Effect of chain stiffness on interfacial slip in nanoscale polymer films: A molecular dynamics simulation study

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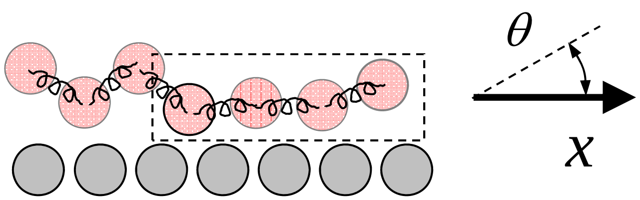

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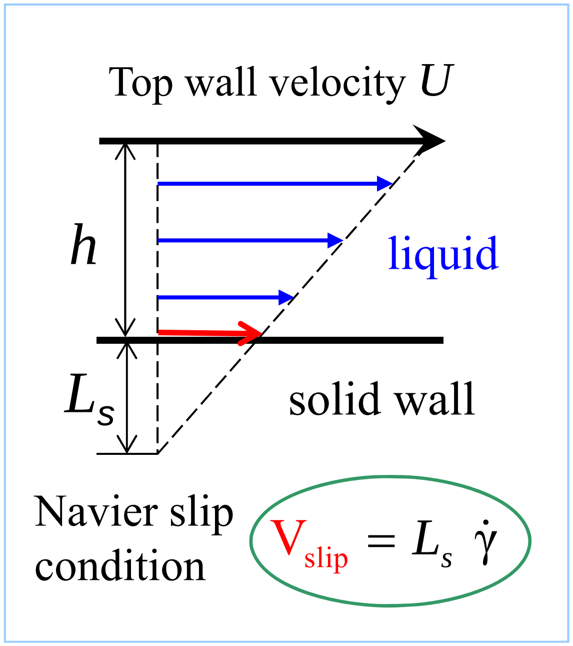
N. V. Priezjev, "Interfacial friction between semiflexible polymers and crystalline surfaces", *J. Chem. Phys.* **136,** 224702 (2012).

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

Motivation for investigation of slip phenomena at liquid/solid interfaces

- Navier model: slip velocity is proportional to shear rate via the slip length. Very important in micro- and nanofluidics and tribology. Slip length L_s as a function of shear rate:

  Thompson and Troian, *Nature* (1997). $L_s(\dot{\gamma}) = L_s^o\,(1-\dot{\gamma}/\dot{\gamma}_c)^{-0.5}$
  Priezjev, *Phys. Rev. E* (2007) Linear & nonlinear dependence.

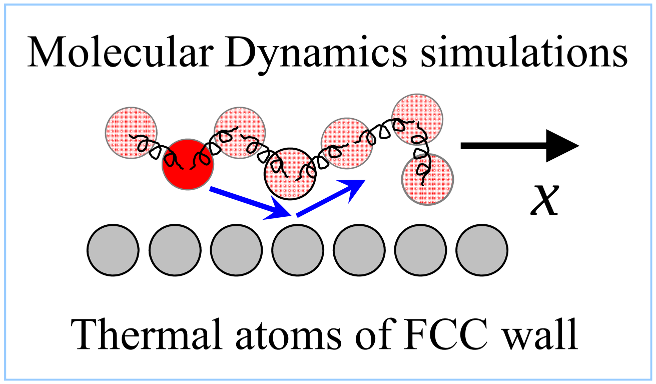


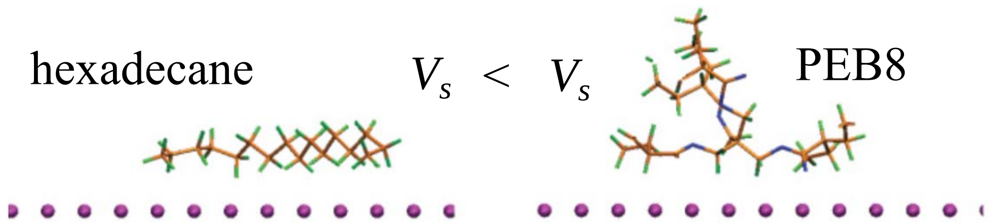
- Degree of slip depends on the structure of the first fluid layer in contact with the periodic surface potential.

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

- ***Polymer chain architecture***: slip velocity is reduced for liquids which consist of molecules that can easily conform their atoms into low-energy sites of the substrate potential.

  Vadakkepatt, Dong, Lichter, Martini, *Phys. Rev. E* (2011).

