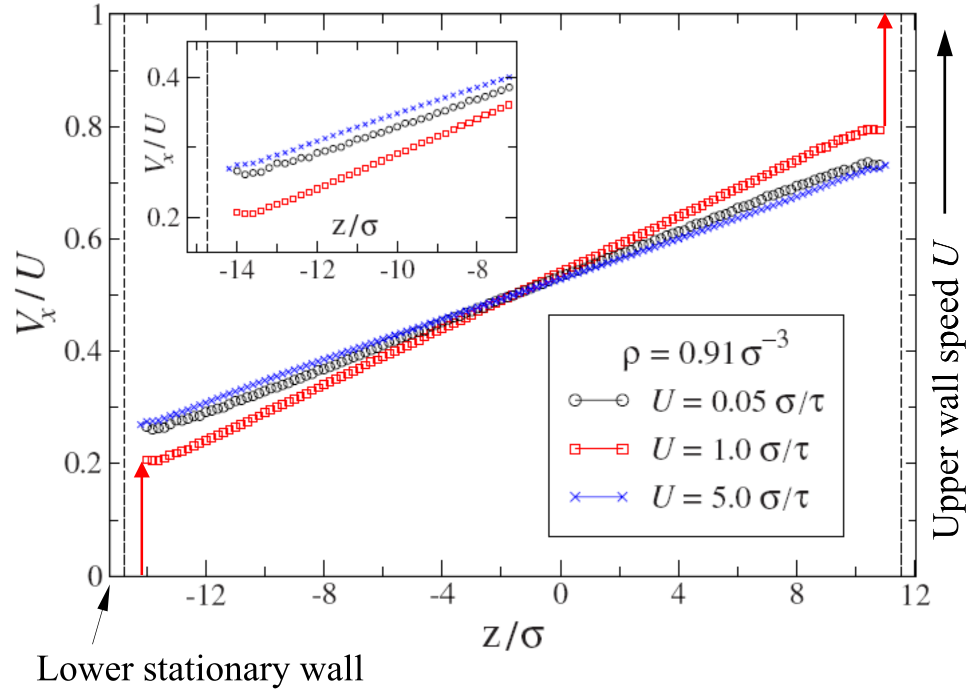
Density profiles near the lower wall:



ρ_c = contact density (max first fluid peak)

The amplitude of density oscillations ρ_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 !?

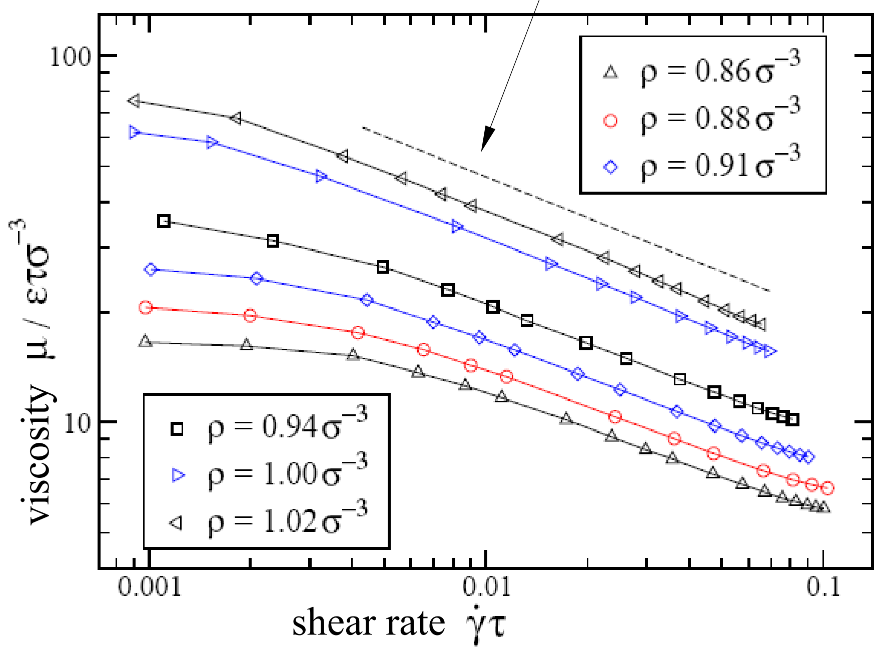
Shear rate $\dot{\gamma}$ = slope of the velocity profiles

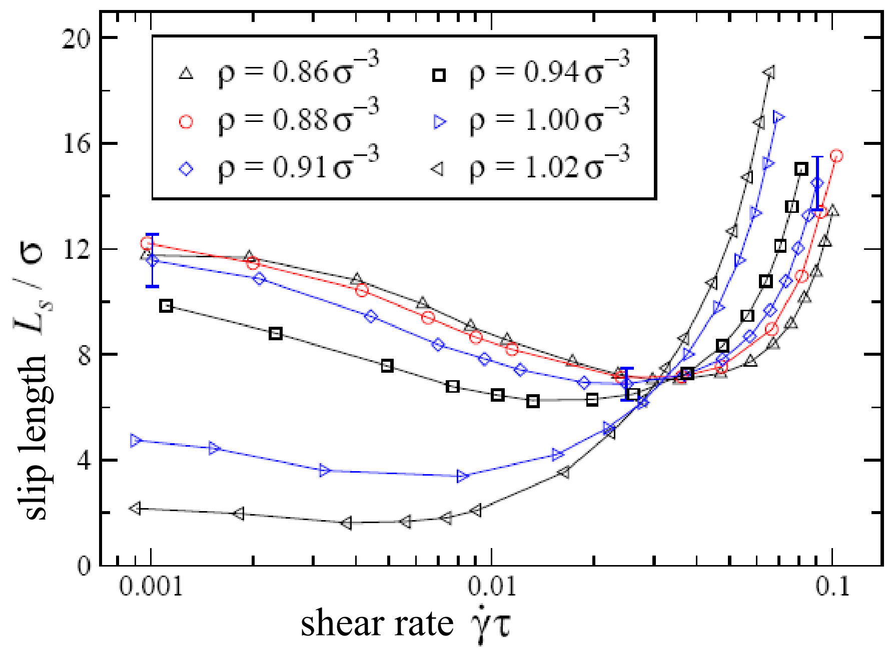
Niavarani and Priezjev, *Phys. Rev. E* **77**, 041606 (2008)

