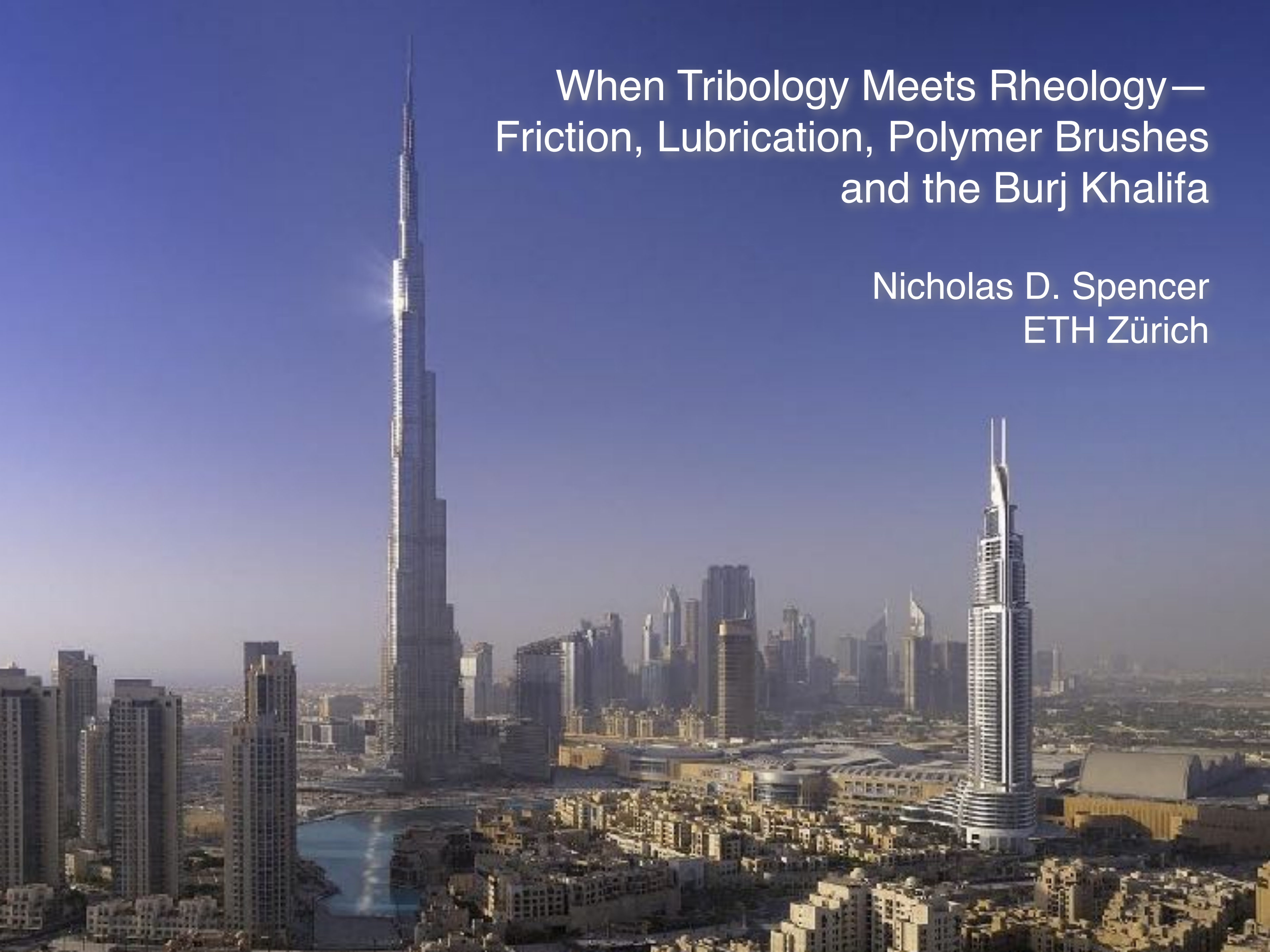
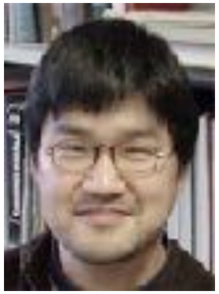
When Tribology Meets Rheology— Friction, Lubrication, Polymer Brushes and the Burj Khalifa

Nicholas D. Spencer
ETH Zürich





Seunghwan Lee

Markus Müller

Robert Bielecki

Nicolas Fernandez

Juliette Cayer-Barrioz

Roman Mani

Hans Herrmann

Lucio Isa

Funding: AFOSR, EOARD, ETH, ESF, KTI, SNSF,

LAFARGE

erc
European Research Council
Established by the European Commission

Outline

- Modes of lubrication
- Polymer brushes
- Polymer brushes and friction
- Polymer brushes and granular flow

Outline

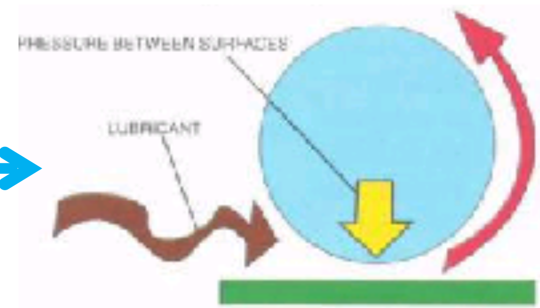
- Modes of lubrication
- Polymer brushes
- Polymer brushes and friction
- Polymer brushes and granular flow

Lubrication

Types of lubrication

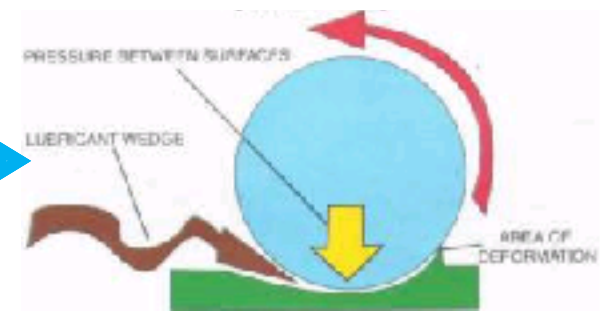
Lubricants are normally employed to reduce frictional forces. Lubricants form a layer of lower shear strength than the sliding surfaces

Hydrodynamic lubrication: the sliding surfaces are separated by a thick lubricant film (thickness > height of the asperities)

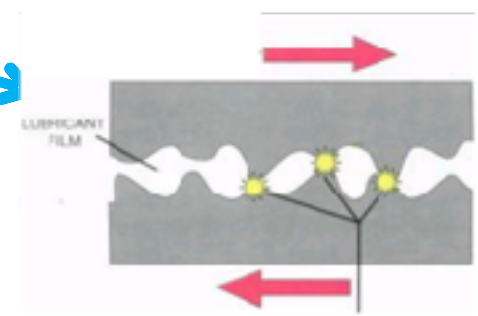


Hydrostatic lubrication: oil is pumped under pressure between the sliding surfaces

Elastohydrodynamic lubrication (EHL): the local pressures are so high that significant elastic deformation of the sliding surfaces occurs



Boundary lubrication: the surfaces are separated by monomolecular (or nearly monomolecular) films



Solid lubrication: based on a solid interfacial layer of low shear strength

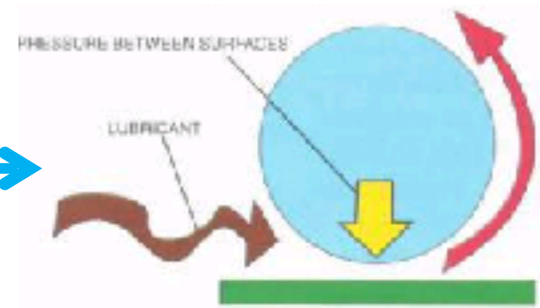
http://images.google.ch

Lubrication

Types of lubrication

Lubricants are normally employed to reduce frictional forces. Lubricants form a layer of lower shear strength than the sliding surfaces

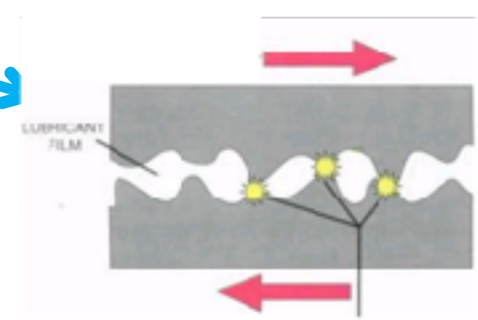
Hydrodynamic lubrication: the sliding surfaces are separated by a thick lubricant film (thickness > height of the asperities)



Hydrostatic lubrication: oil is pumped under pressure between the sliding surfaces

Elastohydrodynamic lubrication (EHL): the local pressures are so high that significant elastic deformation of the sliding surfaces occurs

Boundary lubrication: the surfaces are separated by monomolecular (or nearly monomolecular) films

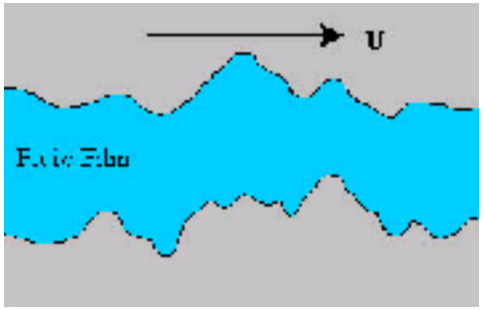


Solid lubrication: based on a solid interfacial layer of low shear strength

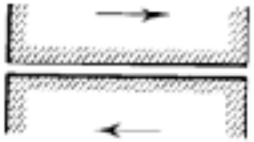
http://images.google.ch

Lubrication

Hydrodynamic lubrication (full fluid film)



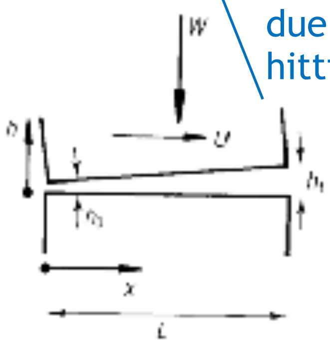
- The asperities on the sliding partners never come into contact with each other
- Surfaces are kept apart by hydrodynamic forces

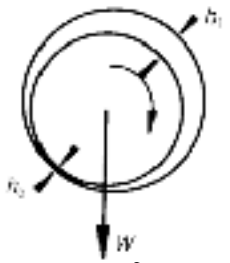


http://images.google.ch

- Sliding surfaces have to be conformal

due to lubricant hitting the surface





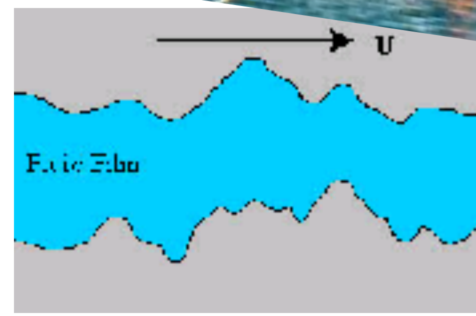
- But not parallel, so upwards momentum supports the load

The pressure that counteracts the normal load originates from the viscous forces in the liquid

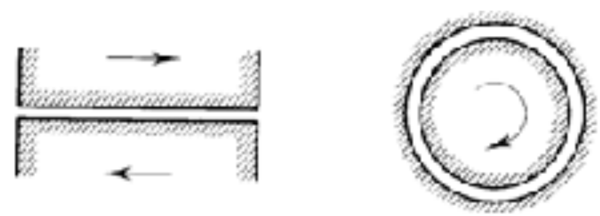
The gap between the surfaces becomes narrower in the direction of motion

Lubrication

Hydrodynamic lubrication (full fluid film)

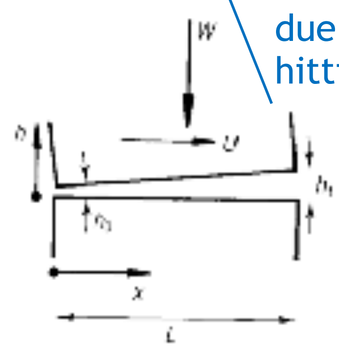


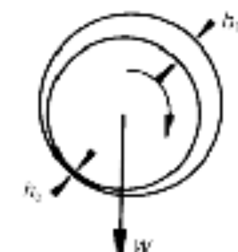
- The asperities on the sliding partners never come into contact with each other
- Surfaces are kept apart by hydrodynamic forces
- Sliding surfaces have to be conformal



http://images.google.ch

due to lubricant hitting the surface





- But not parallel, so upwards momentum supports the load

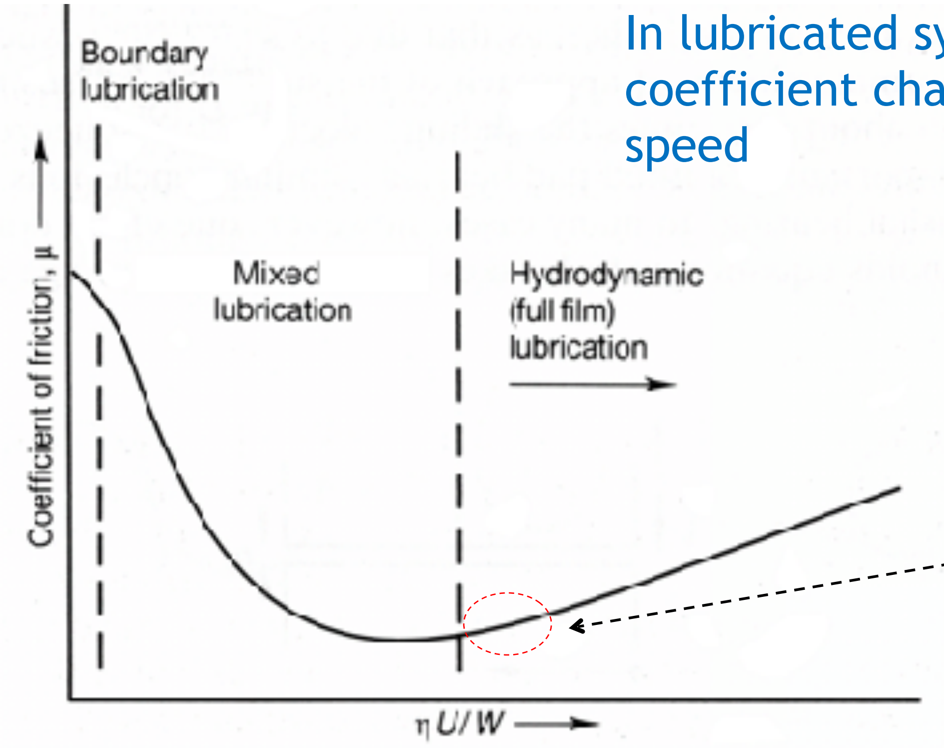
The pressure that counteracts the normal load originates from the viscous forces in the liquid

The gap between the surfaces becomes narrower in the direction of motion

Lubrication

The Stribeck curve

Friction coefficient is displayed as a function of the viscosity multiplied by the tangential velocity, and divided by the normal load (η·U/W)



In lubricated systems, the friction coefficient changes as a function of speed

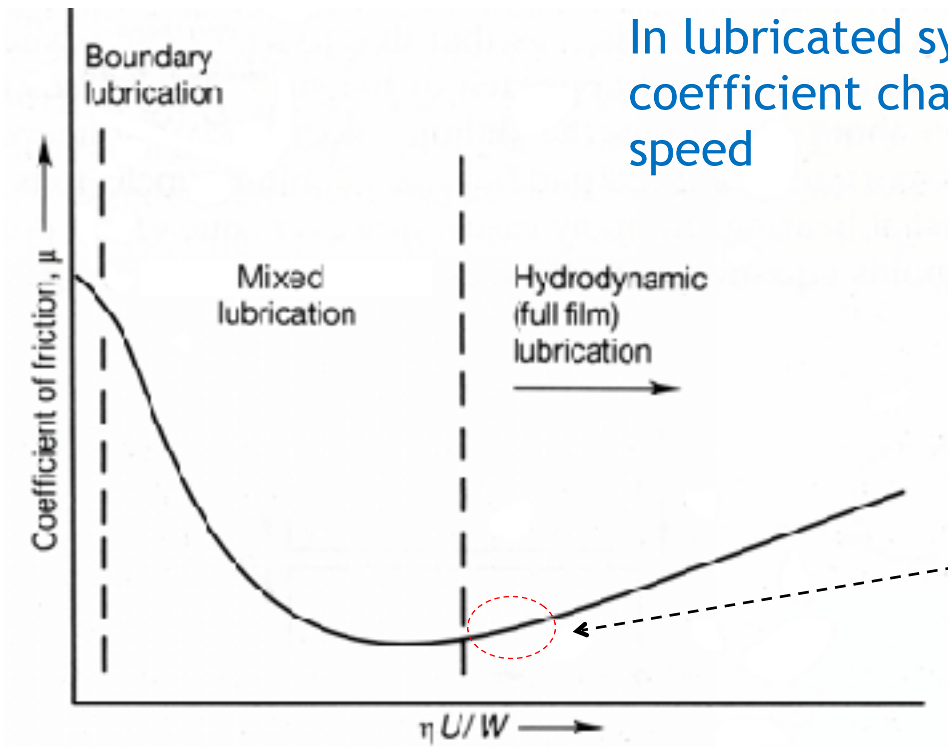
A bearing wants to be operated here!

Close to the minimum but on the right side, so that with slight changes of the parameters, the system is drawn towards the minimum

Lubrication

The Stribeck curve

Friction coefficient is displayed as a function of the viscosity multiplied by the tangential velocity, and divided by the normal load (η·U/W)



In lubricated systems, the friction coefficient changes as a function of speed

A bearing wants to be operated here!