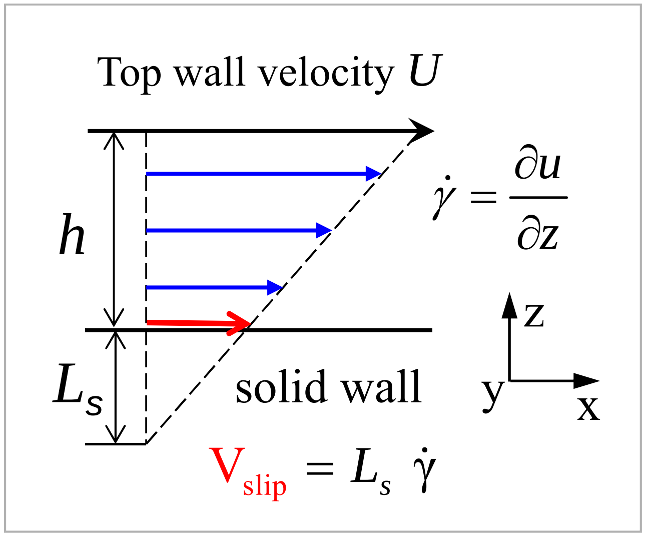




Molecular dynamics simulations: polymer melt with chains N=20 beads

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: $\rho = 0.91\ \sigma^{-3}$



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

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

f_i = Gaussian random force

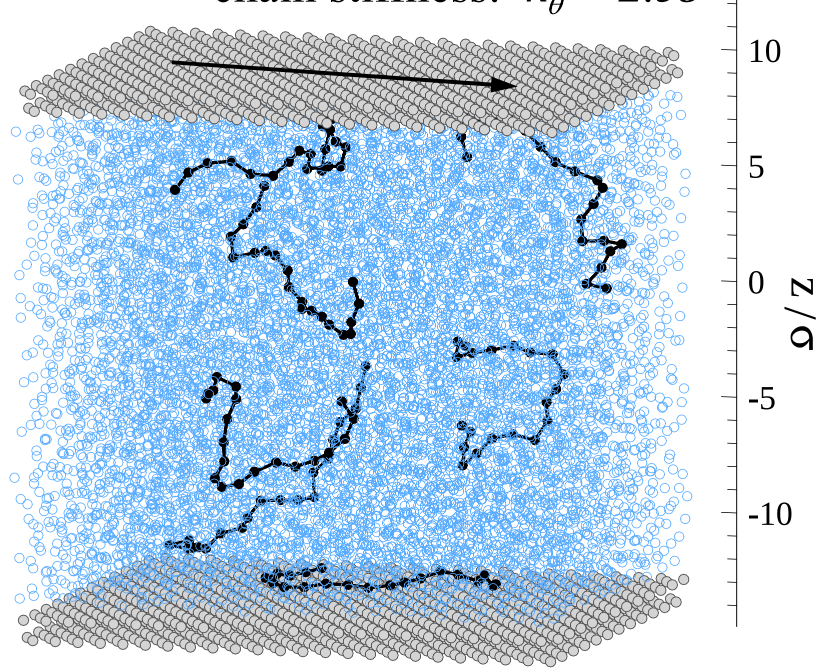
Langevin thermostat: $T = 1.1\varepsilon/k_B$