Shear rate dependence of the slip length L_s and polymer viscosity μ

Shear-thinning μ with the slope –0.37

N = 20 polymer chains;
ρ = polymer melt 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 L_s passes through a minimum as a function of shear rate and then increases rapidly at higher shear rates

Niavarani and Priezjev, *Phys. Rev. E* **77**, 041606 (2008)

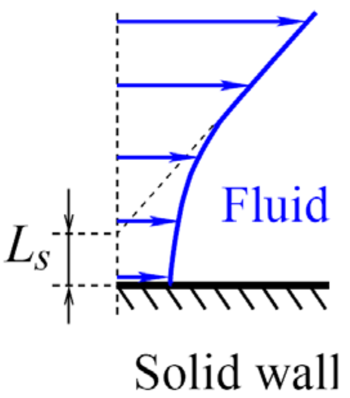
A relation between the slip length L_s and friction coefficient at the interface

Shear stress in steady flow:

In the bulk fluid $\sigma_{xz} = \mu\,\dot{\gamma}$

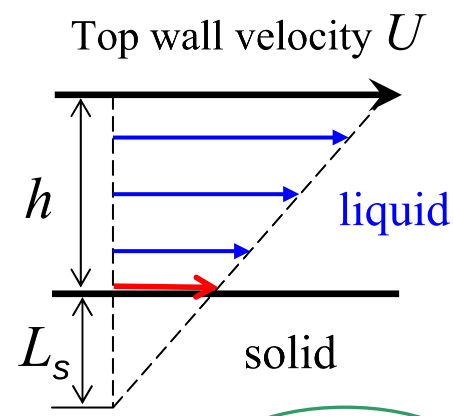
At the interface $\sigma_{xz} = k\,V_{slip}$

Friction coefficient:
$k = \mu / L_s$



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

Shear rate threshold: Priezjev, *Phys. Rev. E* **80**, 031608 (2009).



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

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

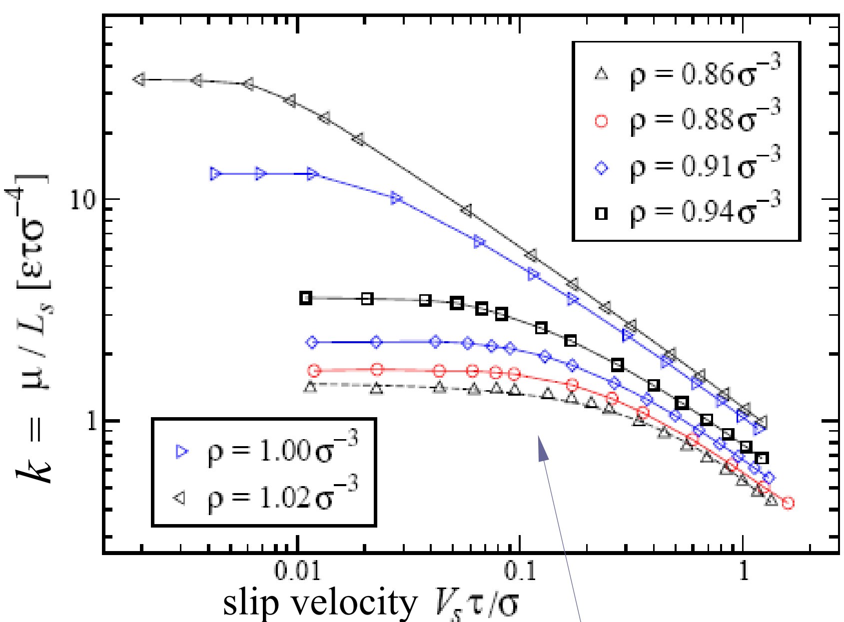
$$\boxed{L_s(\dot{\gamma}) = L_s^o\,(1 - \dot{\gamma}/\dot{\gamma}_c)^{-0.5}} \quad \Longrightarrow \quad k(V_s) = C_1\left(\sqrt{C_2 + V_s^2} - V_s\right)$$