Close to the minimum but on the right side, so that with slight changes of the parameters, the system is drawn towards the minimum

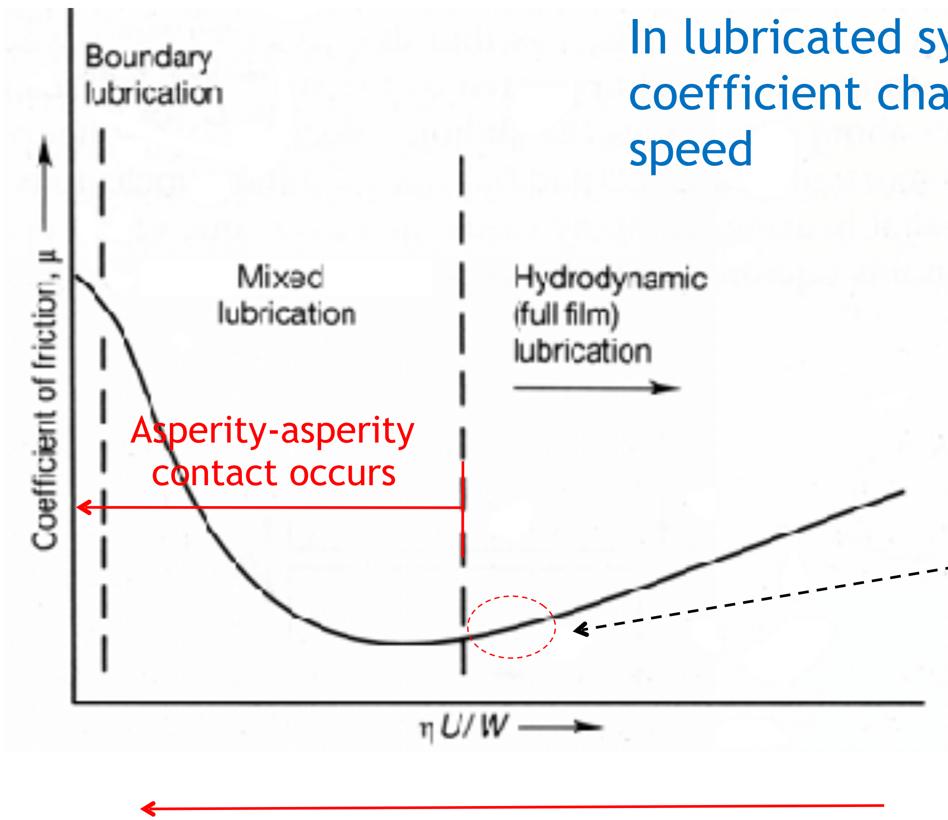
Film thickness decreases

Lubrication

The Stribeck curve

Friction coefficient is displayed as a function of the viscosity multiplied by the tangential velocity, and divided by the normal load (η·U/W)

In lubricated systems, the friction coefficient changes as a function of speed



Film thickness decreases

A bearing wants to be operated here!

Close to the minimum but on the right side, so that with slight changes of the parameters, the system is drawn towards the minimum

Lubrication

Boundary lubrication

Occurs at high loads or low speeds

↓

Hydrodynamic forces can no longer maintain a lubricant film between the sliding surfaces

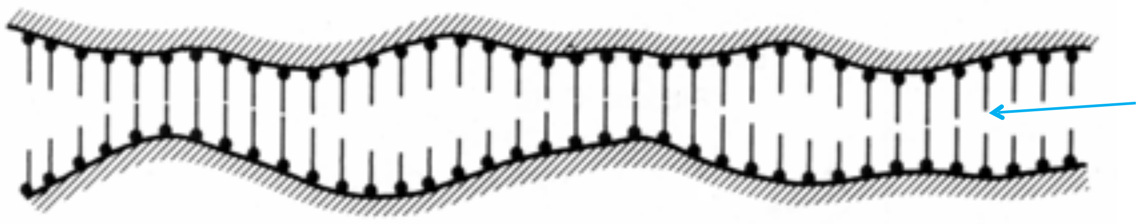
↓

Direct contact between the asperities starts to become dominant

↓

Boundary lubricant is essential under these conditions, in order to avoid excessive friction and wear

Boundary lubricants form adsorbed molecular films on the surfaces (oversimplification)

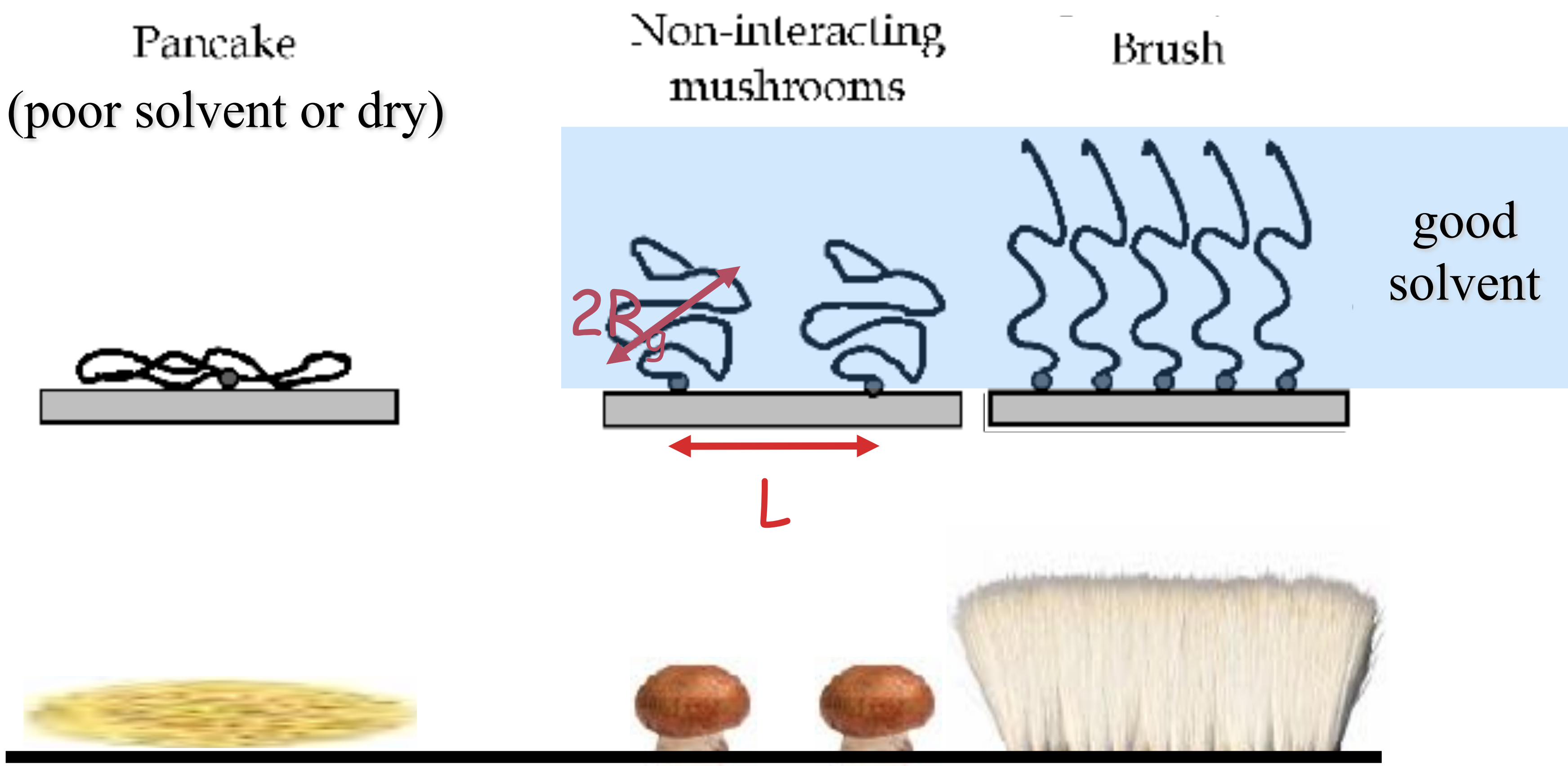


Repulsive forces between the films carry a significant part of the load

Outline

- Modes of lubrication
- Polymer brushes
- Polymer brushes and friction
- Polymer brushes and granular flow

Polymer brushes



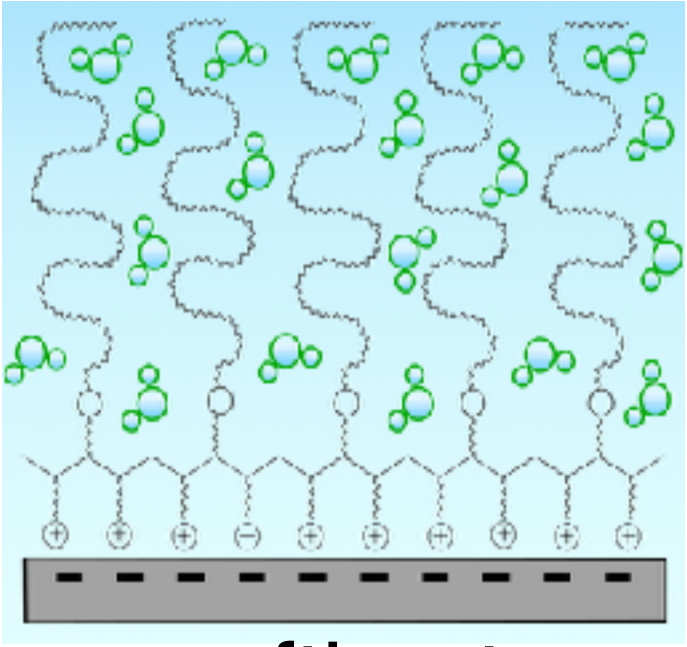
The Brushettes:
World Première, Cargèse, 2010

The Brushettes:
Faraday Meeting on Tribology, 2012

Polymer Brush Demo
Madrid, 2012

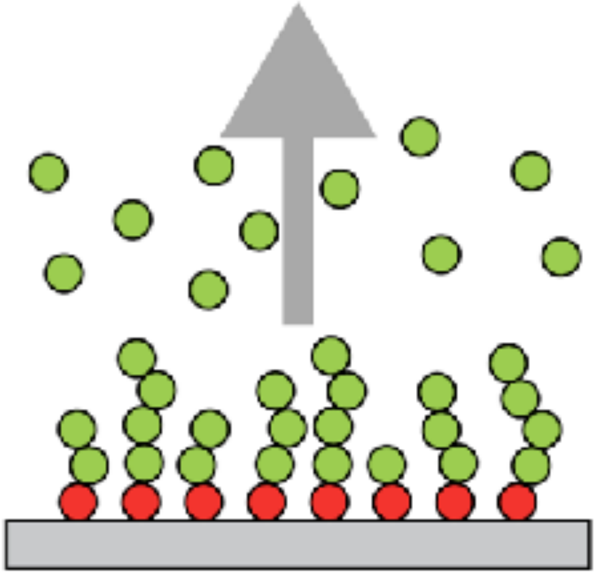
Polymer Brush Demo
Tokyo, 2013

Polymer brushes



grafting to

oxides, polymers



grafting from

almost anything...

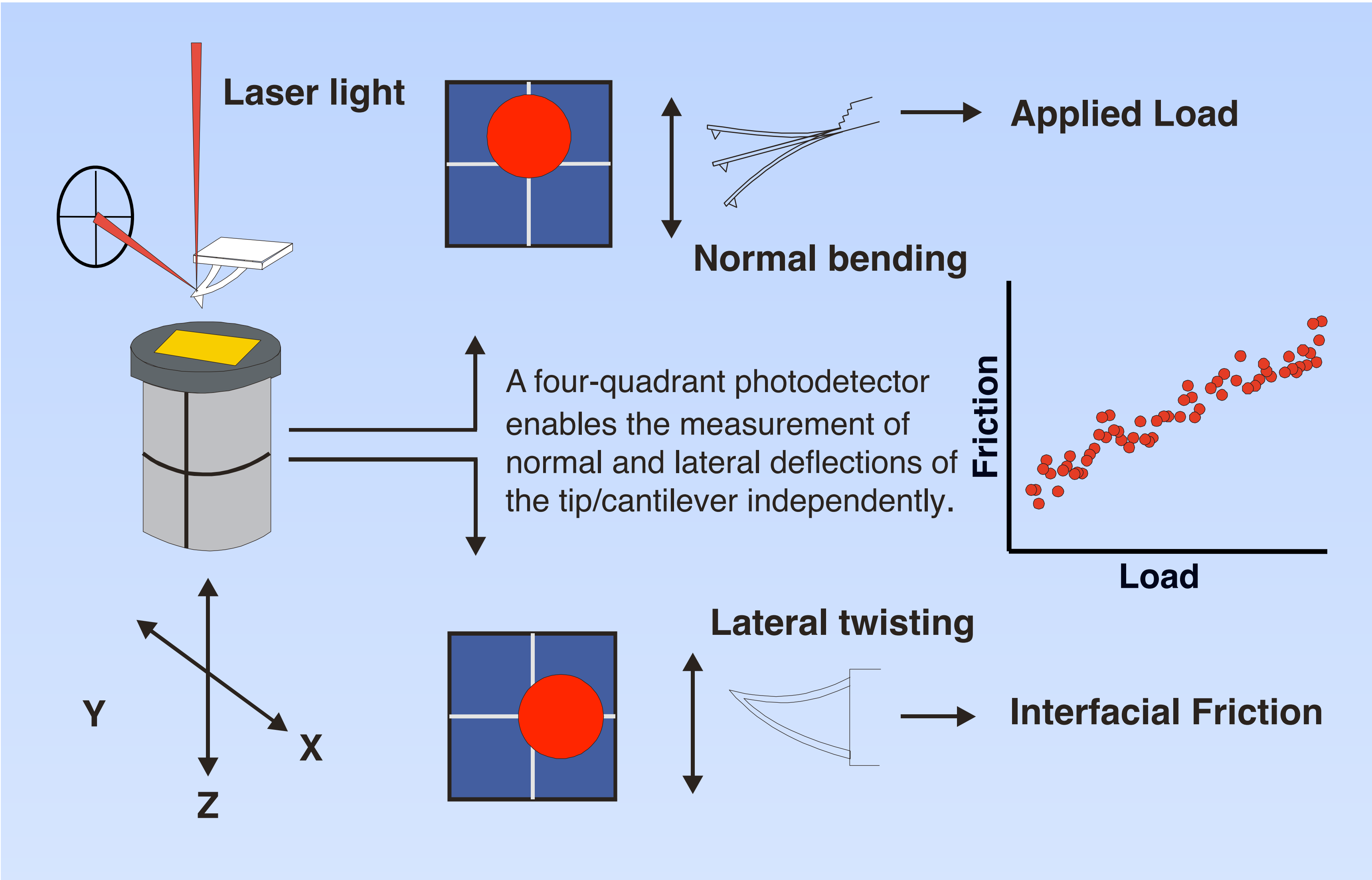
ETHzürich

LSST

Outline

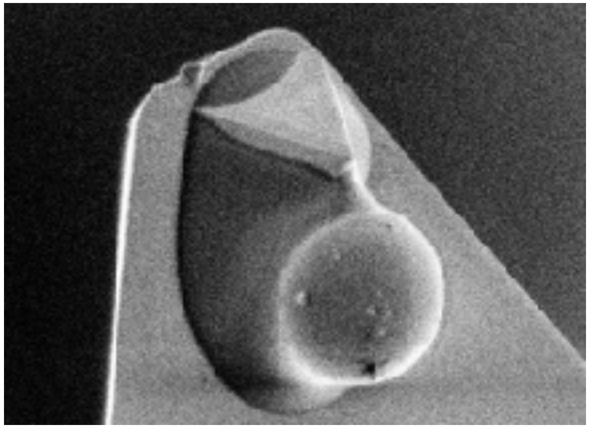
- Modes of lubrication
- Polymer brushes
- Polymer brushes and friction
- Polymer brushes and granular flow
- Brushes in oil lubrication

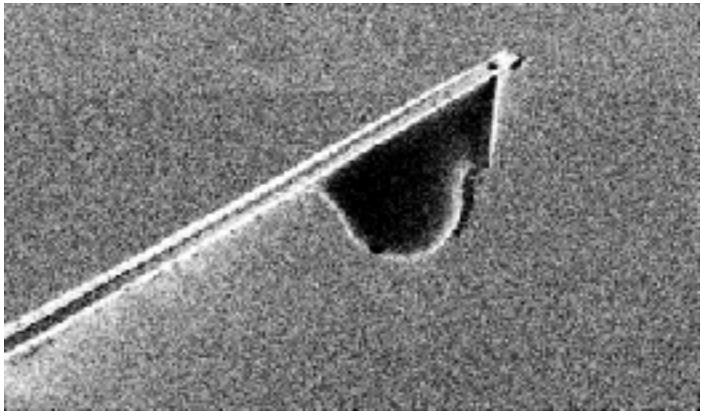
Friction Measurements with Beam Deflection AFM



Sodium Borosilicate Microsphere

Cantilever:	Si_3N_4
Sphere radius:	2.5 μm
Image:	SEM
Beam energy:	1 kV





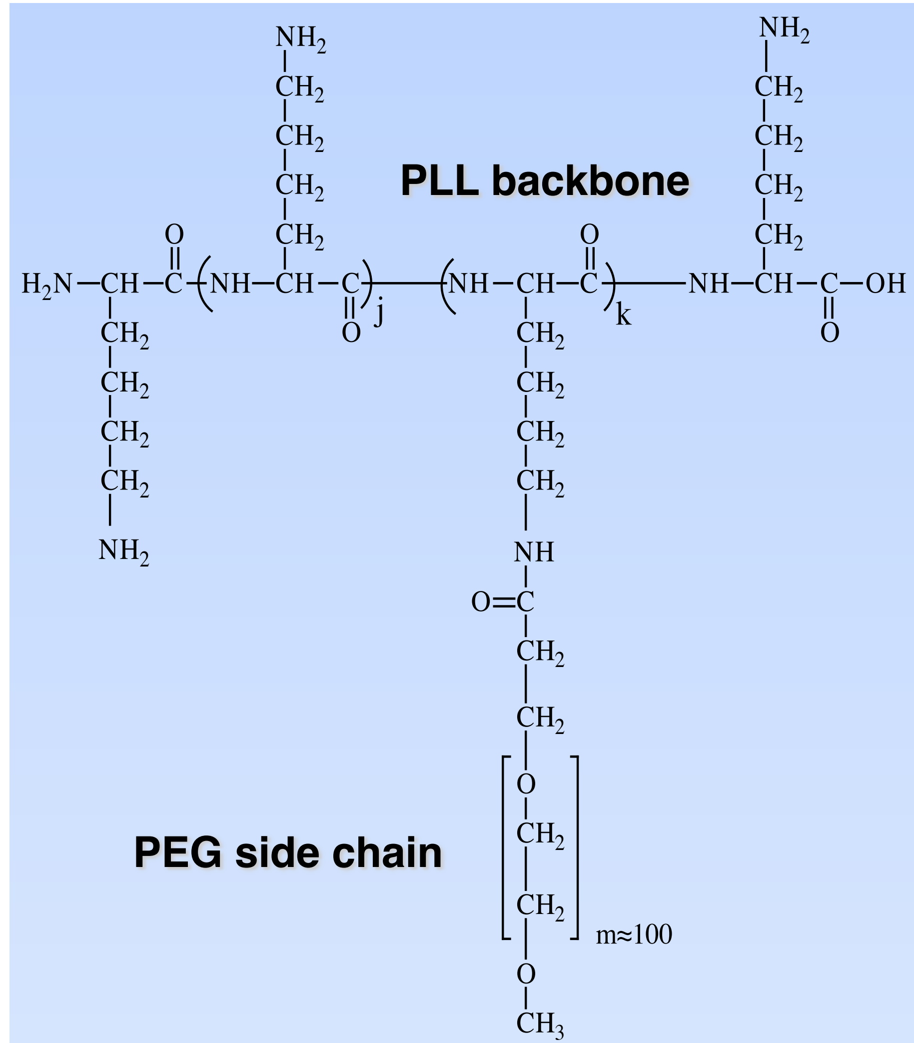
Poly-l-lysine (PLL)-*g*-polyethylene glycol (PEG)