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

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

Bending potential: $V_{bend}(\theta) = k_\theta(1 - \cos\theta)$

chain stiffness: $k_\theta = 2.5\varepsilon$

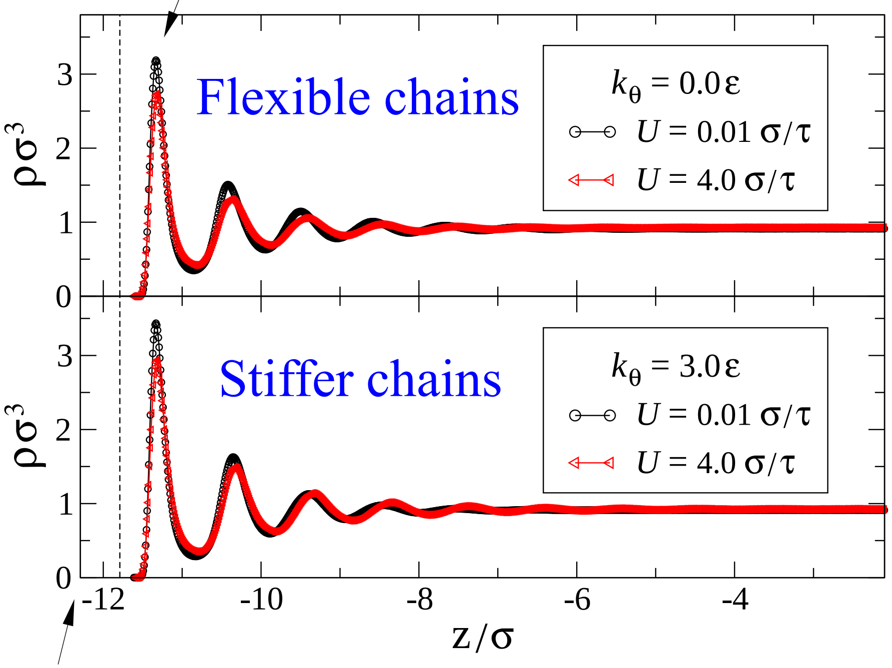


FCC walls with density $\rho_w = 1.40\ \sigma^{-3}$

Weak wall-fluid interactions: $\varepsilon_{wf} = 0.8\ \varepsilon$

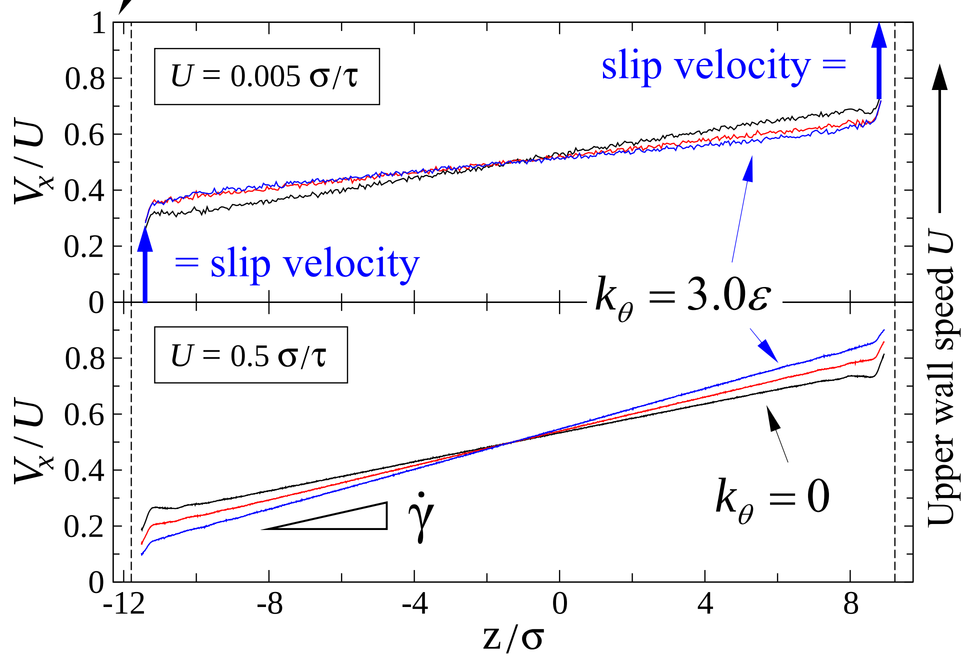
Density and velocity profiles for different chain stiffness coefficients k_θ