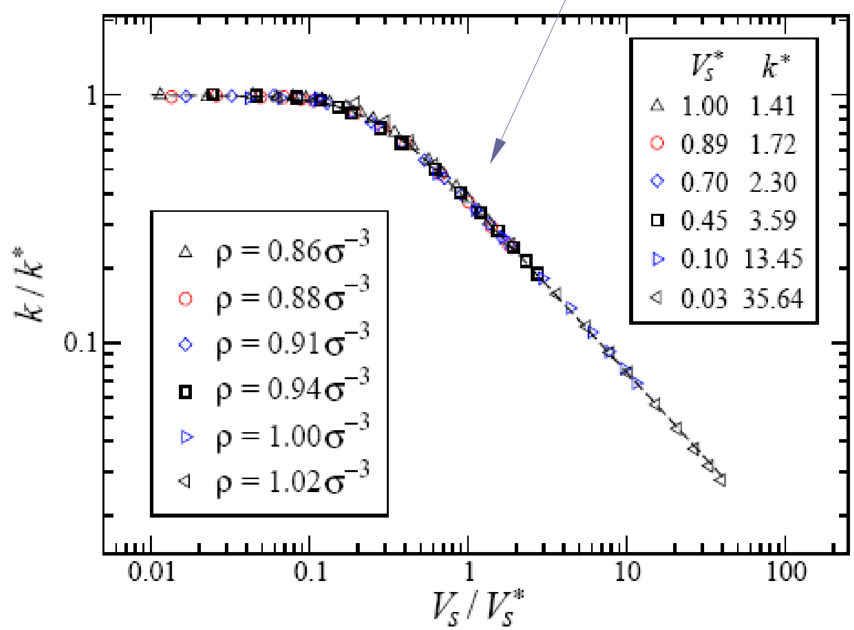
Viscosity μ is rate-independent for simple fluids (N=1) where $C_1 = \mu / 2\dot{\gamma}_c (L_s^o)^2,\ C_2 = (2L_s^o\dot{\gamma}_c)^2$

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

Friction coefficient: $k = \mu / L_s$

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





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

Thompson and Troian (1997)
Friction coeff. for simple fluids

ρ = polymer melt density

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

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

Niavarani and Priezjev, *Phys. Rev. E* **77**, 041606 (2008)

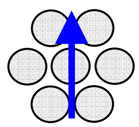
Friction coefficient at the liquid-solid interface as a function of slip velocity