PLL backbone

- MW: 20,000 to 350,000
- Positively charged at pH<10 (R= $-NH_3^+$)
- Approximate length of backbone: 90 to 1000 nm

PEG side chain

- MW: 2000 to 5000
- Adsorbs water and has properties similar to water
- Protein resistant
- Approximate length of side chain:20 nm



J. Hubbell, D. Elbert, Chem Biol 5: (3) 177-183 (1998)

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

LSST
Laboratory for Surface Science and Technology

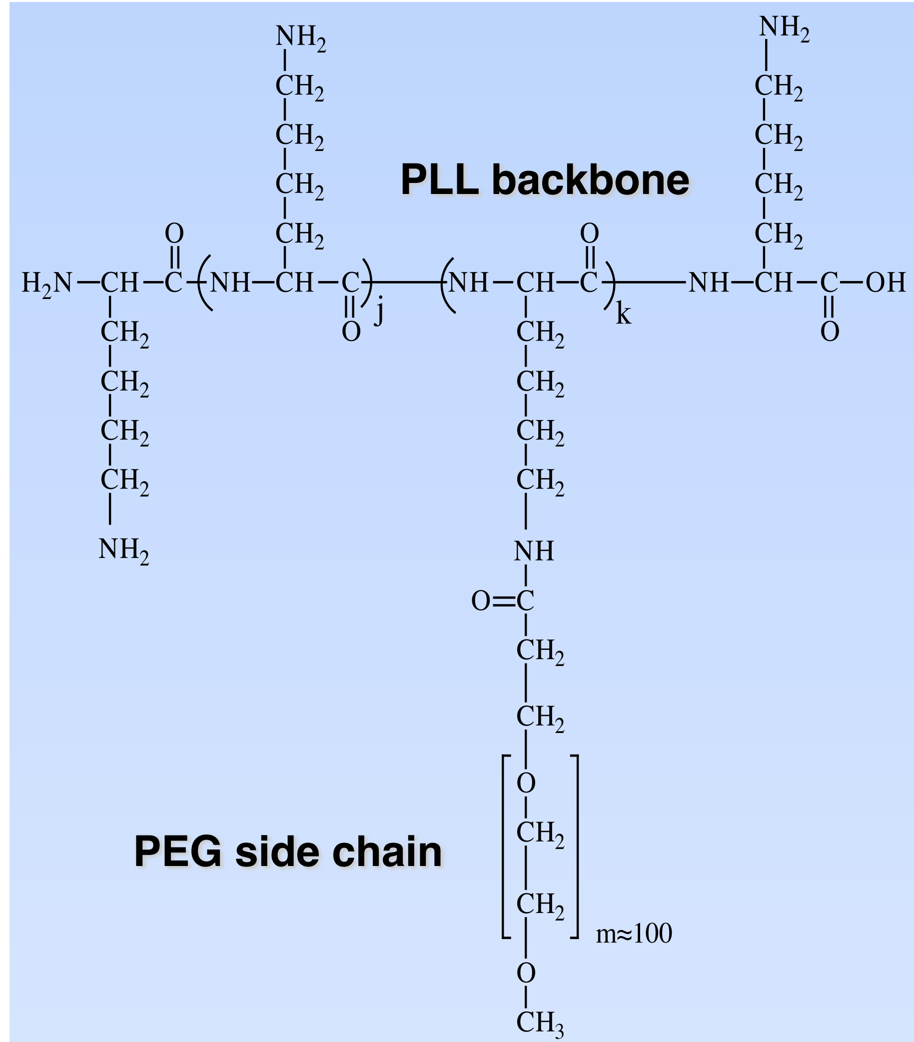
Poly-l-lysine (PLL)-*g*-polyethylene glycol (PEG)

PLL backbone

- MW: 20,000 to 350,000
- Positively charged at pH<10 (R= $-NH_3^+$)
- Approximate length of backbone: 90 to 1000 nm

PEG side chain

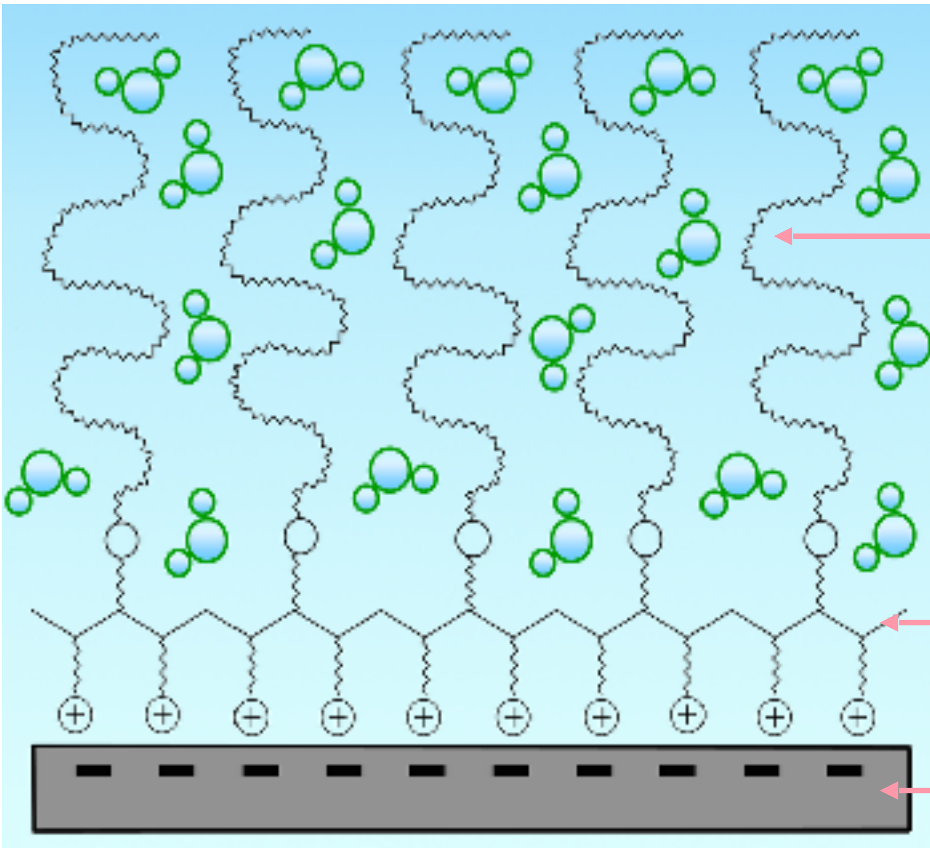
- MW: 2000 to 5000
- Adsorbs water and has properties similar to water
- Protein resistant
- Approximate length of side chain:20 nm



J. Hubbell, D. Elbert, Chem Biol 5: (3) 177-183 (1998)

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

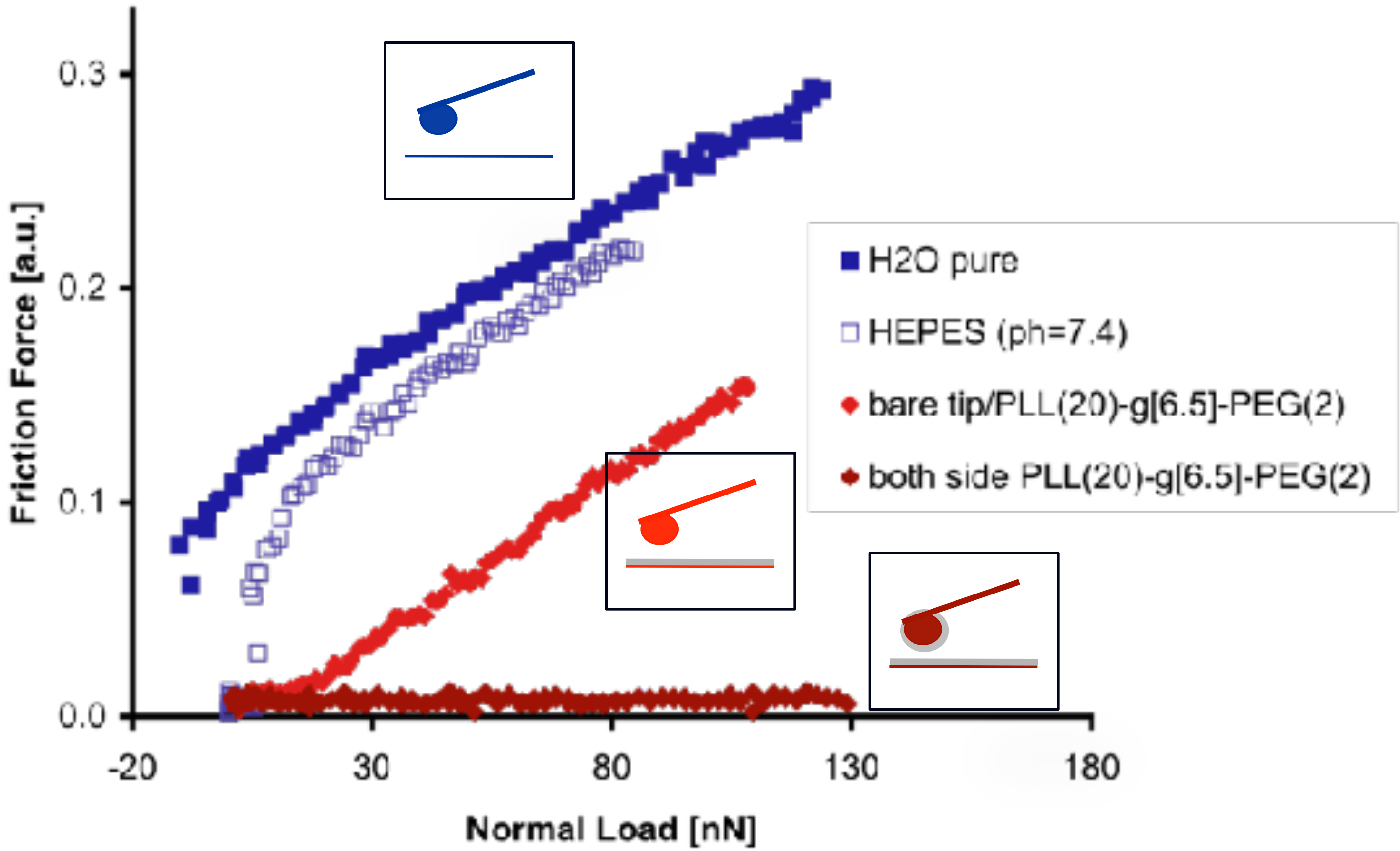
"Grafting to" of PEG, using a backbone



- Hydrophilic
- Uncharged
- Flexible chains
- High water content
- Protein resistant
- Biocompatible

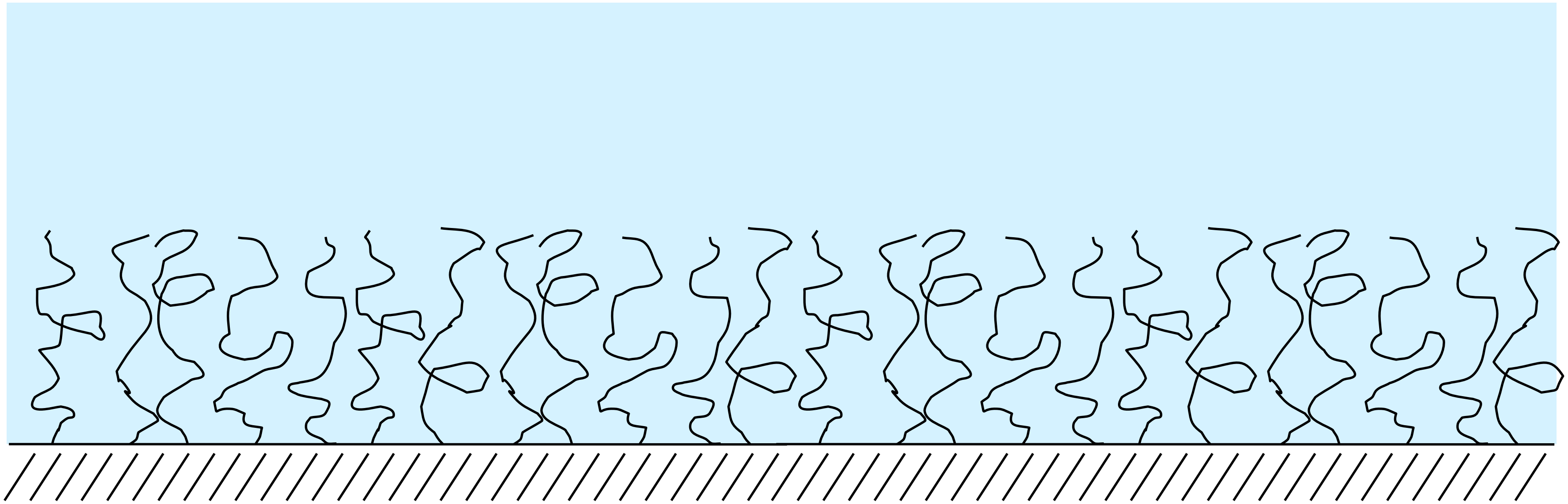
- Positive charge
- High coverage
- Kinetic inertness
- pH dependence