ρ_c = contact density decreases with U



Lower stationary wall

Lower stationary wall

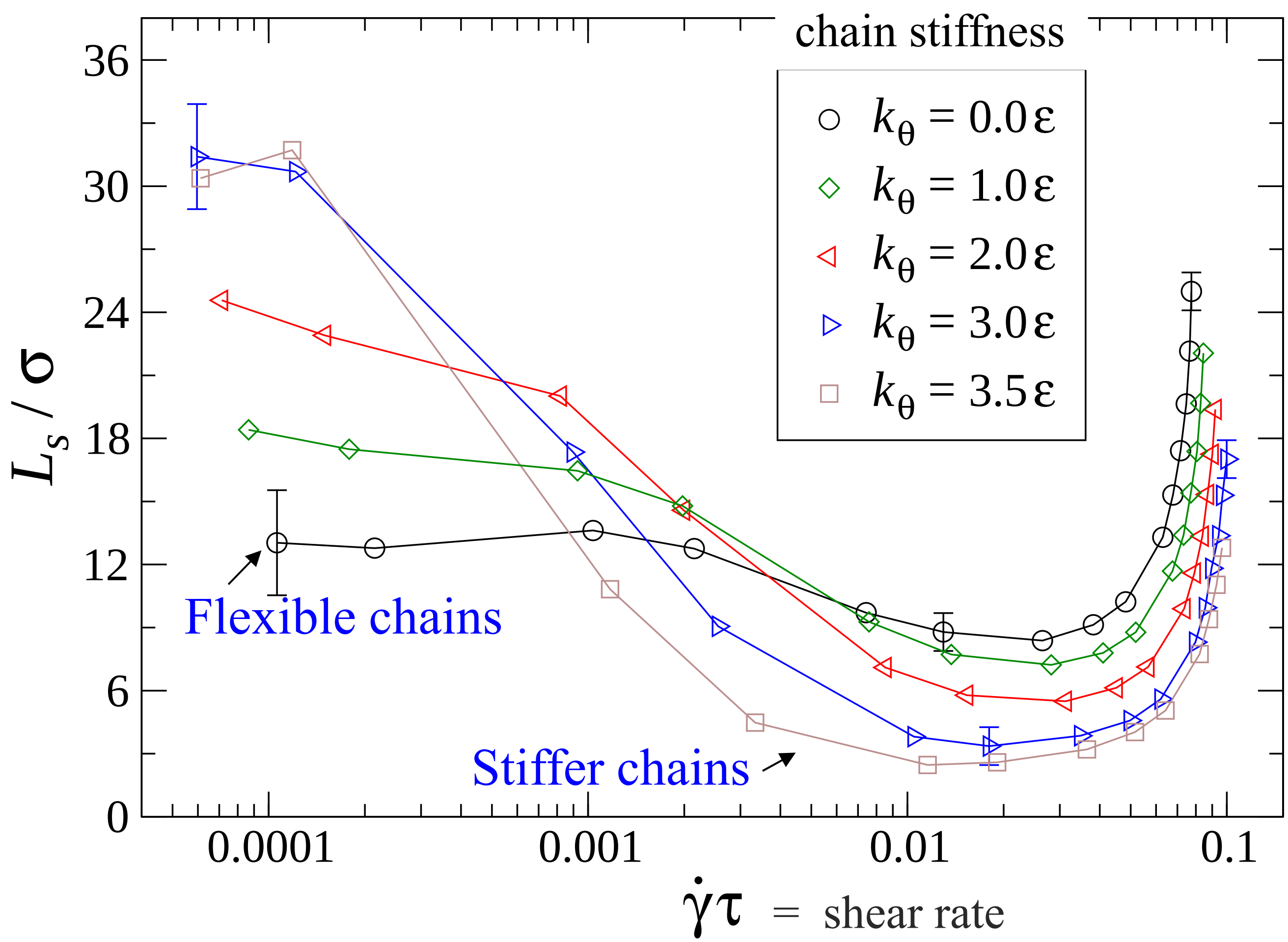


Shear rate $\dot{\gamma}$ = slope of the velocity profiles

- Layering near the walls is more pronounced for stiffer chains.
- Stiffer chains: residual order in shear flow due chain orientation.

- Surprisingly, slip velocity for stiff chains is larger (smaller) for lower (higher) upper wall speed U.

Dependence of the slip length L_s on the chain stiffness coefficient k_θ



- Local minimum in L_s is related to shear-thinning and friction.