Friction coefficient:
$k = \mu / L_s$

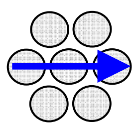
20 liquid-solid systems

Dashed curve = best fit: $k/k^* = [1 + (V_s / V_s^*)^2]^{-0.35}$

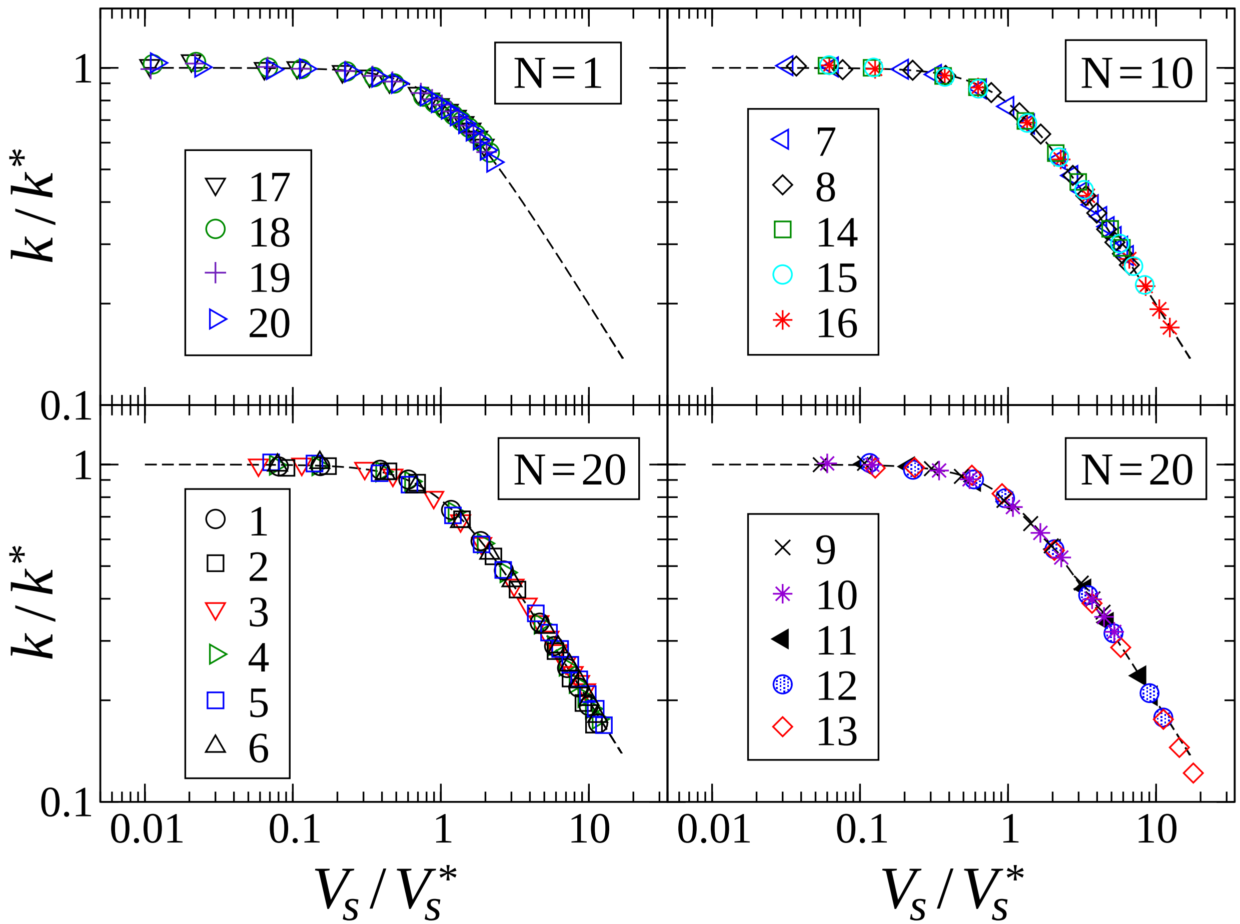
Odd #'s



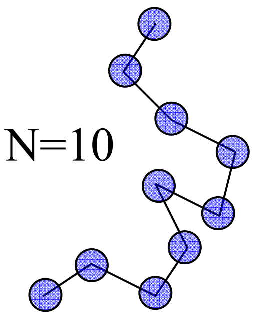
Even #'s



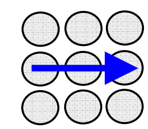
(111) FCC lattice plane



N=10



#'s: 11-16



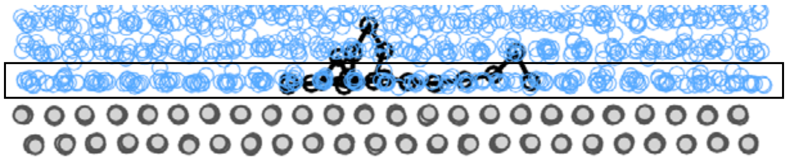
(001) BCC lattice plane

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.

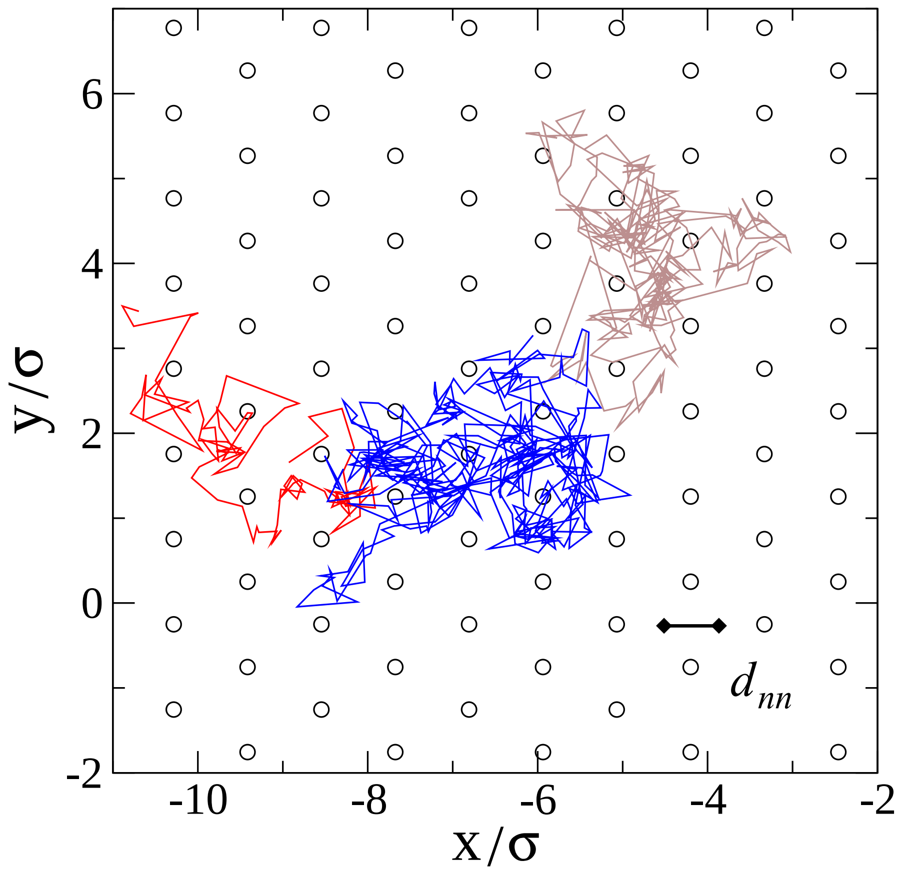
N.V. Priezjev, *Phys. Rev. E* **82**, 051603 (2010)

Diffusion of fluid monomers in the first fluid layer at equilibrium (i.e. U=0)