Polymer adsorption dramatically reduces nanofriction

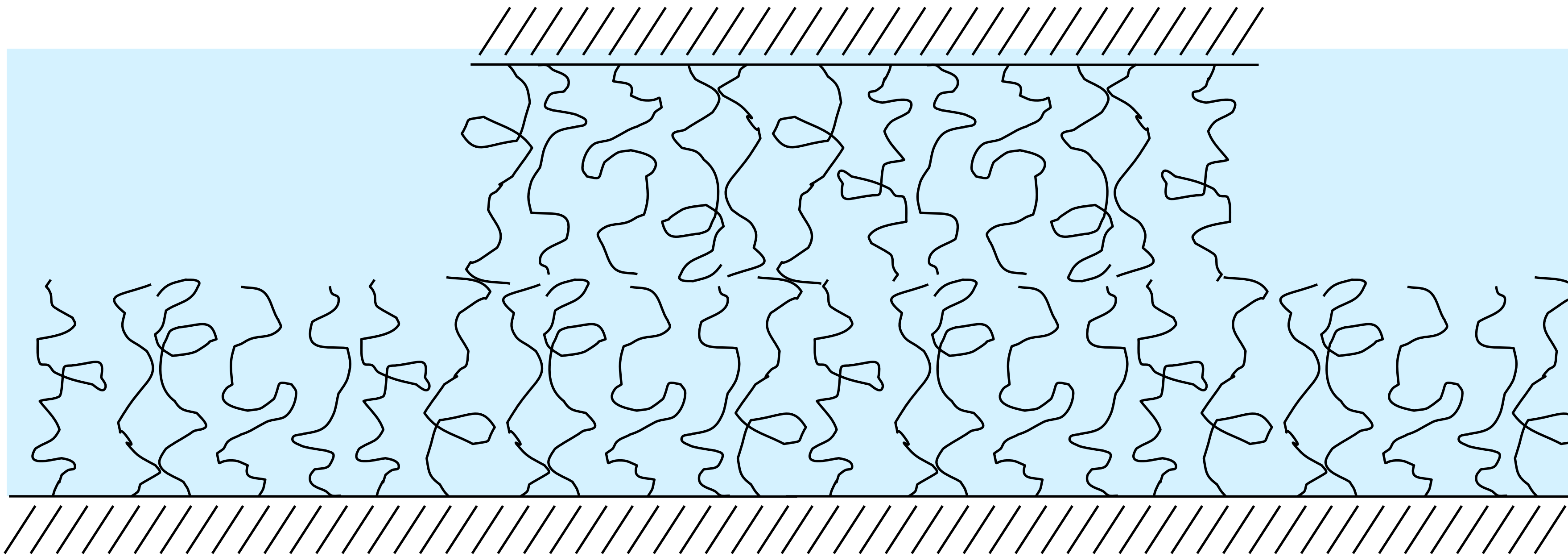


X. Yan, S.S. Perry, N.D. Spencer, S. Pasche, S.M. De Paul, M. Textor, M.S. Lim, *Langmuir* 2004, *20,* 423-428

"Enforced" Fluid-Film Lubrication by Polymer Brushes

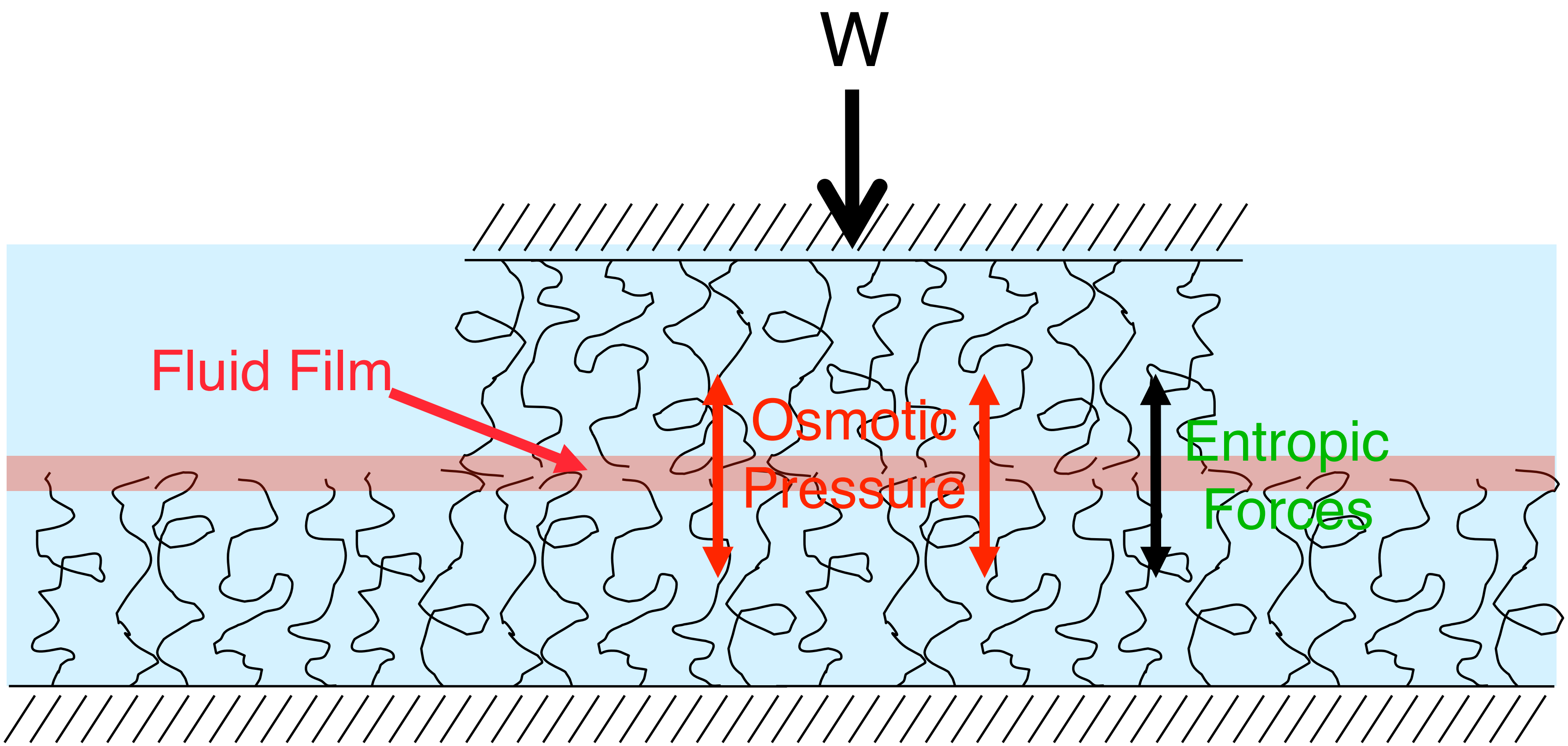


“Enforced” Fluid-Film Lubrication by Polymer Brushes

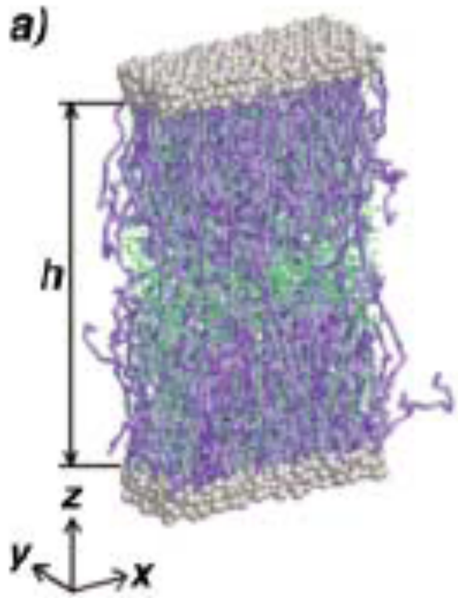


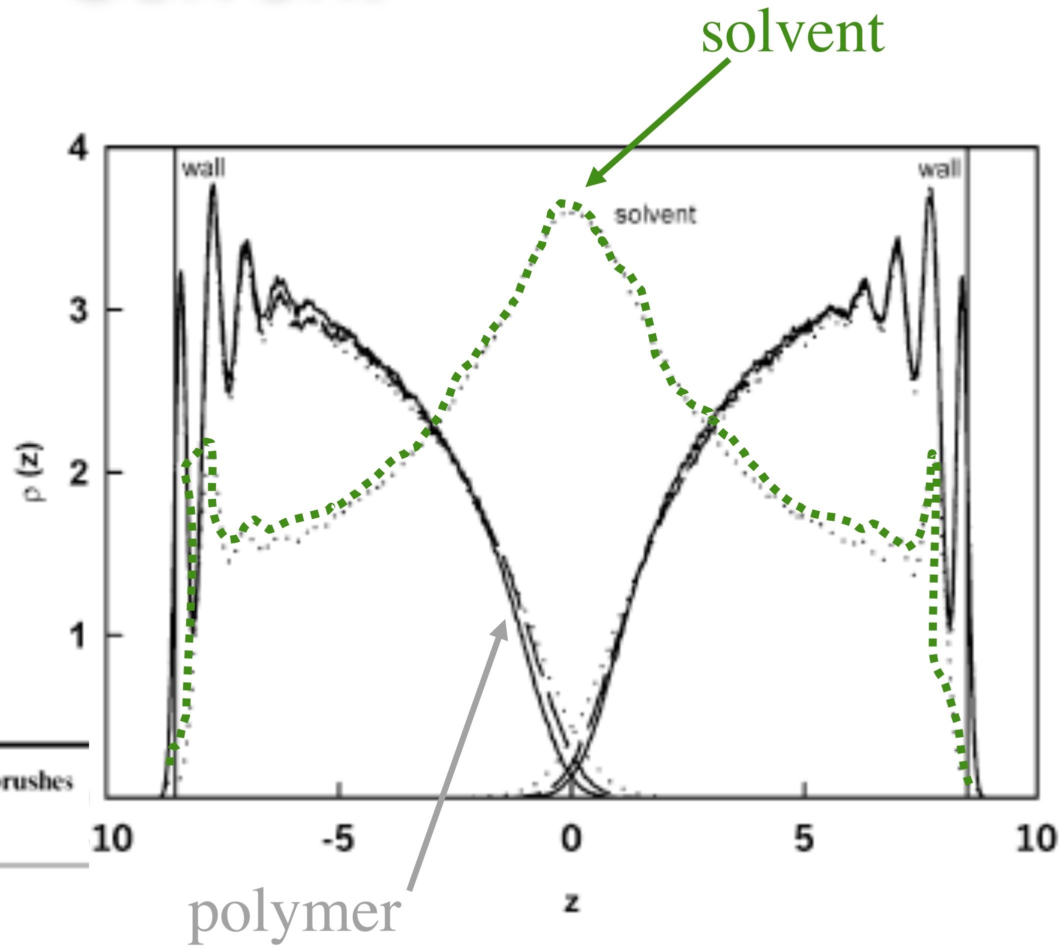
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

"Enforced" Fluid-Film Lubrication by Polymer Brushes



Density Distribution of Polymer and Solvent





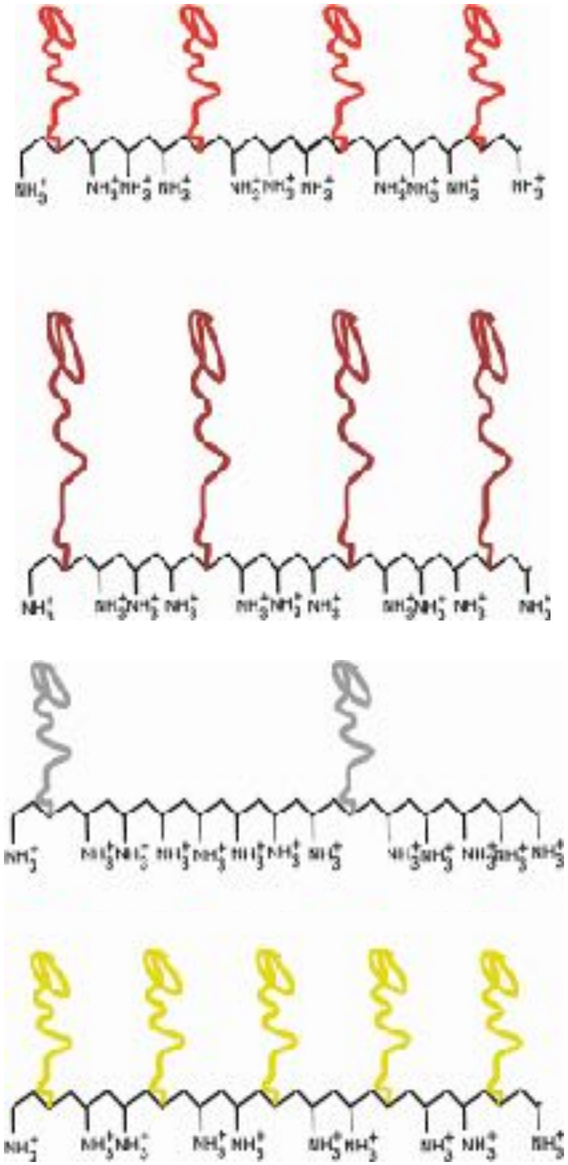
Dissipative particle dynamics simulation of grafted polymer brushes under shear

Danial Irfachsyad,[a] Dominic Tildesley[a] and Patrice Malfreyt[b]

[a] *Uniever Research Port Sunlight, Bebington, Wirral, UK CH63 3JW*
[b] *Laboratoire de Thermodynamique des Solutions et des Polymeres, UMR CNRS 6003, 24 avenue de Landais, Universite Blaise-Pascal, 63177, Aubiere Cedex, France*

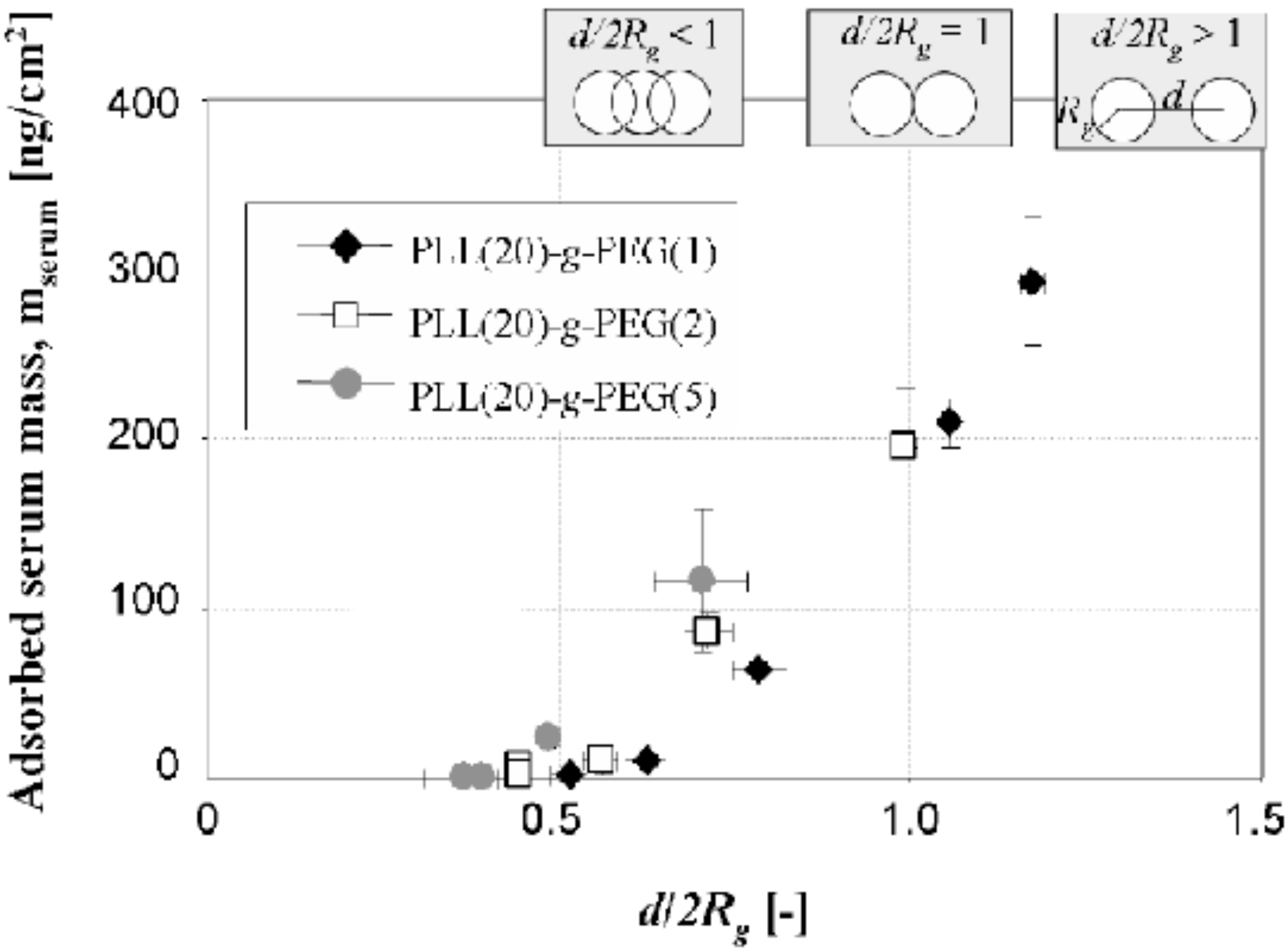
Received 22nd November 2001, Accepted 22nd April 2002
First published as an Advance Article on the web 27th May 2002

Tailoring PLL-g-PEG Architecture



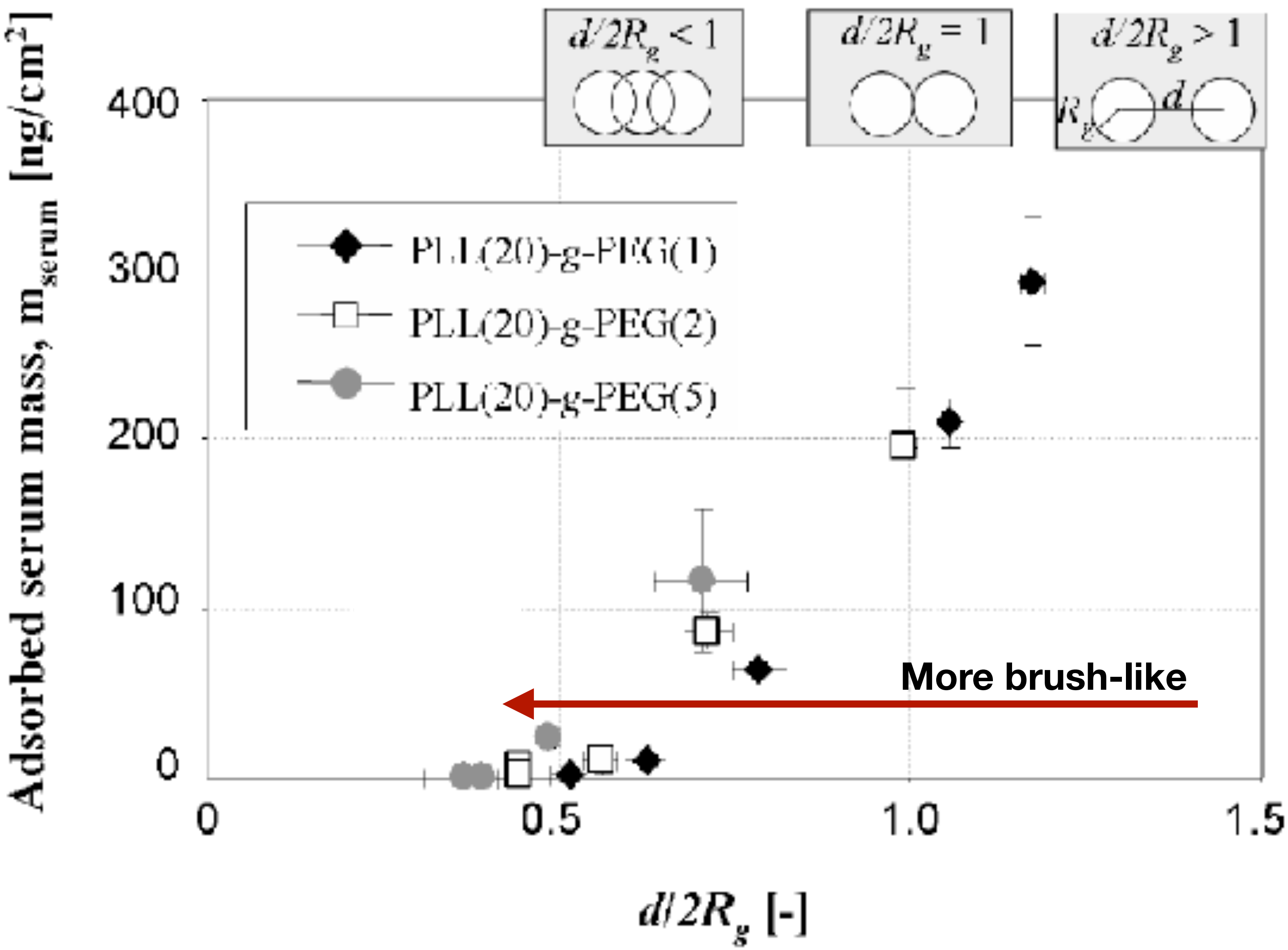
$$g = \frac{PLL}{PEG - chain} = 3.4$$

Effect of Chain Spacing on Protein Adsorption



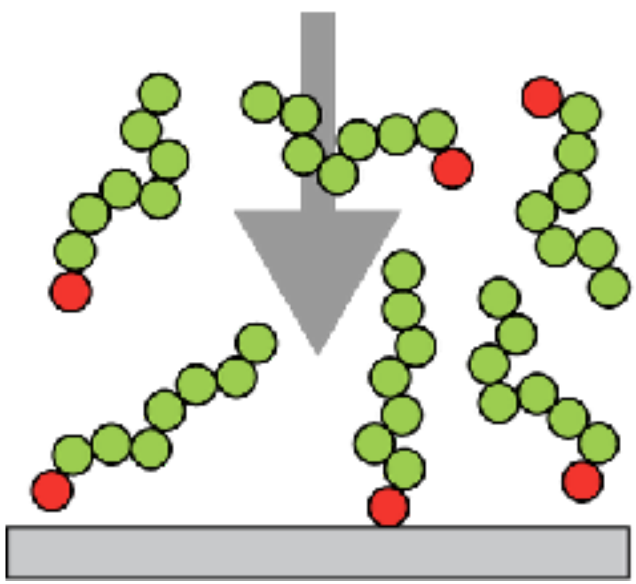
Pasche et al, Langmuir 2003, **19**, 9216-9225