$$L_s = \mu / k$$

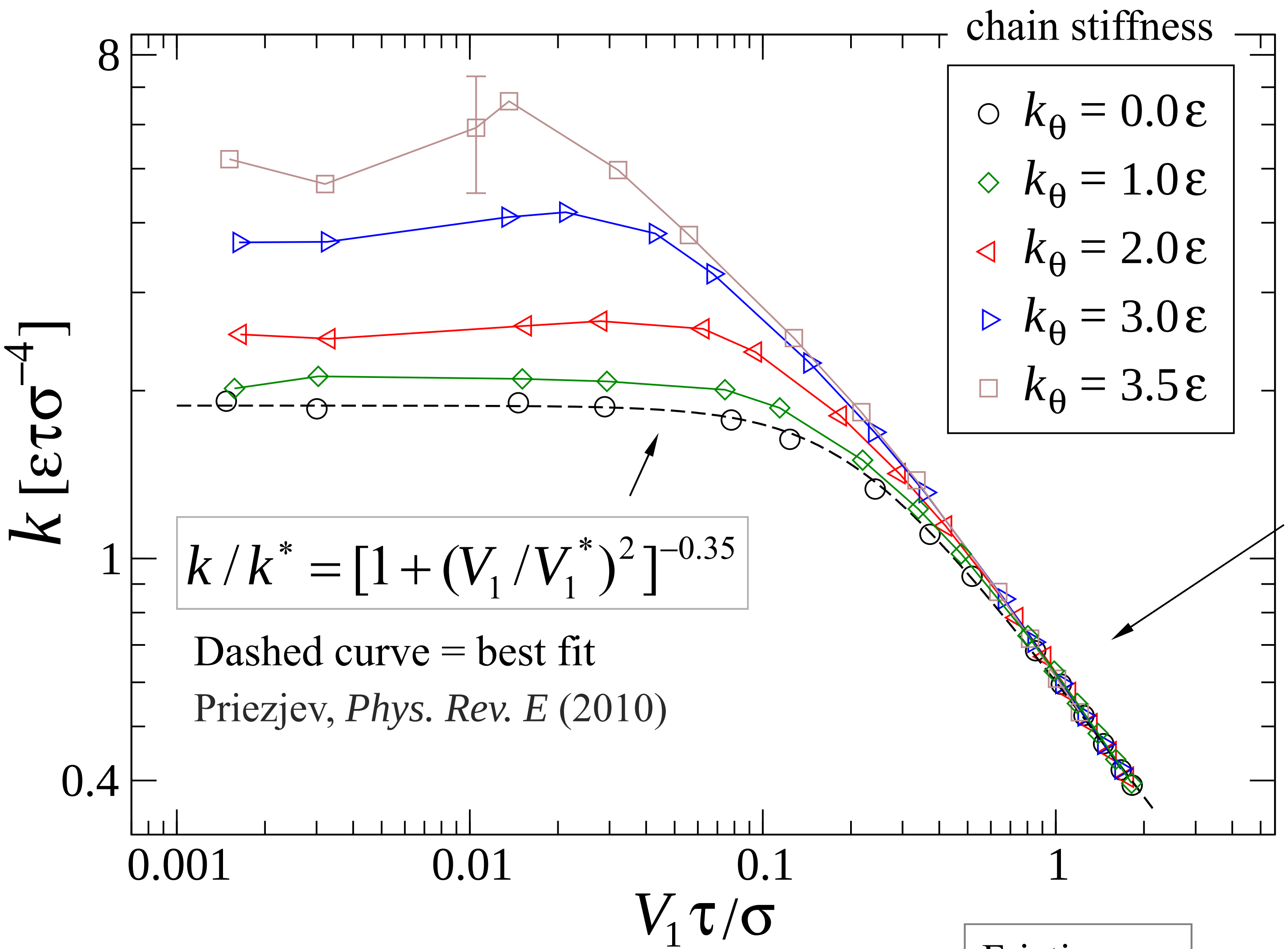
Priezjev, *Phys. Rev. E* (2010).

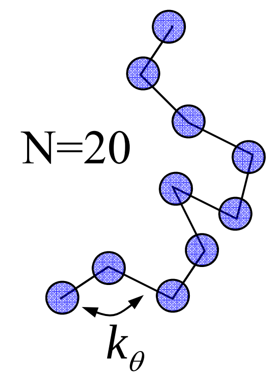
- Unexpectedly, increasing chain stiffness produces larger slip lengths at low shear rates but smaller L_s at high shear rates.

N.V. Priezjev, *J. Chem. Phys.* **136**, 224702 (2012).

Friction coefficient: $k = \mu / L_s$

Friction coefficient at polymer-solid interface k as a function of slip velocity V_1