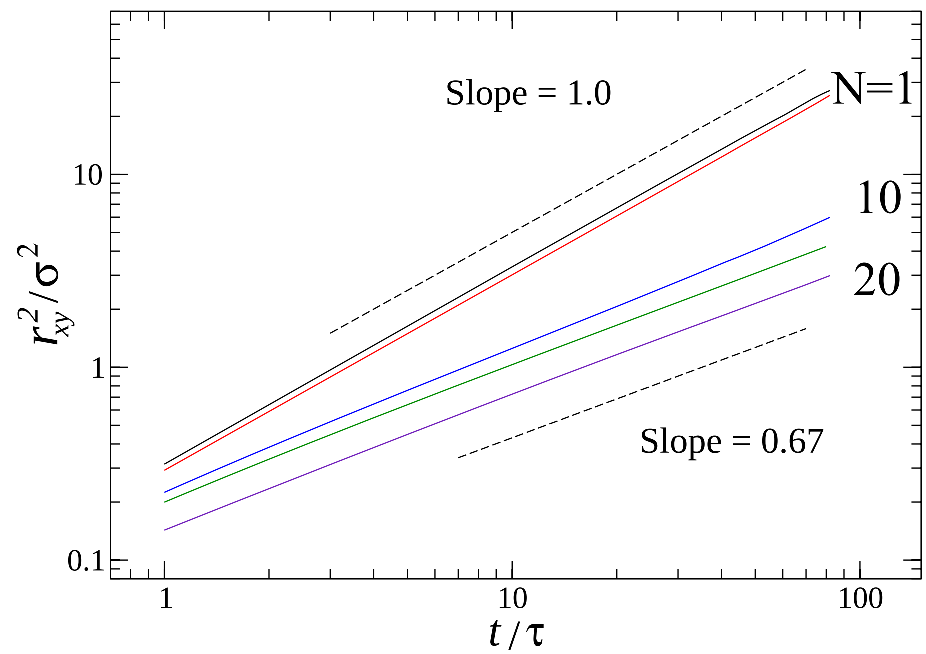
Side view: polymer melt near solid wall



Top view: (111) plane of FCC wall lattice



Mean square displacement in the first layer

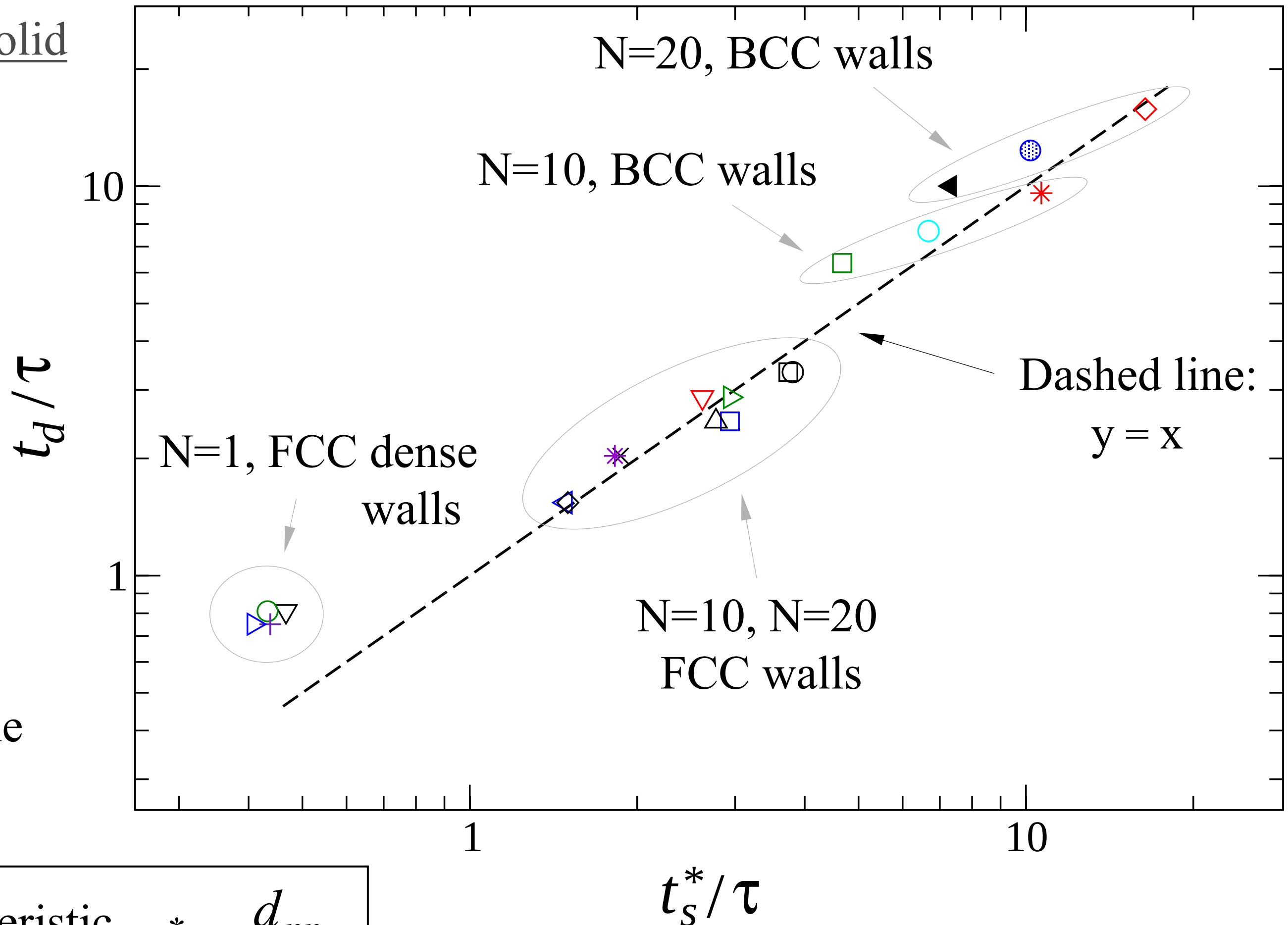


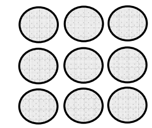
The diffusion time t_d was estimated from the mean square displacement of fluid monomers in the first layer at the distance between nearest minima of the periodic surface potential d_{nn} .

N.V. Priezjev, *Phys. Rev. E* **82**, 051603 (2010)

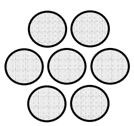
A correlation between the diffusion time t_d and the characteristic slip time t_s^*

20 liquid-solid systems





(001) BCC lattice plane



(111) FCC lattice plane

Characteristic slip time: $t_s^* = \dfrac{d_{nn}}{V_s^*}$

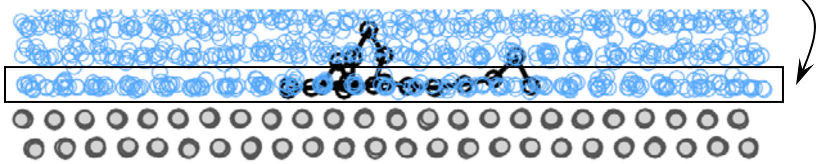
$$k / k^* = [1 + (V_s / V_s^*)^2]^{-0.35}$$

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.