Effect of Chain Spacing on Protein Adsorption

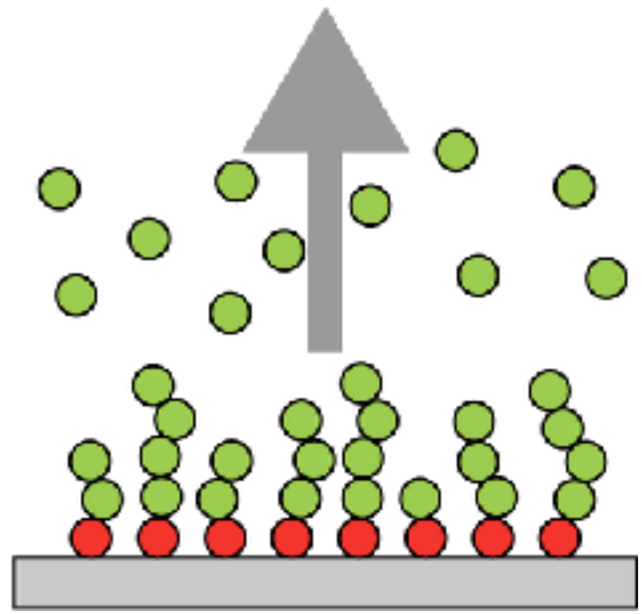


Pasche et al, Langmuir 2003, **19**, 9216-9225

Changing the approach:
"grafting from" vs. "grafting to"



"grafting to"
easy, but relatively low density
e.g. PLL-*g*-PEG, PLL-*g*-dex

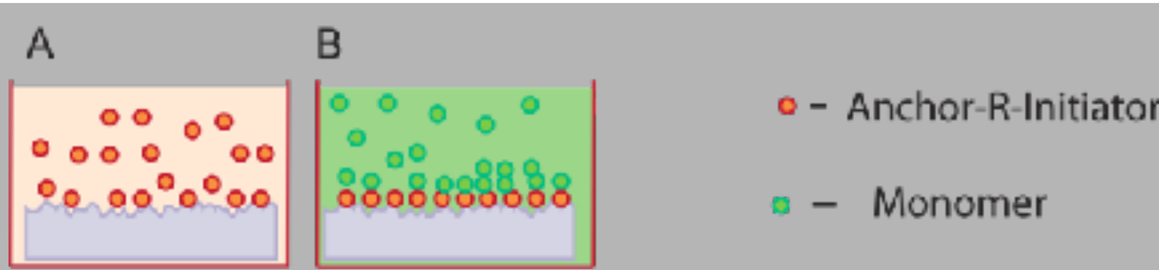


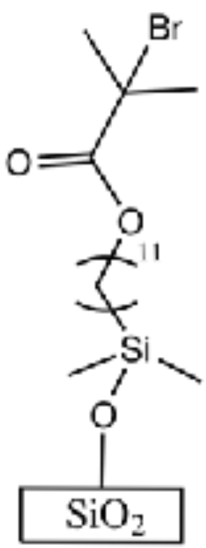
"grafting from"
more effort, but high density

Hydrocarbon-rich brushes by ATRP

Polymer dry thickness up to above 250 nm (8 MDa) in 3 hours

2 steps:





C12

initiator

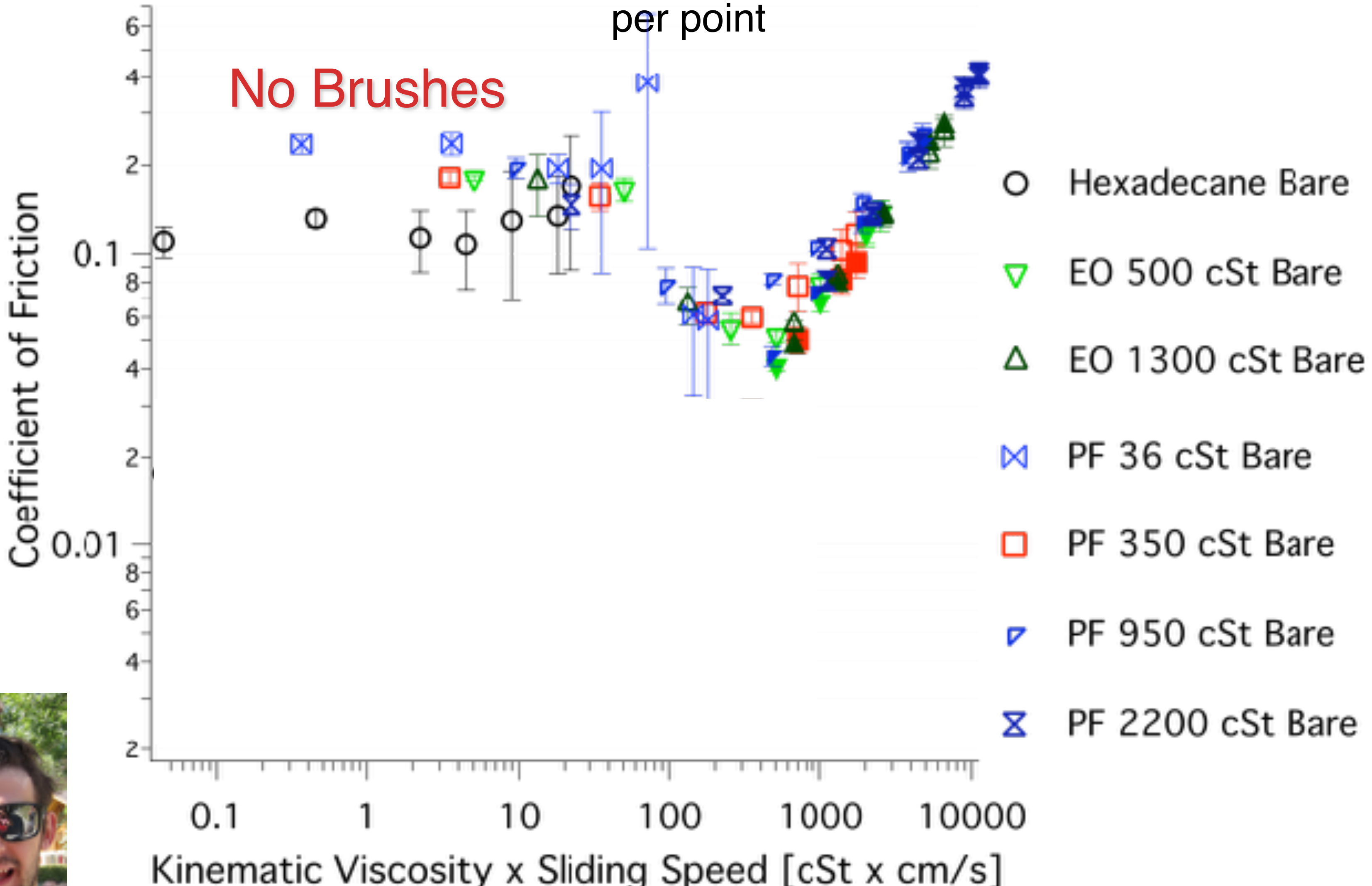
methacrylate monomer

polymers

Stribeck Curve in Microtribometer:

7 Oils, Bare Borosilicate Against Brush or Si Wafer

250nm (dry) Poly(dodecyl methacrylate), 20 mN, rotating, reciprocating, 20 cycles per point

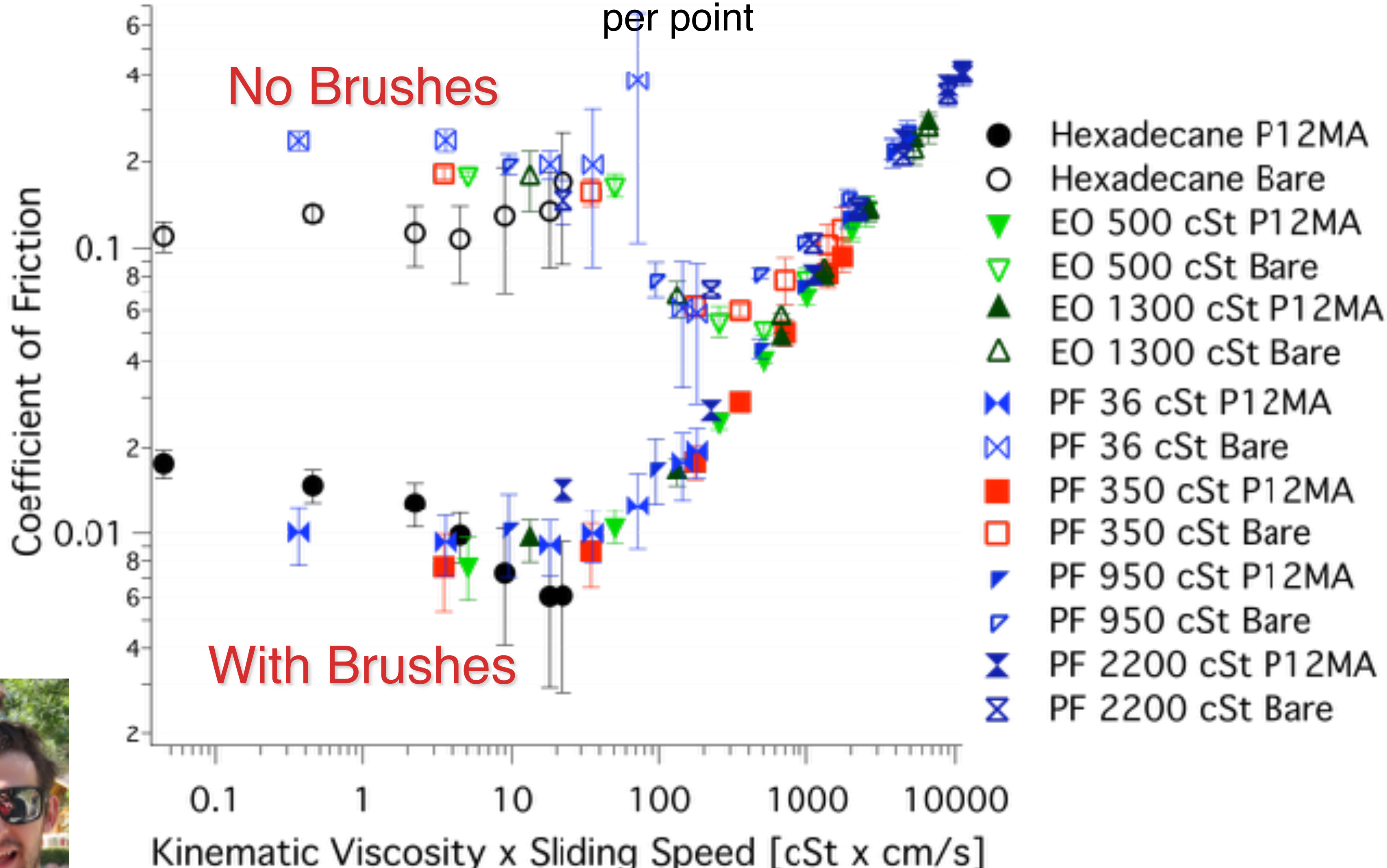


Robert M. Bielecki, Maura Crobu, and Nicholas D. Spencer *Tribol Lett* (2013) **49**:263–272

Stribeck Curve in Microtribometer:

7 Oils, Bare Borosilicate Against Brush or Si Wafer

250nm (dry) Poly(dodecyl methacrylate), 20 mN, rotating, reciprocating, 20 cycles per point

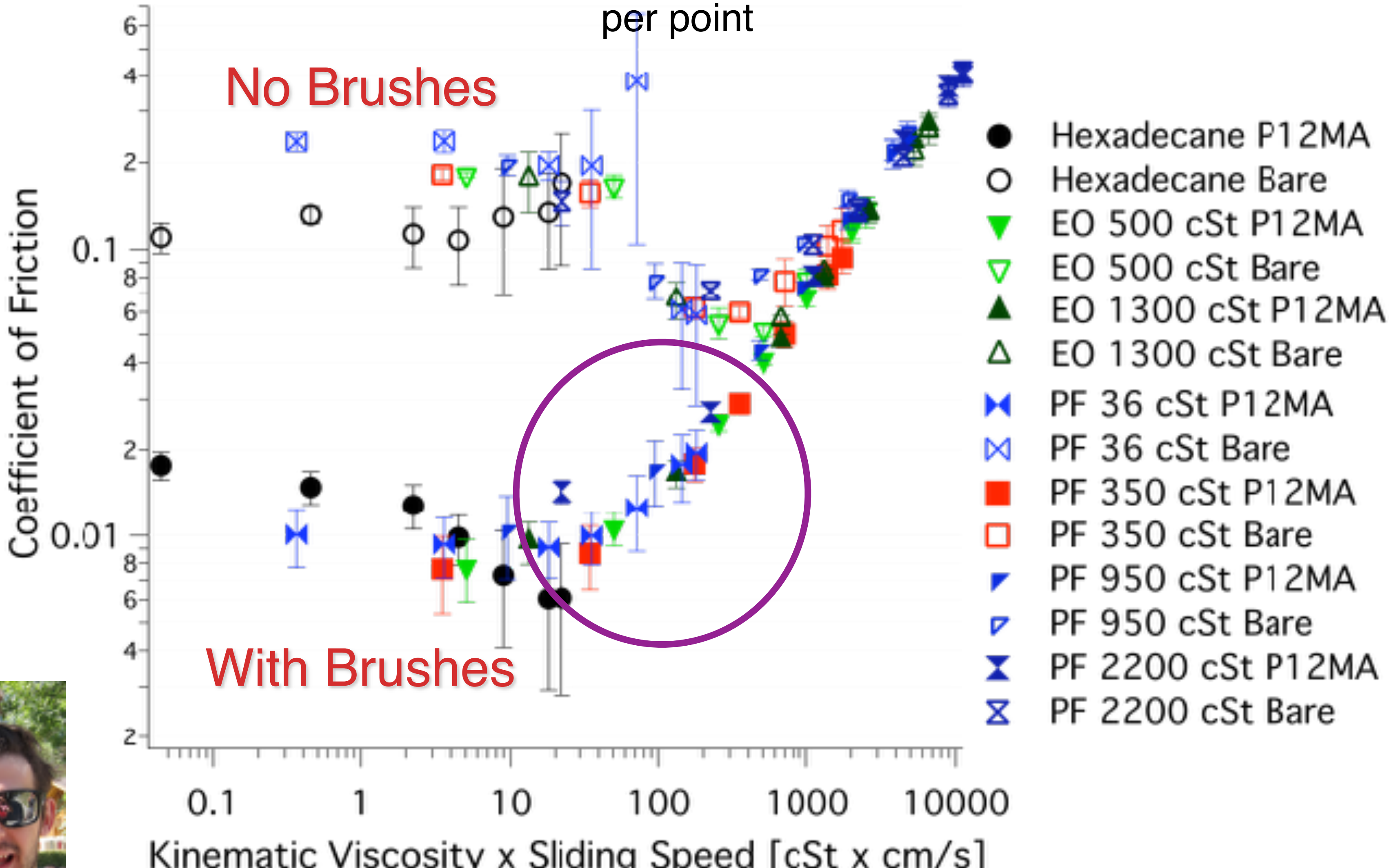


Robert M. Bielecki, Maura Crobu, and Nicholas D. Spencer *Tribol Lett* (2013) **49**:263–272

Stribeck Curve in Microtribometer:

7 Oils, Bare Borosilicate Against Brush or Si Wafer

250nm (dry) Poly(dodecyl methacrylate), 20 mN, rotating, reciprocating, 20 cycles per point

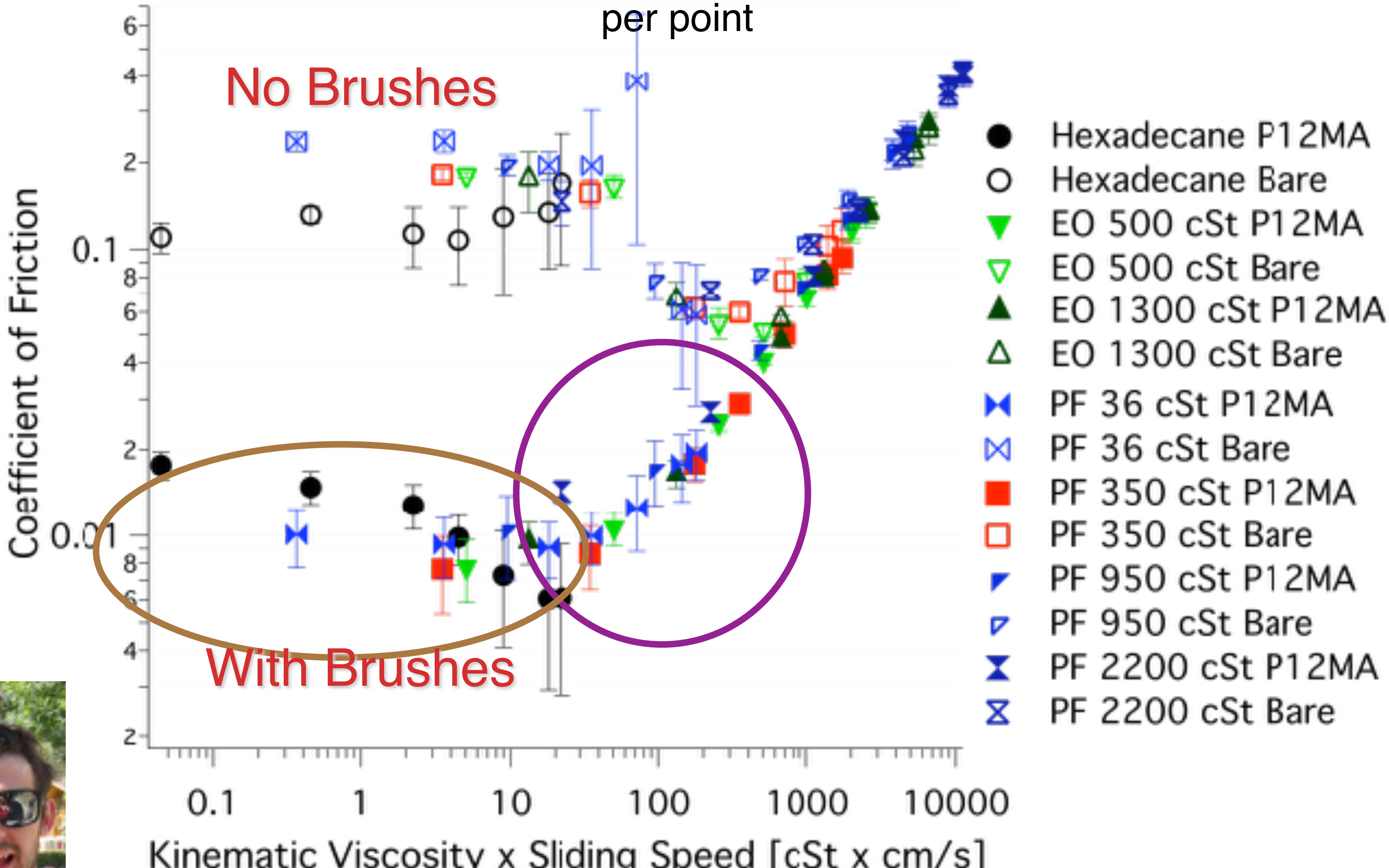


Robert M. Bielecki, Maura Crobu, and Nicholas D. Spencer *Tribol Lett* (2013) **49**:263–272

Stribeck Curve in Microtribometer:

7 Oils, Bare Borosilicate Against Brush or Si Wafer

250nm (dry) Poly(dodecyl methacrylate), 20 mN, rotating, reciprocating, 20 cycles per point



Robert M. Bielecki, Maura Crobu, and Nicholas D. Spencer *Tribol Lett* (2013) **49**:263–272

Outline

- Modes of lubrication
- Polymer brushes
- Polymer brushes and friction
- Polymer brushes and granular flow


Burj al Khalifa


Burj al Khalifa
Pumping cement slurries!