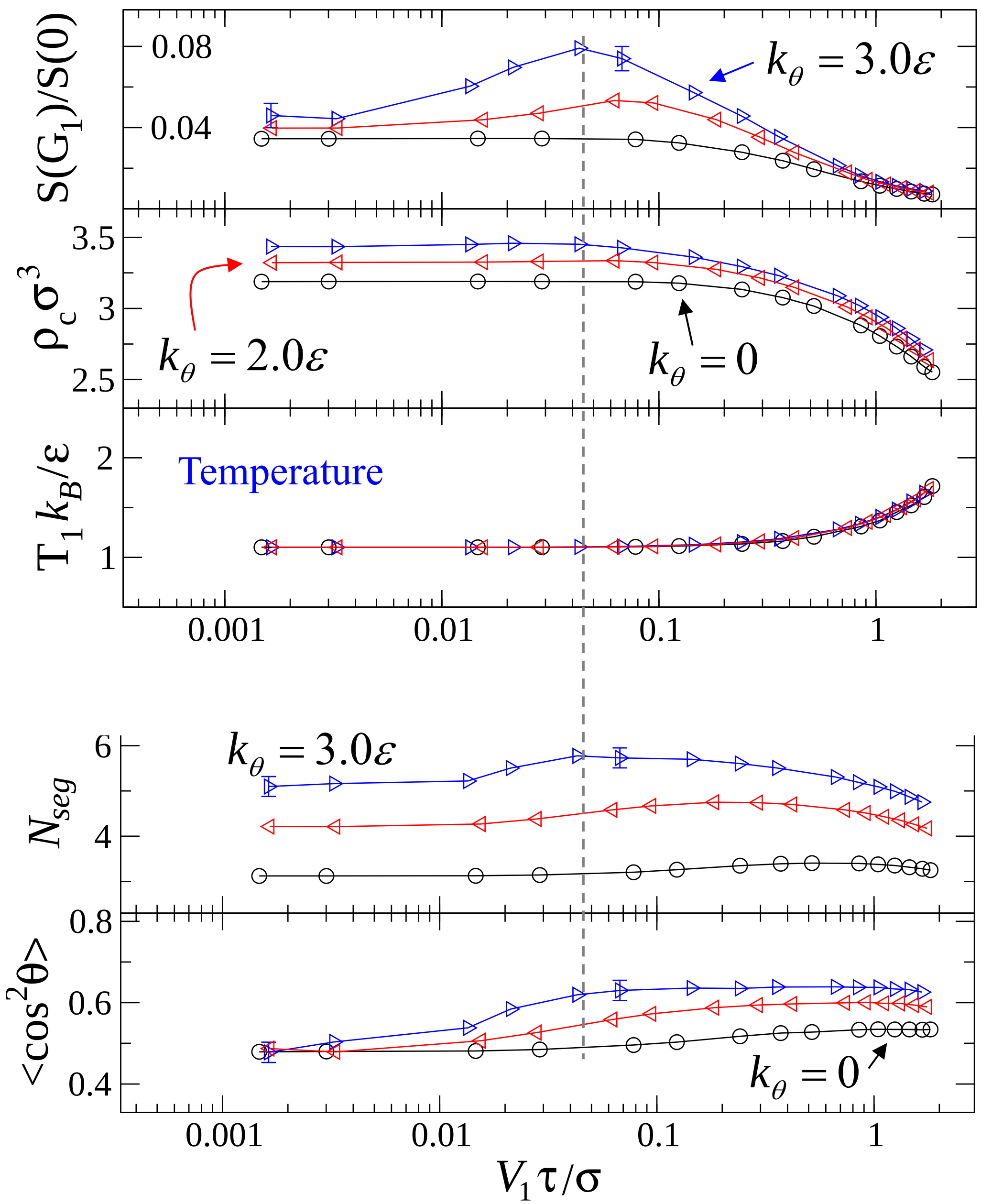
When $V_1 > V_1^*$ the friction coefficient is independent of the chain stiffness.

Local maximum in friction for stiffer chains: shear-induced alignment of chain segments.

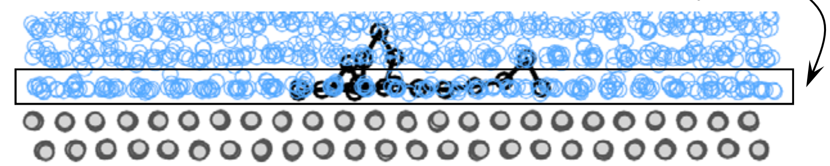
Friction coefficient: $k = \mu / L_s$

N.V. Priezjev, *J. Chem. Phys.* **136**, 224702 (2012).

Fluid structure in the first layer near the wall as a function of slip velocity V_1



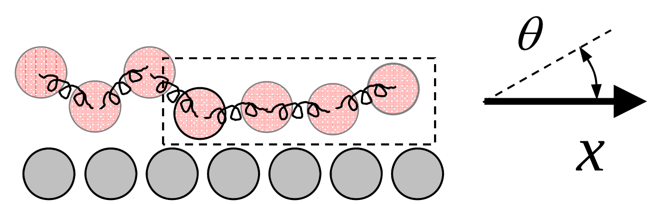
Structure factor in the first fluid layer:



$$S(\mathrm{G}_1) = \frac{1}{N_l}\left|\sum e^{i\,\mathrm{G}_1 \cdot \mathrm{r}_j}\right|^2$$

- Shear-induced alignment of semiflexible chain segments.