N.V. Priezjev, *Phys. Rev. E* **82**, 051603 (2010)

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

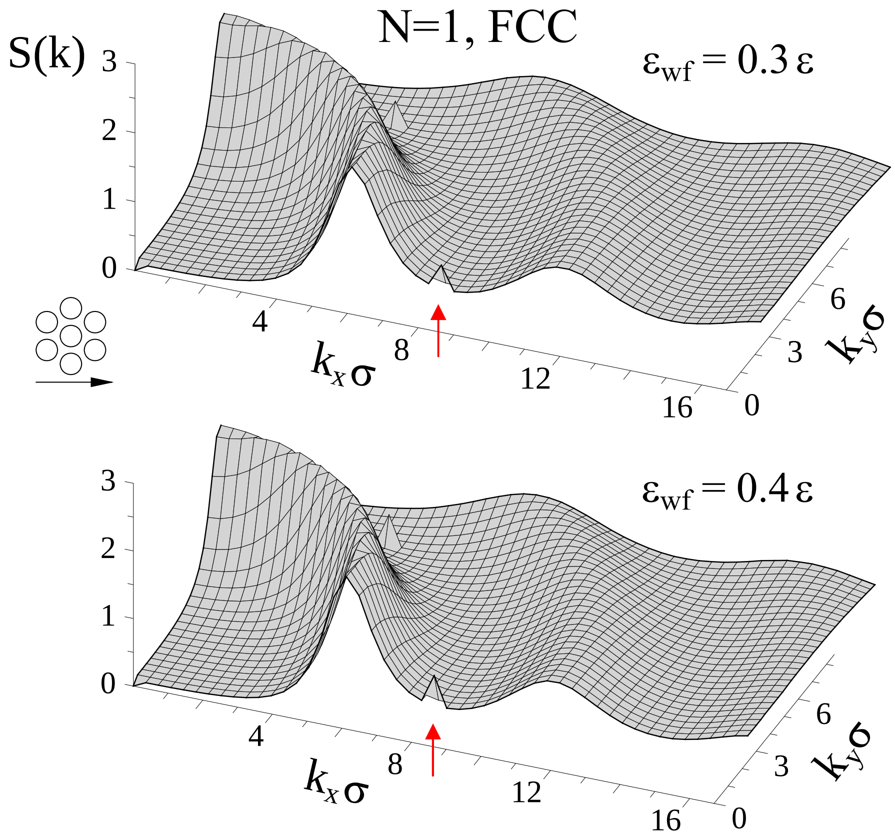
Structure factor in the first fluid layer:

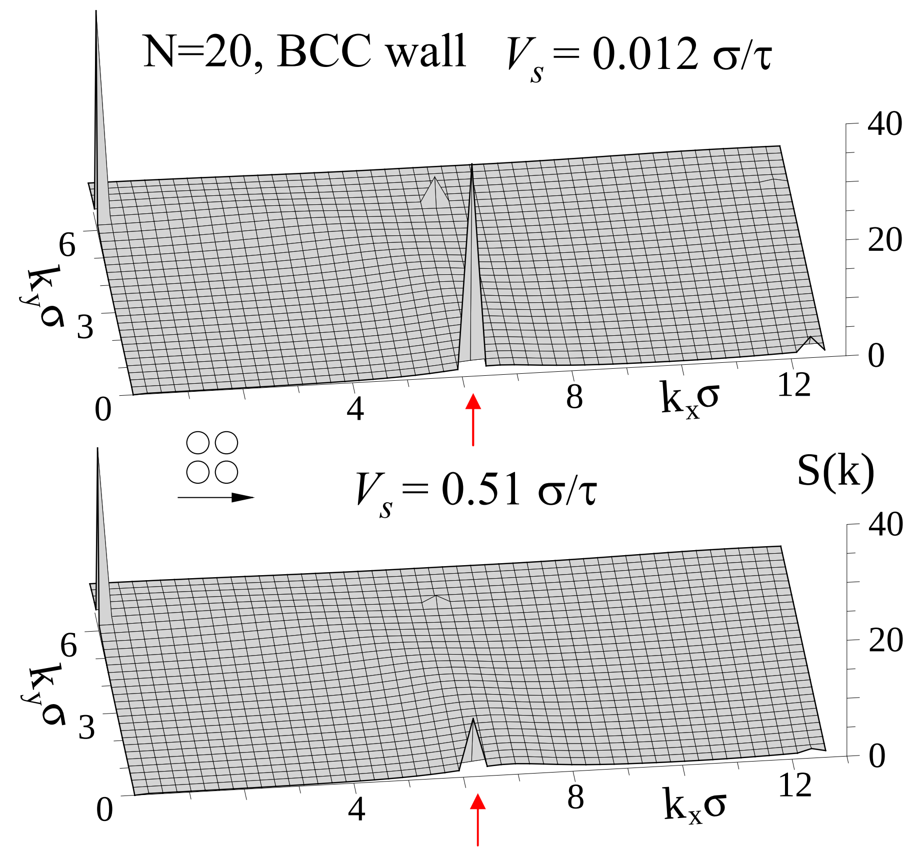


$$S(\mathbf{k}) = \frac{1}{N_l}\left|\sum e^{i\,\mathbf{k}\cdot\mathbf{r}_j}\right|^2$$

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 ε_{wf}.