Environmental issues around concrete

sources: US EPA and Columbia U

Environmental issues around concrete

- Concrete is the second most consumed substance on Earth after water

sources: US EPA and Columbia U

Environmental issues around concrete

- Concrete is the second most consumed substance on Earth after water
- Each year, three tons of concrete are consumed by every person on the planet

sources: US EPA and Columbia U

Environmental issues around concrete

- Concrete is the second most consumed substance on Earth after water
- Each year, three tons of concrete are consumed by every person on the planet
- Cement production is growing by 2.5% annually, and is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050.

sources: US EPA and Columbia U

Environmental issues around concrete

- Concrete is the second most consumed substance on Earth after water
- Each year, three tons of concrete are consumed by every person on the planet
- Cement production is growing by 2.5% annually, and is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050.
- Producing a ton of cement generates a ton of CO_2 (reaction product, heat and electricity required)

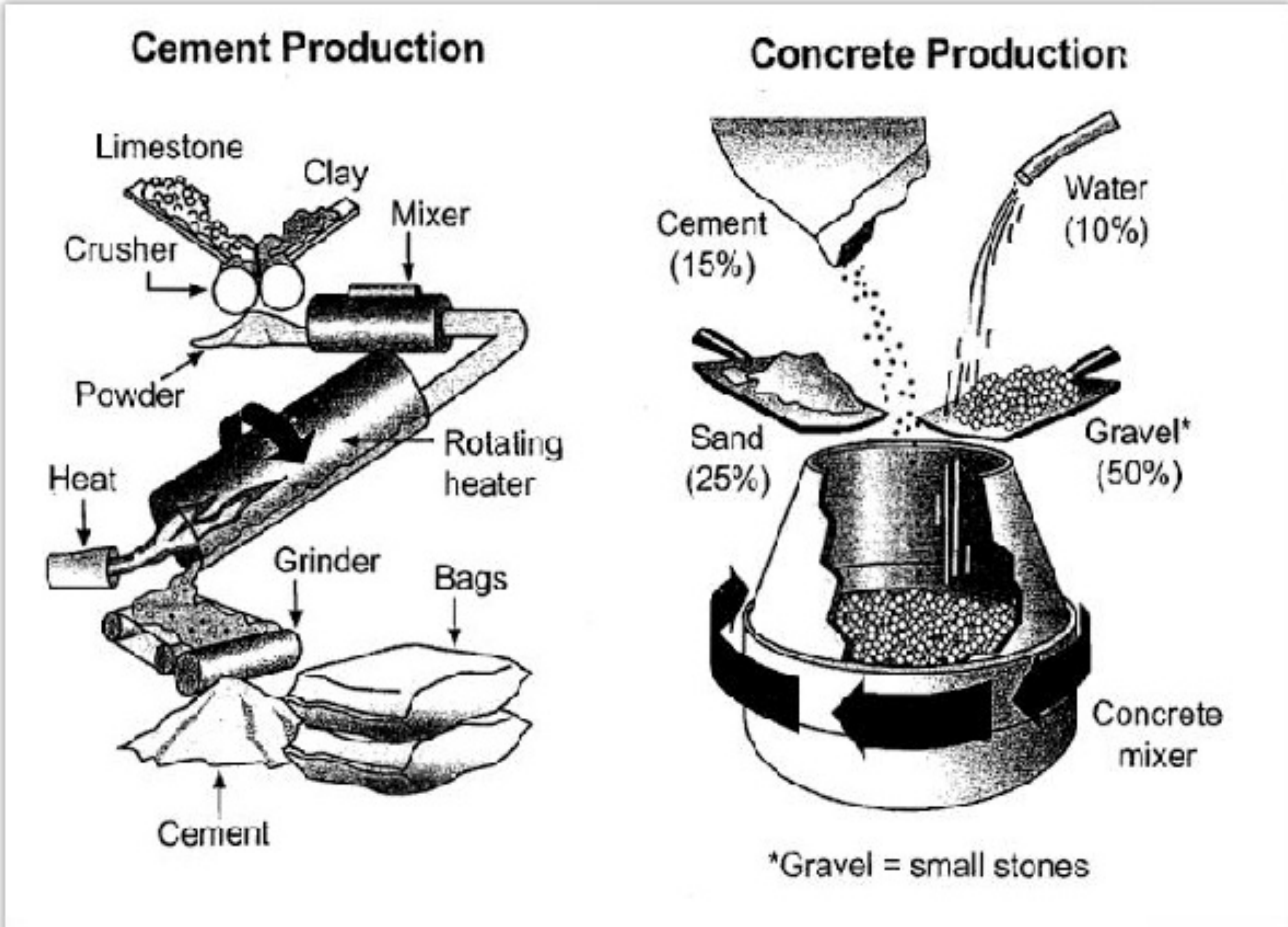
sources: US EPA and Columbia U

Environmental issues around concrete

- Concrete is the second most consumed substance on Earth after water
- Each year, three tons of concrete are consumed by every person on the planet
- Cement production is growing by 2.5% annually, and is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050.
- Producing a ton of cement generates a ton of CO_2 (reaction product, heat and electricity required)
- 5% of world CO_2 emissions are due to cement production

sources: US EPA and Columbia U

Cement and Concrete Production



One Approach to Improving the C-footprint of Cement

One Approach to Improving the C-footprint of Cement

- Making concrete with fillers (e.g. ash) mixed in with cement improves C-footprint of system

One Approach to Improving the C-footprint of Cement

- Making concrete with fillers (e.g. ash) mixed in with cement improves C-footprint of system
- but…reaction of water with cement is stoichiometric, and excess water lowers concrete performance.

One Approach to Improving the C-footprint of Cement

- Making concrete with fillers (e.g. ash) mixed in with cement improves C-footprint of system
- but…reaction of water with cement is stoichiometric, and excess water lowers concrete performance.
- So slurry of cement + filler is more viscous than slurry of cement alone

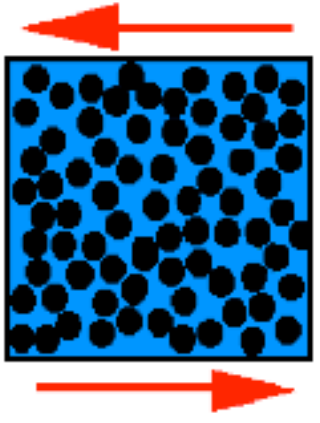
One Approach to Improving the C-footprint of Cement

- Making concrete with fillers (e.g. ash) mixed in with cement improves C-footprint of system
- but…reaction of water with cement is stoichiometric, and excess water lowers concrete performance.
- So slurry of cement + filler is more viscous than slurry of cement alone
- New rheological situation brings challenges…

Dense Flows (“slurries”):

Shear Thickening of non-Brownian suspensions

- Newtonian Fluid
- Non-Brownian, Rigid, Hard Spheres
- High Volume Fraction (>50%)
- High Shear

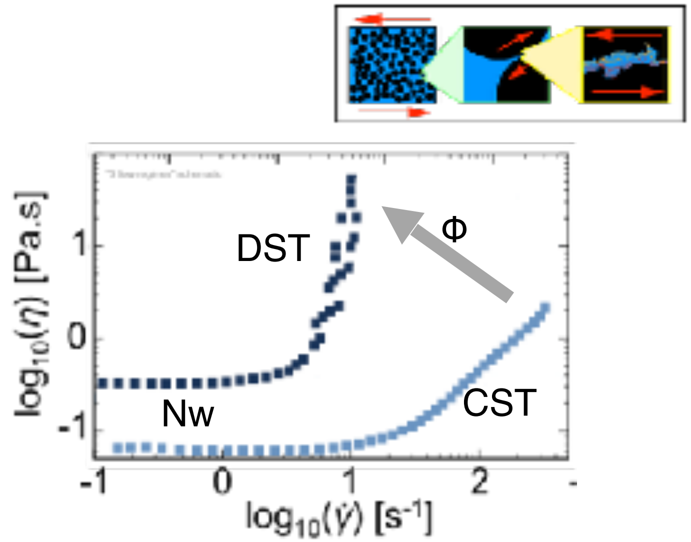


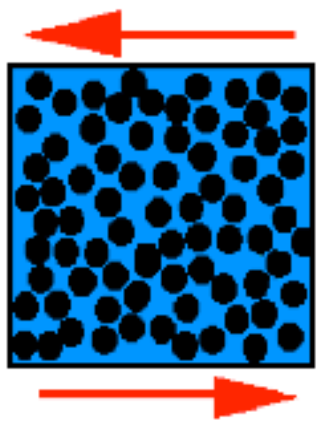
ETH zürich

LSST Laboratory for Surface Science and Technology

Shear Thickening of non-Brownian suspensions

- Newtonian Fluid
- Non-Brownian, Rigid, Hard Spheres
- High Volume Fraction (>50%)
- High Shear





- 3 Flow Regimes:
  - Newtonian Plateau
  - Continuous Shear Thickening
  - Discontinuous Shear Thickening

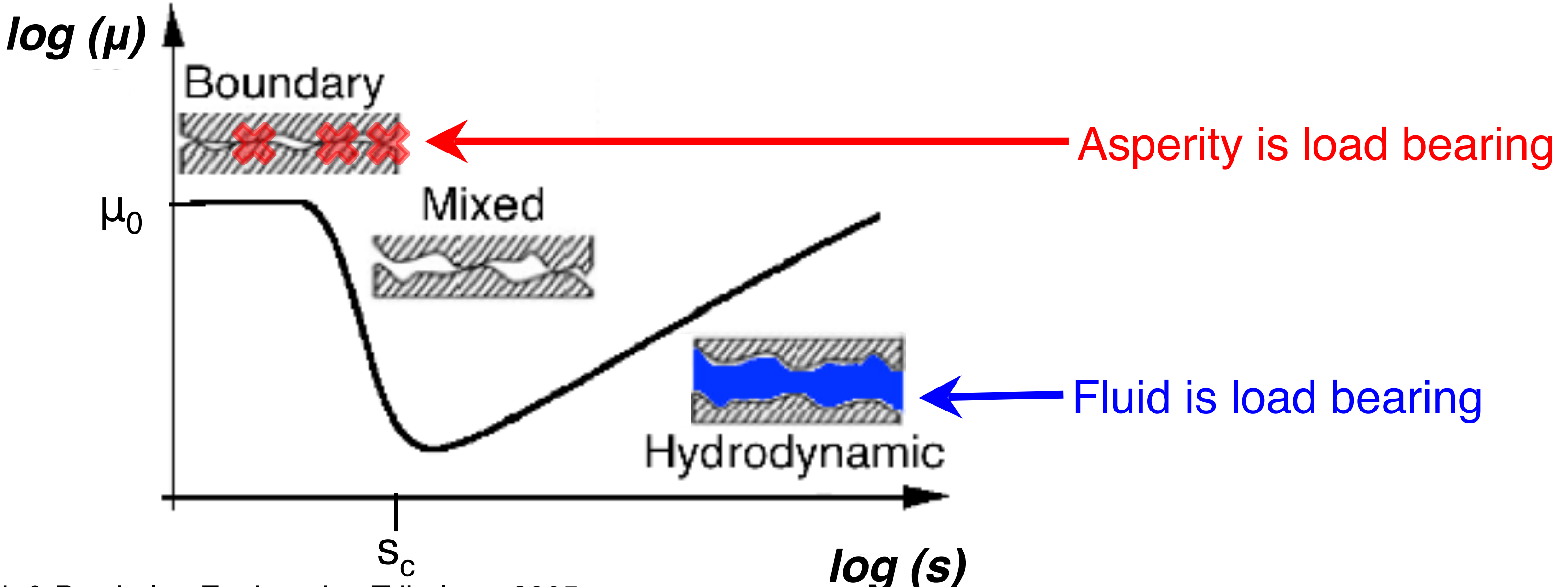
Barnes, J. Rheol, 1989

Theoretical Framework

Particle-contact model

- Lubrication regimes:
  - Sommerfeld number: **s =**

$$\frac{\eta_f R_p v_{sliding}}{F_N}$$

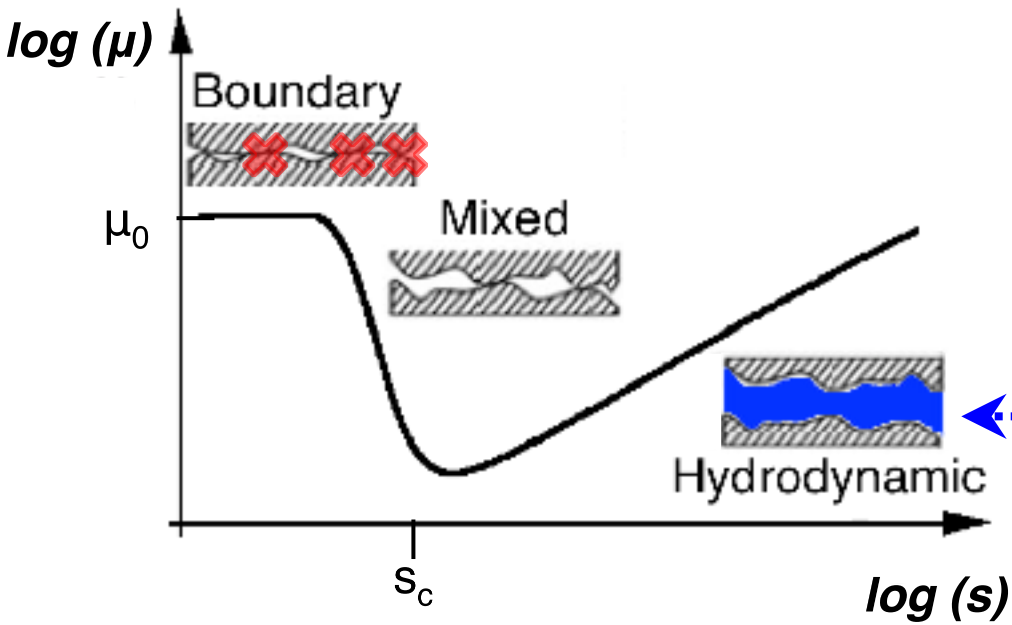


Stachowiak & Batchelor, Engineering Tribology, 2005

Theoretical Framework

Particle-contact model

- Lubrication regimes:
  - Sommerfeld number: **s =** $\frac{\eta_f R_p v_{sliding}}{F_N}$



Corresponding Flow Regimes

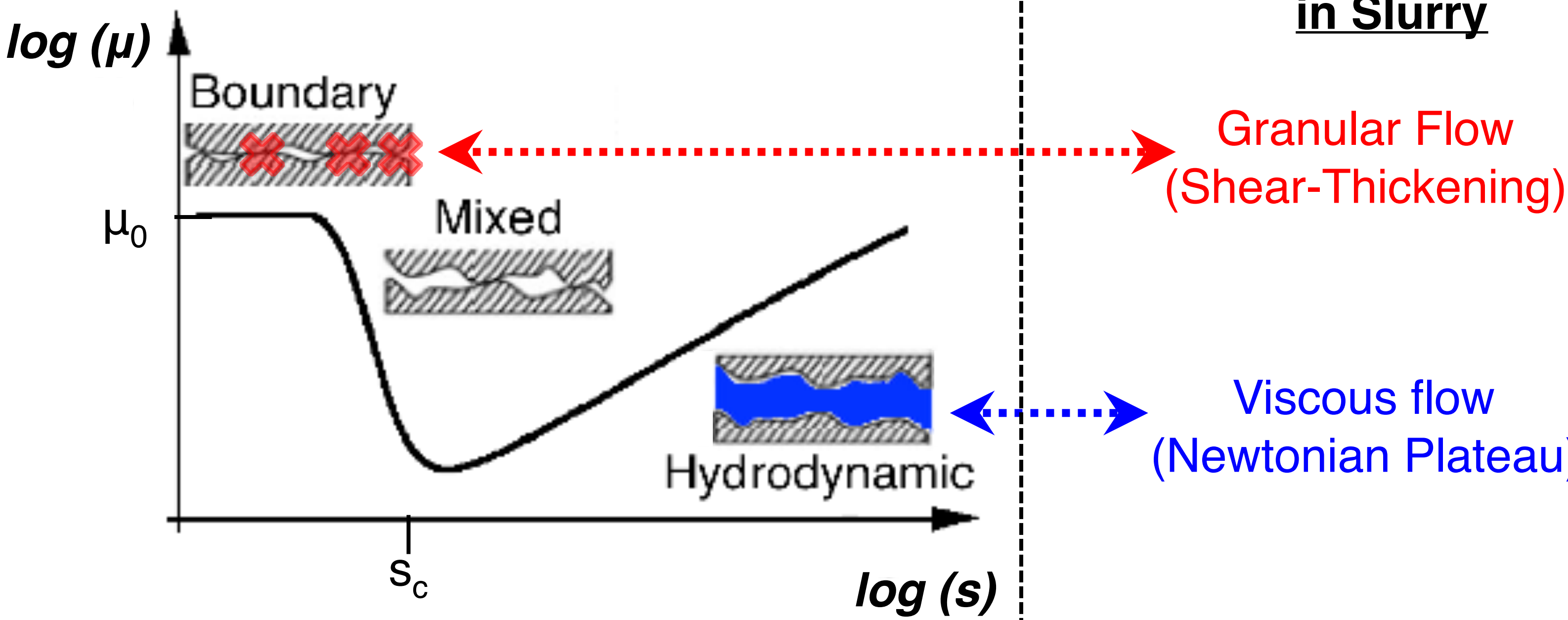
Viscous flow
(Newtonian Plateau)

