(viscous) dissipation in confined liquid films

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Physics of Complex Fluids
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Computational Biophysics
nanolubrication

sliding friction (Couette flow)

\[ F_C = \mu A \frac{v}{D} \]

squeeze-out damping (Reynolds damping)

\[ F_R = \frac{6\pi \mu R^2}{D} \delta \]
β confined simple liquids – macroscopic contacts (SFA)

β dynamic AFM measurements on confined liquids:
non-monotonic evolution of dissipation

β Molecular Dynamics simulations of simple confined Lennard-Jones fluids
• non-monotonic evolution of dissipation
• anisotropy of force fluctuations & dissipation
• breakdown of Stokes-Einstein relation
force measurements on confined liquid films

Surface Forces Apparatus

normal force

log viscosity

film thickness

film thickness

SFA:
Klein 1995
Granick 1996
Mugele 2003,
Bureau 2008
layer-by-layer squeeze-out in macroscopic contacts (SFA)

OctaMethylCyclo-TetraSiloxane ∅ : ≈ 9 Å

2D potential flow: \( \Delta \Phi = 0 \)

\[
\Phi = - \frac{\rho_{2D}}{\left( \rho_{2D} \eta_{\text{eff}} \right)}
\]

Persson, Tosatti PR B 1994
combined squeeze-out and shear measurements

L. Bureau, PRE 2008; PRL 2010

- no stick slip motion
- squeeze-out: $\eta \approx \eta_{\text{bulk}}$
- shear: $\eta \approx 100 \times \eta_{\text{bulk}}$
force measurements on confined liquid films

Surface Forces Apparatus

- SFA: Klein 1995
  - Bureau 2008
  - Mugele 2003
  - Bureau 2008
  - Horn 1985

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nano-asperity contacts

squeeze-out damping
(Reynolds damping)

\[ F_R = \frac{6\pi \mu R^2}{D} \delta_x \]

Au:Si
OMCTS
HOPG

dynamic AFM

R = 17…35nm
Artifc-free dynamic atomic force microscopy reveals monotonic dissipation for a simple confined liquid

G. B. Kaggwa, J. L. Kilpatrick, J. E. Sader, and S. P. Jarvis

Solid or Liquid? Solidification of a Nanoconfined Liquid under Nonequilibrium Conditions

Shivprasad Patil, George Matei, Ahmet Oral, and Peter M. Hoffmann
tip-sample interaction in OMCTS

deBeer et al. Nanotechnology 2010
a growing consensus

![Graphs and data plots]

C12OH (Hofbauer et al. PRB 2009)

H2O (Khan et al. PRL 2010)

H2O (Ulcinas et al. Langmuir 2011)

OMCTS (deBeer et al. JPCM 2011)
open issues

- relative position of maxima in stiffness & damping
- dependence on tip shape
- dependence on approach rate
- interpretation in term of solidification, glass transition, viscoelastic behavior, …
- epitaxy
how to interpret the excess dissipation?

hydrodynamic damping (Reynolds):

$$\gamma_{\text{hydro}} = \frac{F_R}{\mathcal{D}} = \frac{6\pi \mu R^2}{D}$$

$$\mu = 500 \times \mu_{\text{bulk}}$$
molecular dynamics simulations

in collaboration with Wouter den Otter & Wim Briels

prior art: Thompson, Robbins, Landmann, Lynden-Bell, Schön

Lennard-Jones particles ($\approx 10^5$)

$$V_{ij}(r) = 4\varepsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right)$$

$T=300K$

$\sigma_{OMCTS} = 0.77\text{nm}$

60ns PT equilibration

10ns NVE simulation

$3\text{dim}$

$R=15\text{nm}$

$\text{HOPG}$

$\text{Au}$

$\text{HOPG}$

$d=5\sigma$
density profiles vs. film thickness
diffusion vs. layer thickness

$D_{\text{bulk}} = 0.11$ (r.u.)

$D / D_{\text{bulk}}$

$z [\sigma]$
but AFM does not measure diffusion
the force on the tip is noisy

fluctuation-dissipation theorem: noise \& damping

(without excessive shear rates!)
mean force and number of particles

\[ \langle F_{\text{cyl}} \rangle [10^5 \varepsilon/\sigma] \]

\[ \langle N_{\text{gap}} \rangle [10^3] \]

\[ \text{distance [nm]} \]
noise correlations

**time autocorrelation:**

\[ I(\tau) = \langle \delta F(0) \delta F(\tau) \rangle \]

\[ \delta F(t) = F(t) - \langle F \rangle \]
damping coefficient

fluctuation-dissipation theorem: \[
\gamma = \lim_{T \to \infty} \gamma(T) = \lim_{T \to \infty} \frac{1}{k_B T} \int_{0}^{T} I(\tau) \, d\tau
\]
damping coefficient

![Graph showing norm. excess damping vs. tip surface distance in nm]

- MD simulations
- exp. data

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anisotropy matters

lateral damping shows little structure
structure matters

disordered films display stronger diffusivity & damping

very heterogeneous dynamics
Stokes-Einstein relation does not hold

\[ D \not\propto \frac{1}{\text{mobility}} \propto \frac{1}{\gamma} \]

\[ \gamma = \frac{6\pi \eta R^2}{h} \]

‡ continuum hydrodynamic description of fluid is no longer applicable
tips size matters

more complex behavior for more complex tip shapes?

Luan, Robbins 2005
outlook: nano-rheology

\[ C' = \int \zeta(\tau) \cos \omega \tau \, d\tau \]

\[ C'' = \int \zeta(\tau) \sin \omega \tau \, d\tau \]

elastic response  
dissipative response

on peak  
off peak
conclusions

³ nano-confined liquids display non-monotonous dissipation

³ disordered layer structure entails excess damping & diffusivity (violation of the Stokes-Einstein relation)

³ well-ordered layers display solid-like structure and little dissipation (linear response hardly sensitive to solidification)

³ strong anisotropy between z- and xy-directions
come to Leiden next April

Lorentz Center workshop
Fundamental Aspects of Friction and Lubrication
April 16 – 20

co-organized by the PI’s FOM program FaF (Fundamentals of Friction)