N.V. Priezjev, *Phys. Rev. E* **82**, 051603 (2010)





Review of current slip models

Bocquet & Barrat (1999) Kubo relation

Faraday Disc. **112**, 109 (1999)

$$\frac{1}{k} = \frac{L_s^o}{\mu} \propto \frac{D_{q_\parallel}}{S(q_\parallel)\rho_c \varepsilon_{wf}^2}$$

simple fluids (N=1)

$S(q_\parallel)$ = in-plane structure factor

$D_{q_\parallel}$ = in-plane diffusion coefficient

$q_\parallel$ = reciprocal lattice vector in the shear flow direction

ρ_c = contact density

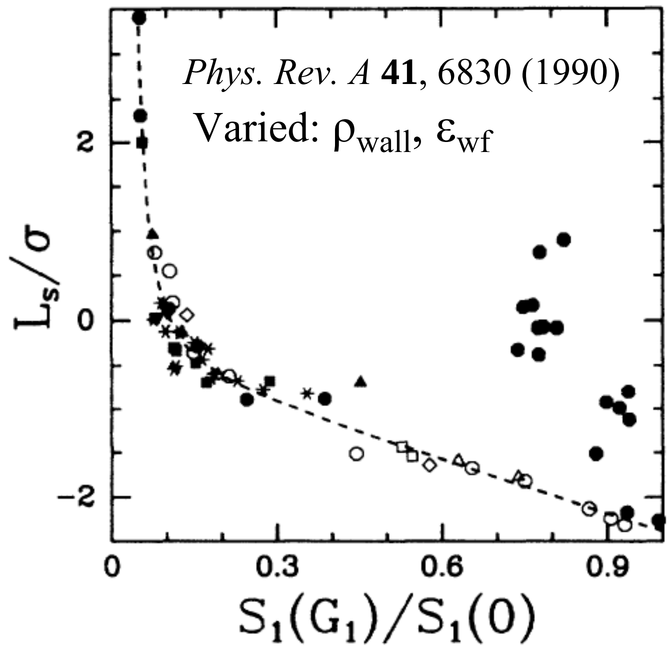
All parameters evaluated in first fluid layer from equilibrium simulations = low shear rates

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

Phys. Rev. Lett. **92**, 018302 (2004)

For chain length $N > 10$ $\quad L_s^o(N) \propto \mu(N)$

Thompson & Robbins (1990) simple fluids (N=1)



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

Smith *et al.* (1996) Friction on monolayers

$$\text{Slip time } \tau = \frac{S_1(0)}{S_1(\mathbf{G}_1)} t_{ph}$$

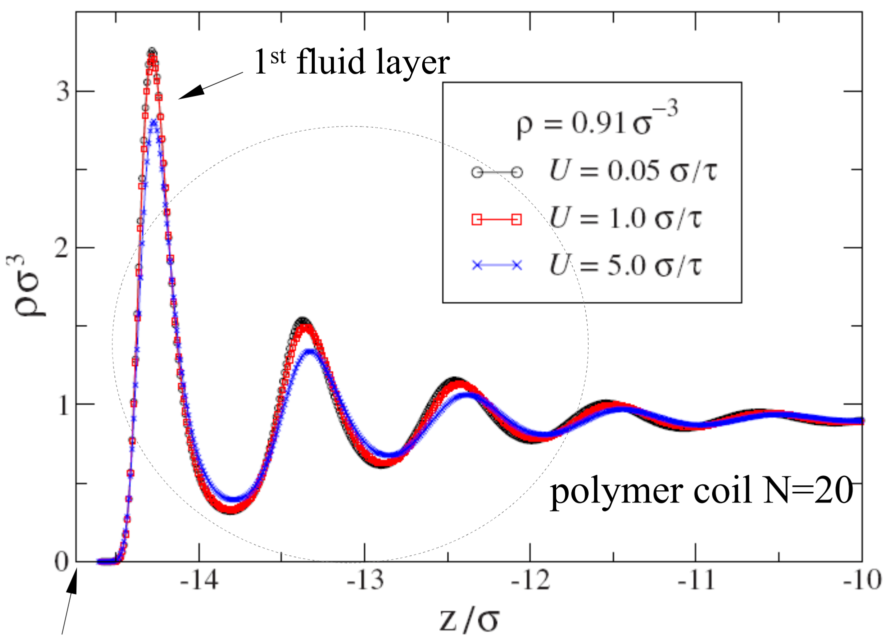
phonon lifetime

in-plane structure factor

Smith, Robbins & Cieplak, *Phys. Rev. E* **54**, 8252 (1996)

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

Density profiles near the lower wall:



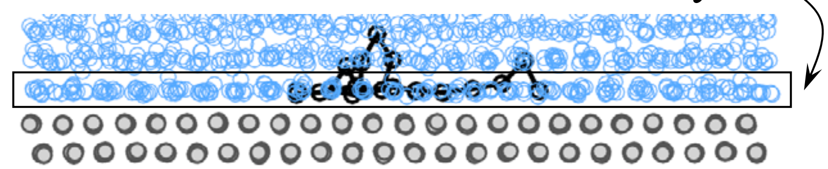
Liquid-solid interface

ρ_c = <u>contact density (max first fluid peak)</u>

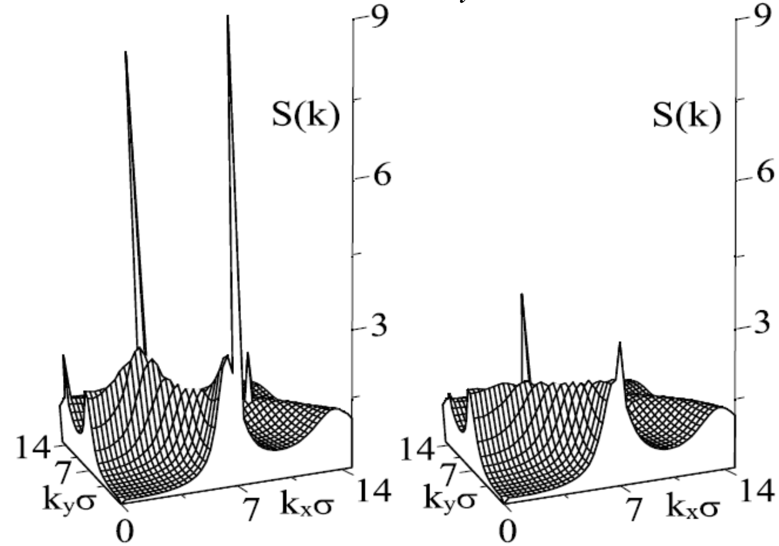
The amplitude of density oscillations ρ_c is reduced at higher values of the top wall speed U (by about 10%)

Niavarani and Priezjev, *Phys. Rev. E* **77**, 041606 (2008)

Structure factor in the first fluid layer:



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

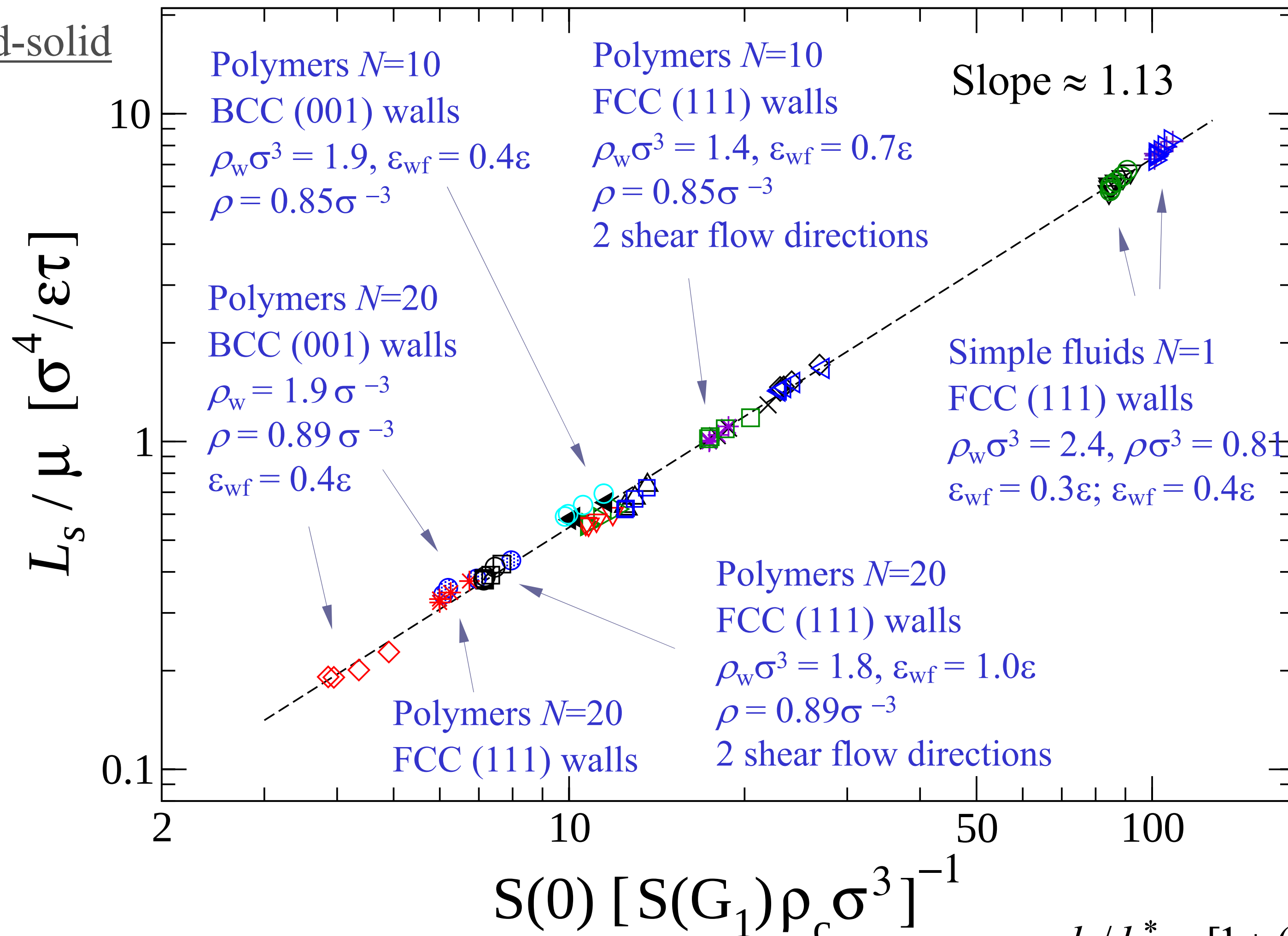


$V_s = 0.012\,\sigma/\tau$ $\qquad$ $V_s = 0.95\,\sigma/\tau$

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

20 liquid-solid systems



Friction coefficient:

$k = \mu / L_s$

$V_s < V_s^*$

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

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.

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.

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

- For *linear velocity profiles,* the friction coefficient k is determined by the product of the surface-induced peak in the structure factor $\mathrm{S}(\mathbf{G}_1)$ and the contact density ρ_c in the first fluid layer near the solid wall.

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

- 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.

Acknowledgement:
NSF, ACS, MSU