Theoretical Framework

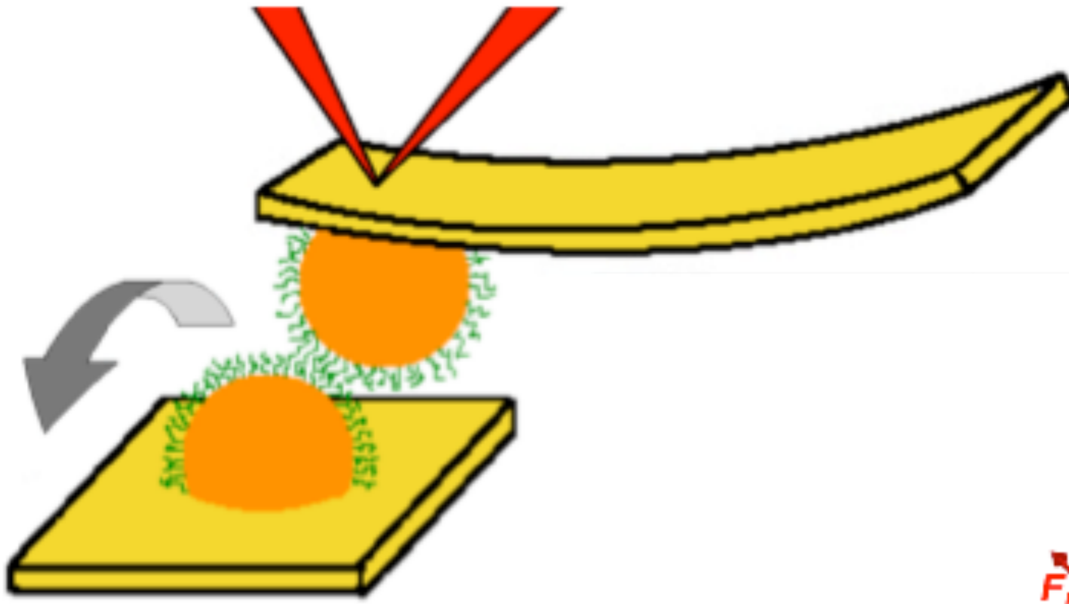
Particle-contact model

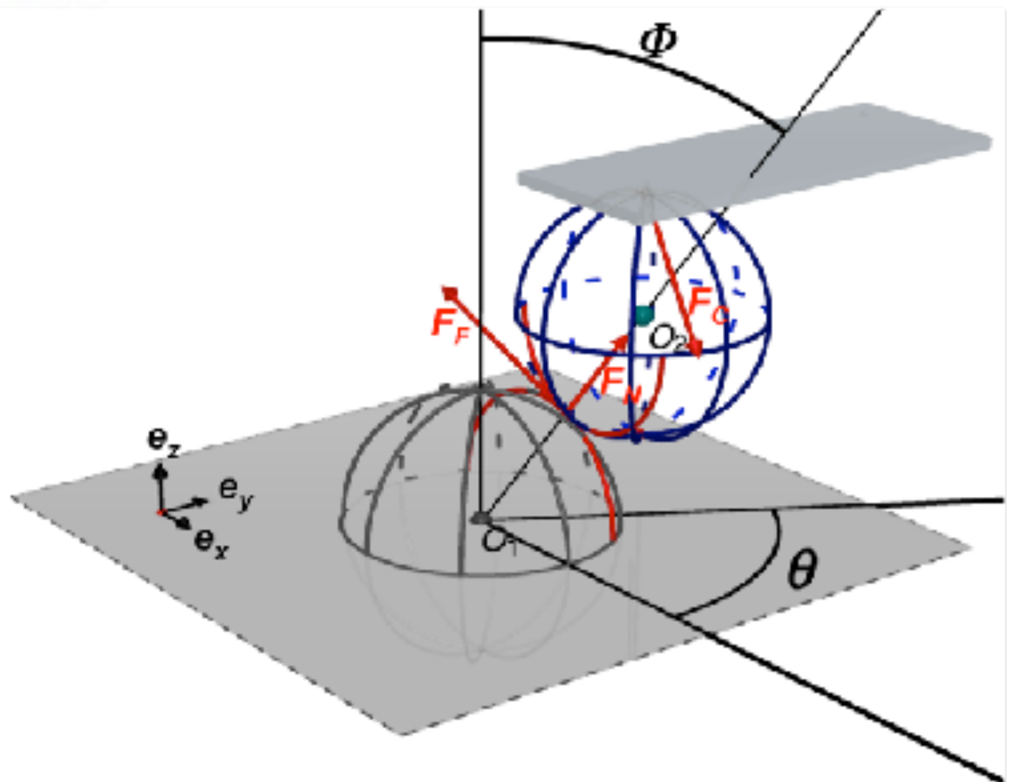
- Lubrication regimes:
  - Sommerfeld number: **s =** $\frac{\eta_f R_p v_{sliding}}{F_N}$

Corresponding Flow Regimes in Slurry



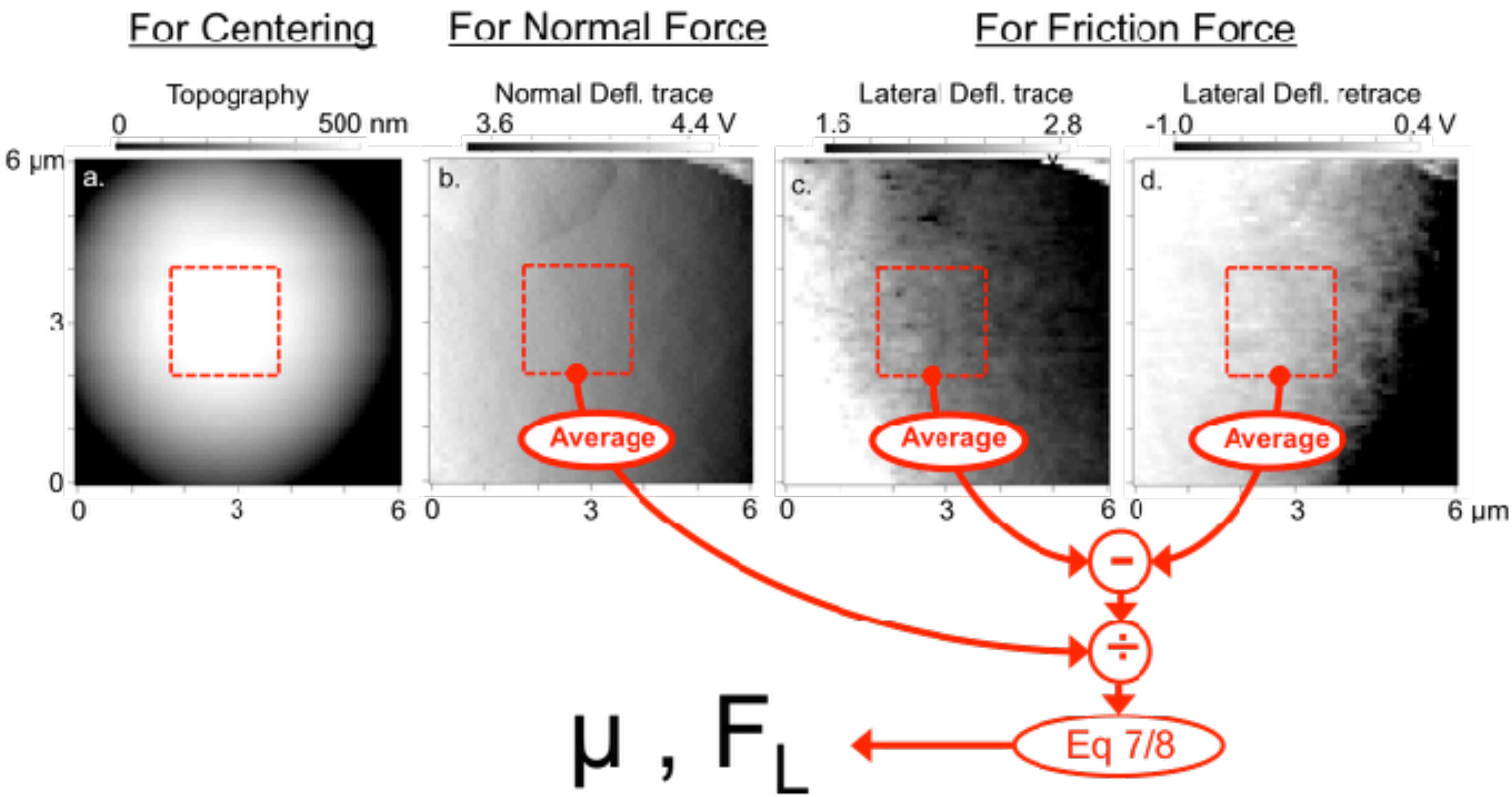
Measuring Friction Between Spheres





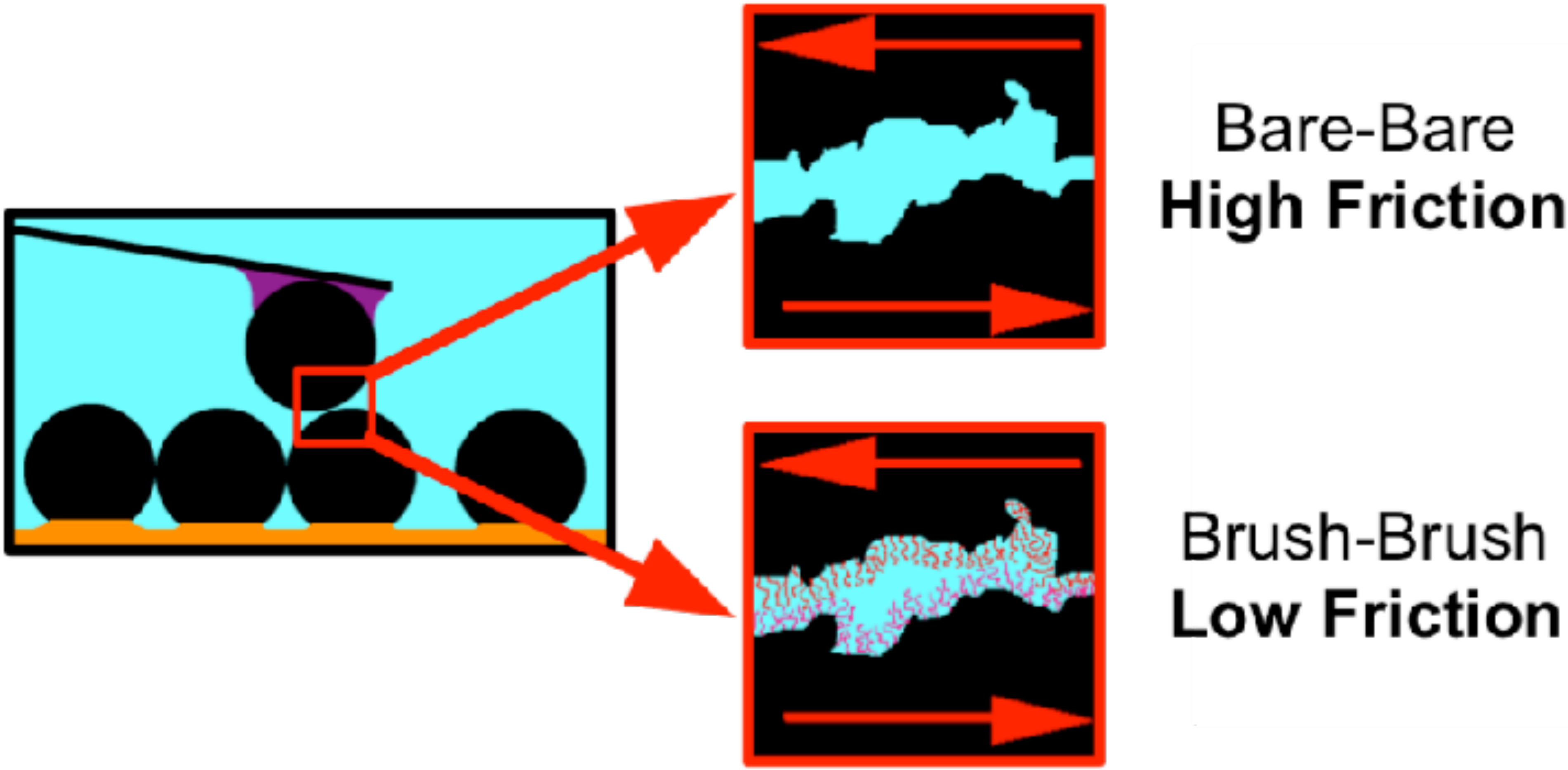
Nicolas Fernandez, Juliette Cayer-Barrioz, Lucio Isa, and Nicholas D. Spencer *Langmuir* (2015) **31**:8809-8817

Measuring Friction Between Spheres



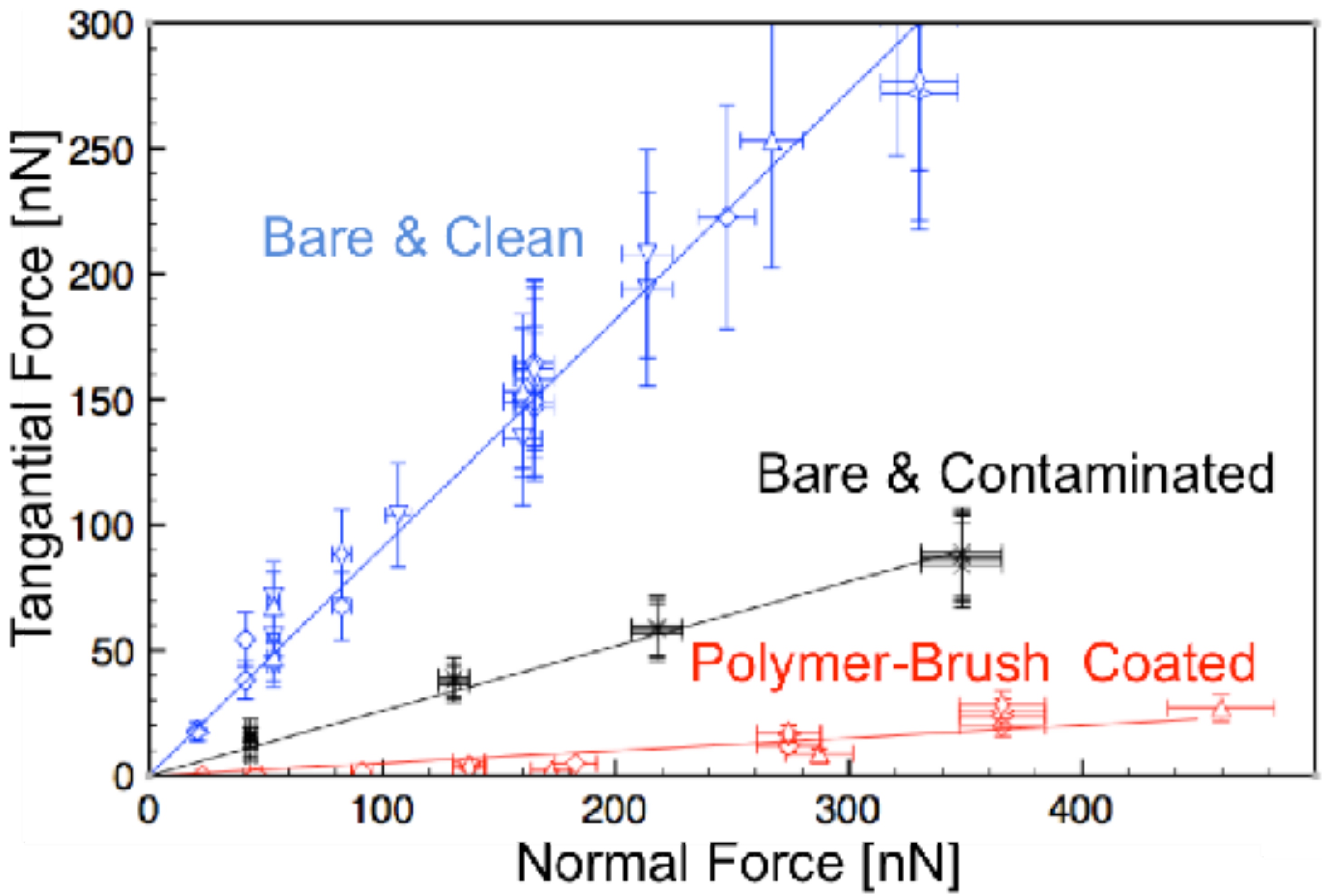
Nicolas Fernandez, Juliette Cayer-Barrioz, Lucio Isa, and Nicholas D. Spencer *Langmuir* (2015) **31**:8809-8817

Measuring Friction Between Spheres



Nicolas Fernandez, Juliette Cayer-Barrioz, Lucio Isa, and Nicholas D. Spencer *Langmuir* (2015) **31**:8809-8817

Measuring Friction Between Silica Spheres

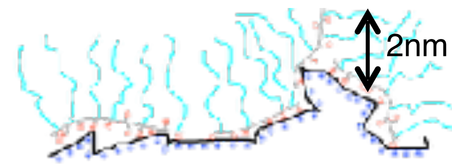


Nicolas Fernandez, Juliette Cayer-Barrioz, Lucio Isa, and Nicholas D. Spencer *Langmuir* (2015) **31**:8809-8817

Experimental Validation

Tribology - Rheology comparison

- μ_0 – tunable system:
  - Quartz Powder (12μm) + PMAA-g-PEG (+ $Ca(OH)_2$)
  - Tunable BL friction coefficient ($\mu_0 = 0.6 \rightarrow 1.1$)



Lee & Spencer, Science, 2008

N Fernandez et al., Physical Review Letters, 111, 108301, 2013

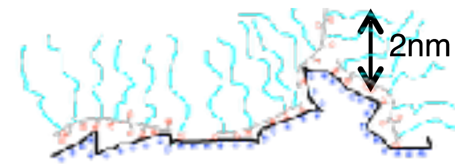
ETH zürich

LSST Laboratory for Surface Science and Technology

Experimental Validation

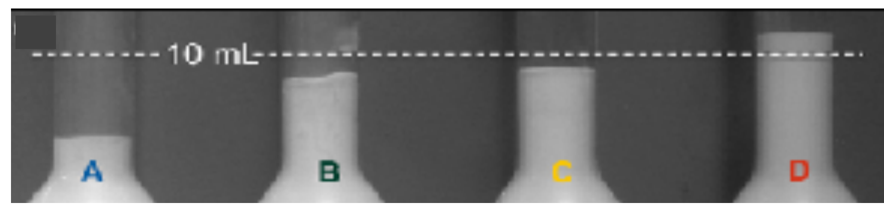
Tribology - Rheology comparison

- μ_0 – tunable system:
  - Quartz Powder (12μm) + PMAA-g-PEG (+ $Ca(OH)_2$)
  - Tunable BL friction coefficient ($\mu_0 = 0.6 \rightarrow 1.1$)



- Φ_{max}^{BL} measurement:
  - Compressive rheology

(Centrifugation up to 2000g)