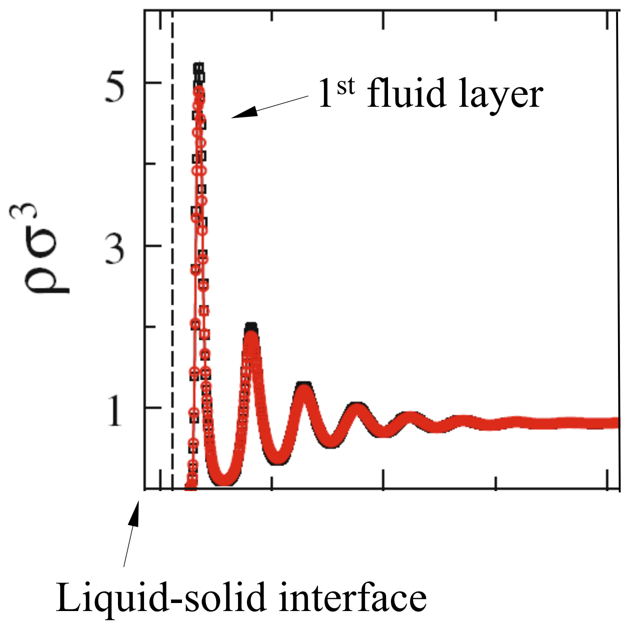
N_{seg} = average number of consecutive monomers per chain in the first layer



θ = average bond orientation

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

Fluid density profiles near the solid wall:

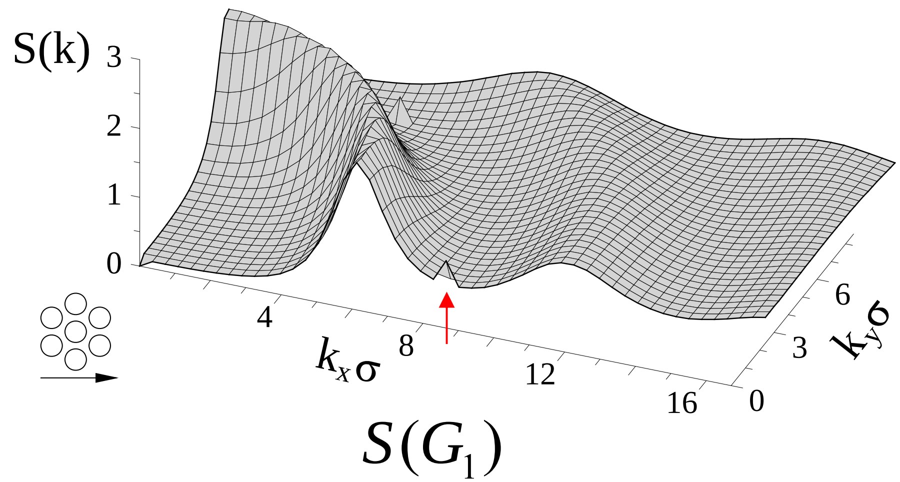


ρ_c = <u>contact density (max first fluid peak)</u>

The amplitude of density oscillations ρ_c is reduced at higher slip velocities V_s (by about 10%).

Structure factor in the first fluid layer:

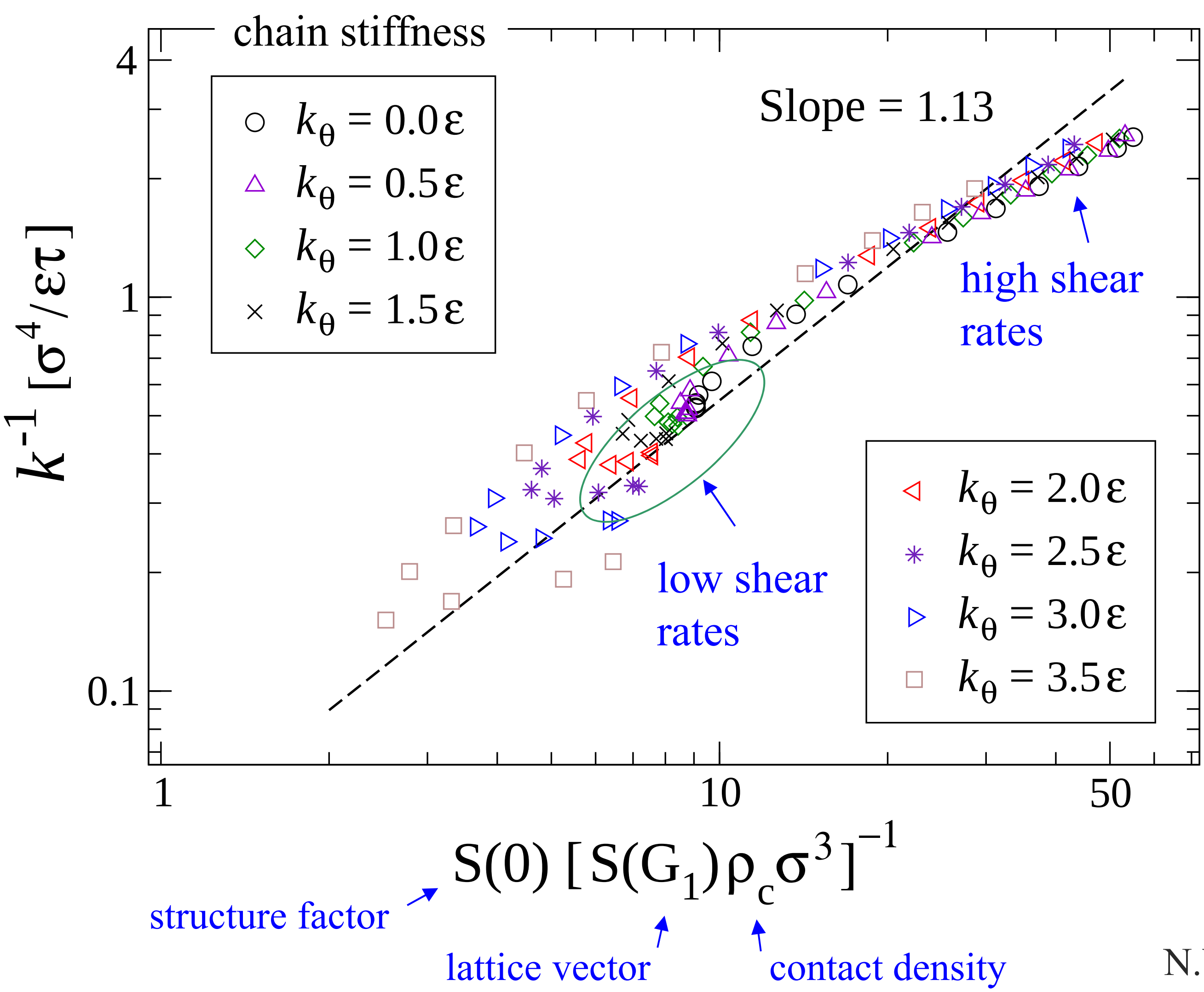
$$S(\mathbf{k}) = \frac{1}{N_l}\left|\sum e^{i\,\mathbf{k}\cdot\mathbf{r}_j}\right|^2$$



Sharp peaks in the structure factor (due to periodic surface potential) are reduced at higher slip velocities V_s

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

Correlation between *k* and fluid structure in the first layer near the solid wall



In-plane structure factor:

$$S(G_1) = \frac{1}{N_l}\left|\sum e^{i\,G\cdot r_j}\right|^2$$

Friction coefficient *k* at the polymer-solid interface correlates well with the structure of the first fluid layer near the solid wall.

Friction coefficient: $k = \mu / L_s$

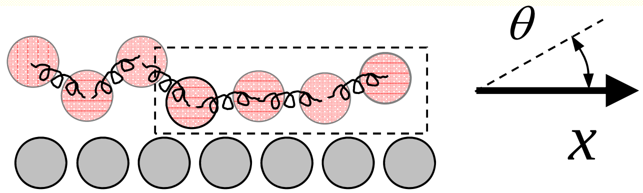
N.V. Priezjev, *J. Chem. Phys.* **136**, 224702 (2012).

Conclusions:

NSF (CBET-1033662)

- Nonlinear shear rate dependence of the slip length is determined by the ratio of the shear-rate-dependent polymer viscosity and the dynamic friction coefficient. $L_s = \mu / k$
- Stiff chains: large slip length at low shear rates and almost no-slip at higher rates.
- A strong correlation between the friction coefficient and fluid structure in the first layer near the solid wall. $k = k\,[S(\mathbf{G}_1)\rho_c]$
- The friction coefficient at small slip velocities exhibits a distinct maximum which appears due to shear-induced alignment of semiflexible chain segments in contact with solid walls.

Friction coefficient: $k = \mu / L_s$



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