N Fernandez et al., Physical Review Letters, 111, 108301, 2013

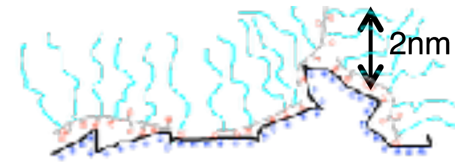
ETH zürich

LSST

Experimental Validation

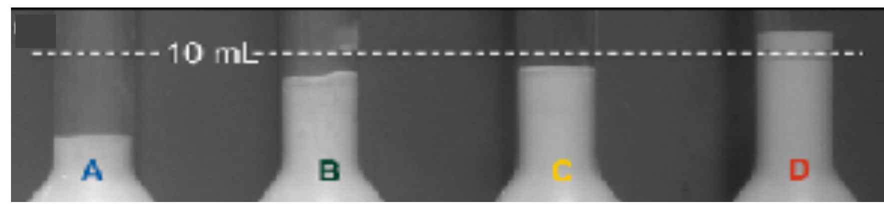
Tribology - Rheology comparison

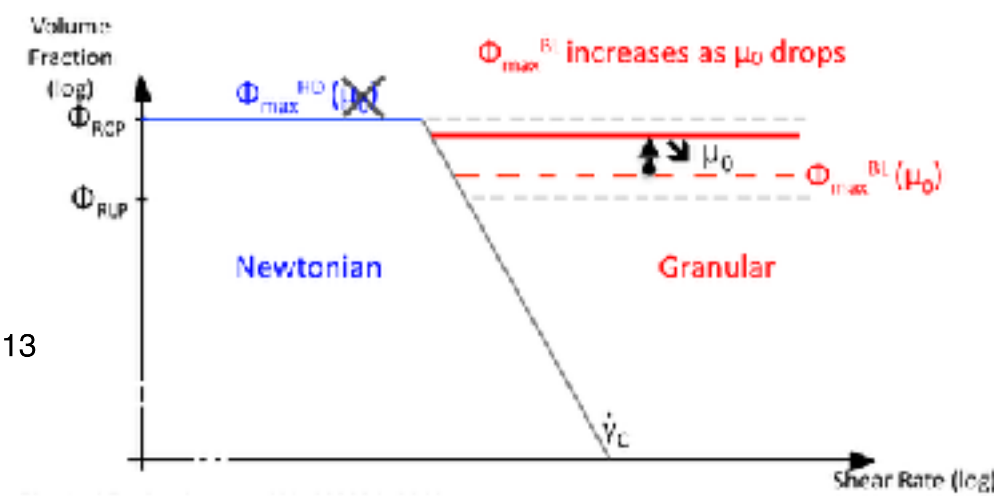
- μ_0 – tunable system:
  - Quartz Powder (12μm) + PMAA-g-PEG (+ $Ca(OH)_2$)
  - Tunable BL friction coefficient (μ_0 = 0.6 → 1.1)



- Φ_{max}^{BL} measurement:
  - Compressive rheology

  (Centrifugation up to 2000g)



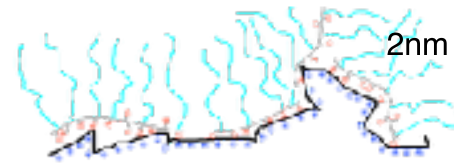


N Fernandez et al., Physical Review Letters, 111, 108301, 2013

Experimental Validation

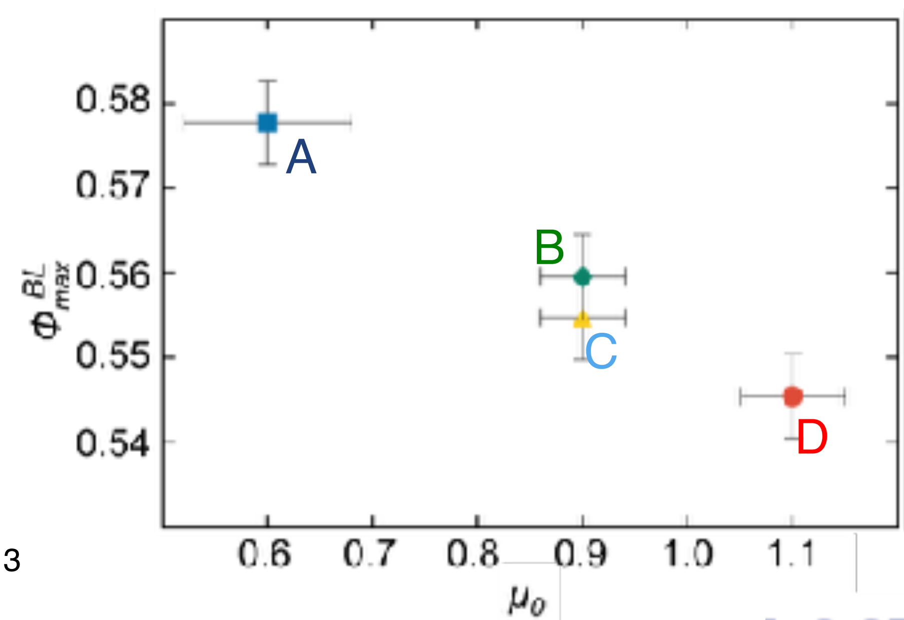
Tribology - Rheology comparison

- μ_0 – tunable system:
  - Quartz Powder (12μm) + PMAA-g-PEG (+ $Ca(OH)_2$)
  - Tunable BL friction coefficient ($\mu_0 = 0.6 \rightarrow 1.1$)



- Φ_{max}^{BL} measurement:
  - Compressive rheology

(Centrifugation up to 2000g)



Silbert, Soft Matter, 2010

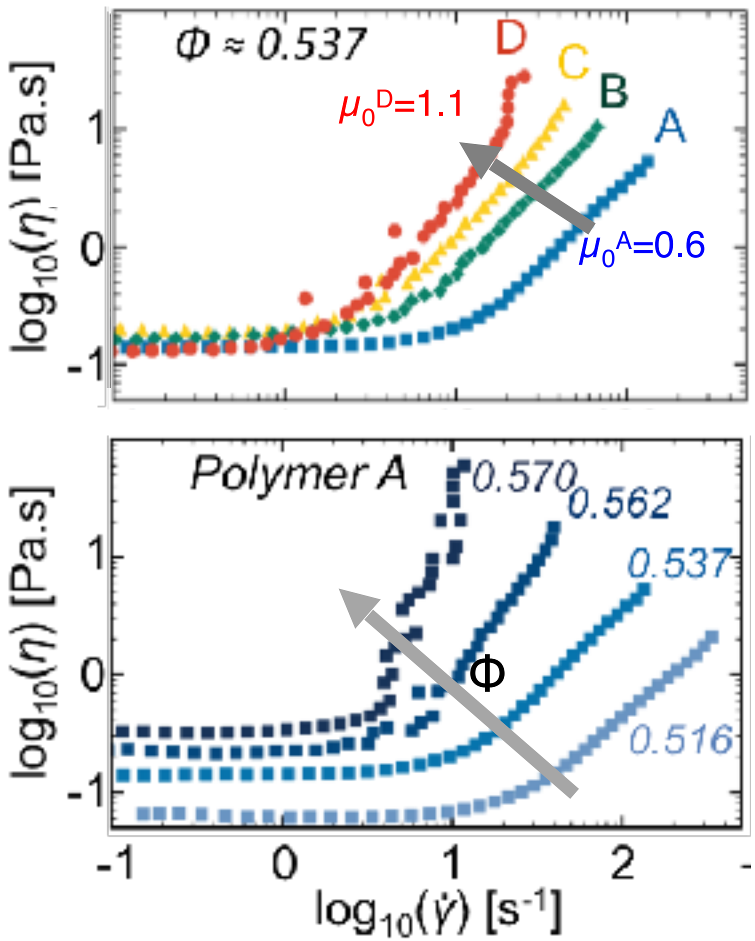
N Fernandez et al., Physical Review Letters, 111, 108301, 2013

ETH zürich

LSST

Experimental Validation

Tribology - Rheology comparison



Nw/ST Transition with $\dot{\gamma}$

CST/DST Transition with μ_0

CST/DST Transition with Φ

ETH zürich

LSST

Conclusions: Dense flows—Friction and Shear Thickening

Conclusions: Dense flows—Friction and Shear Thickening

Conclusions: Dense flows—Friction and Shear Thickening

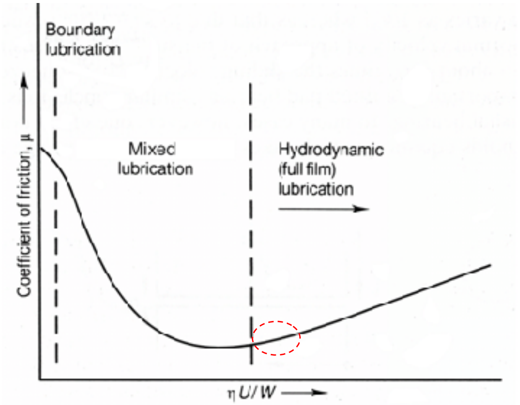
- Direct connection between the transitions in flow regimes and those in lubrication regimes

Conclusions: Dense flows—Friction and Shear Thickening

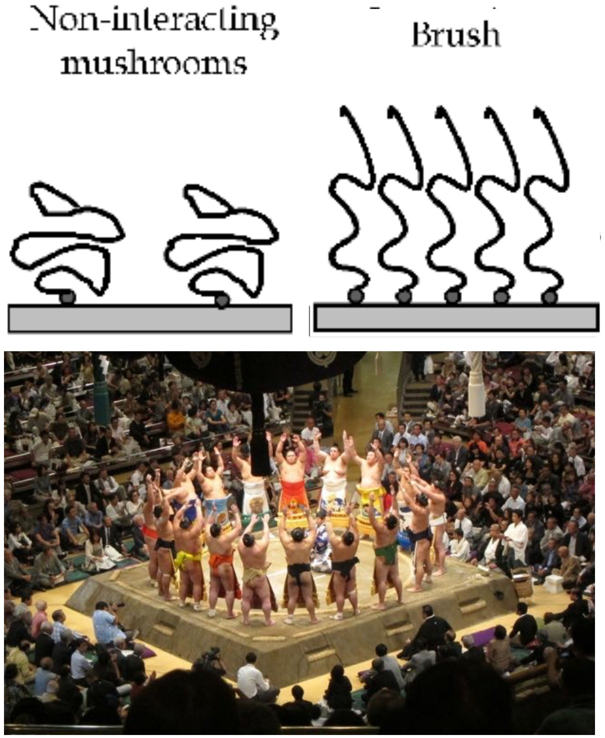
- Direct connection between the transitions in flow regimes and those in lubrication regimes
- Friction determines the maximum volume fraction in boundary-lubricated flows

Conclusions: Dense flows—Friction and Shear Thickening

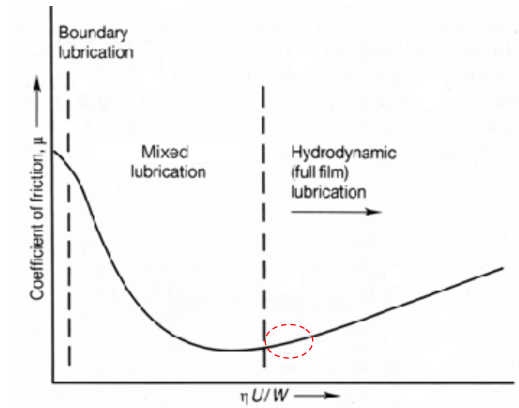
- Direct connection between the transitions in flow regimes and those in lubrication regimes
- Friction determines the maximum volume fraction in boundary-lubricated flows
- Onset and nature of the shear-thickening transition can be controlled by controlling the lubrication between particles
- **can optimised polymer-brush lubricant additive to achieve better flow properties!**



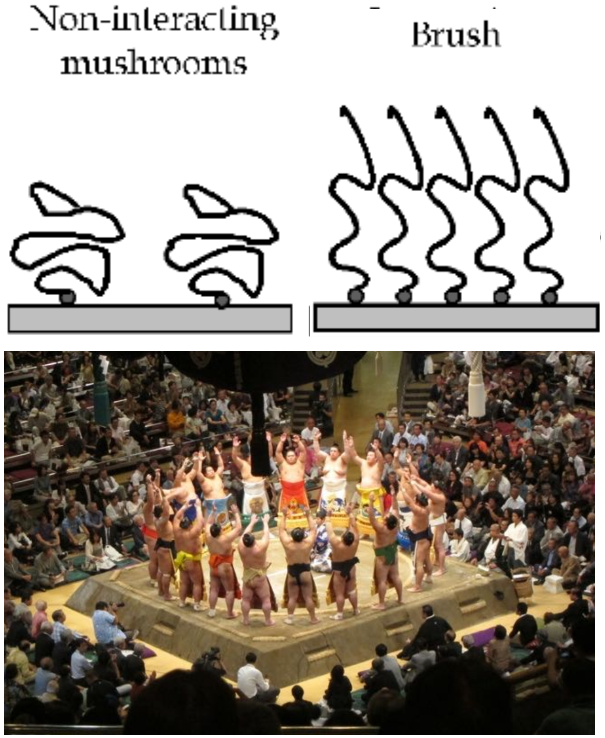
Modes of Lubrication



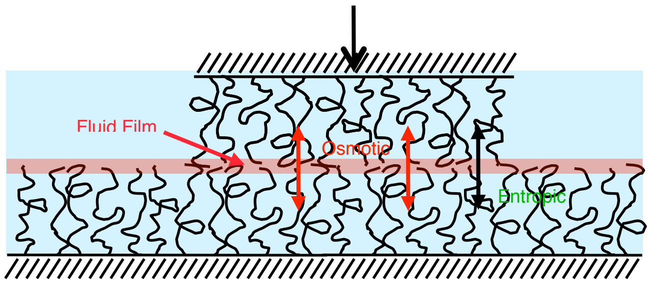
Polymer Brushes



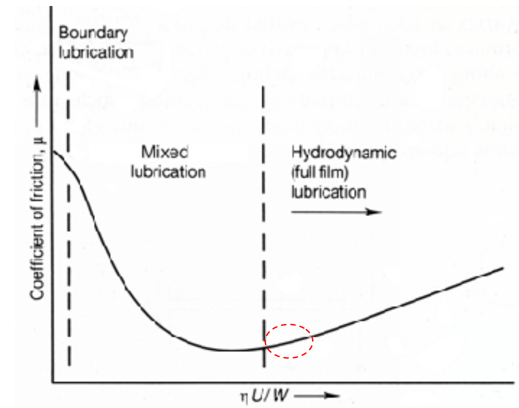
Modes of Lubrication



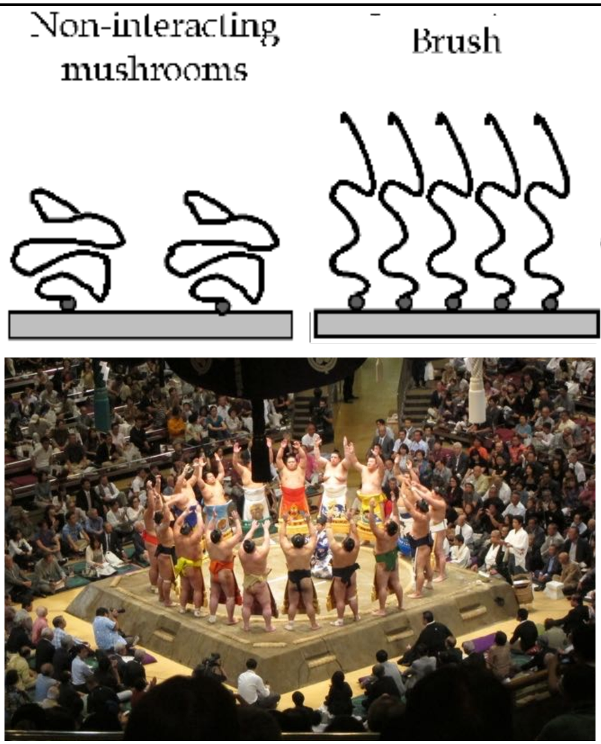
Polymer Brushes



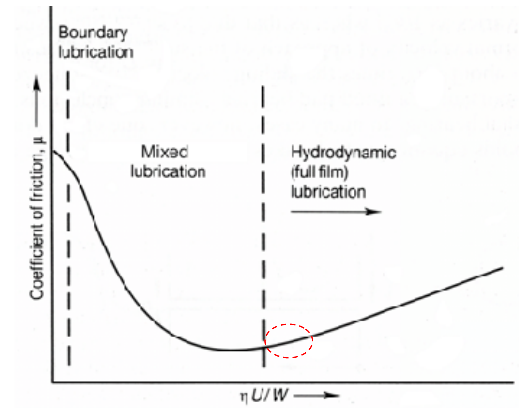
Enforced Fluid-Film Lubrication



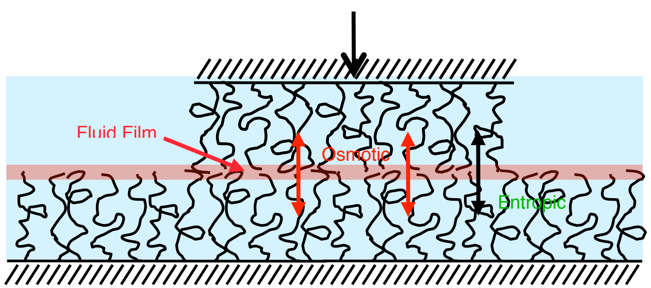
Modes of Lubrication



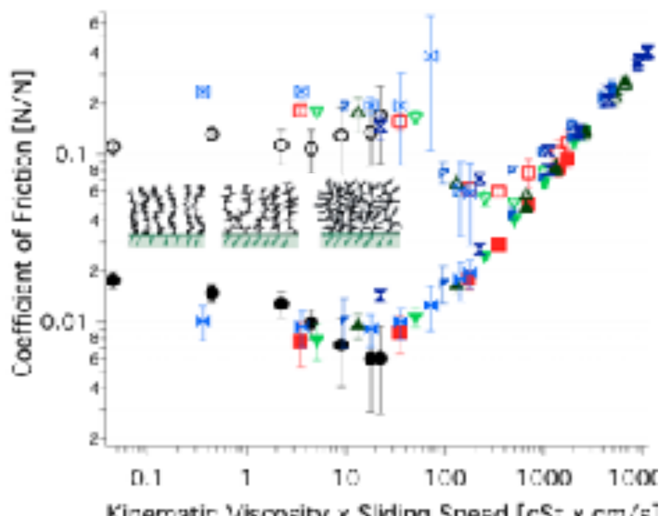
Polymer Brushes



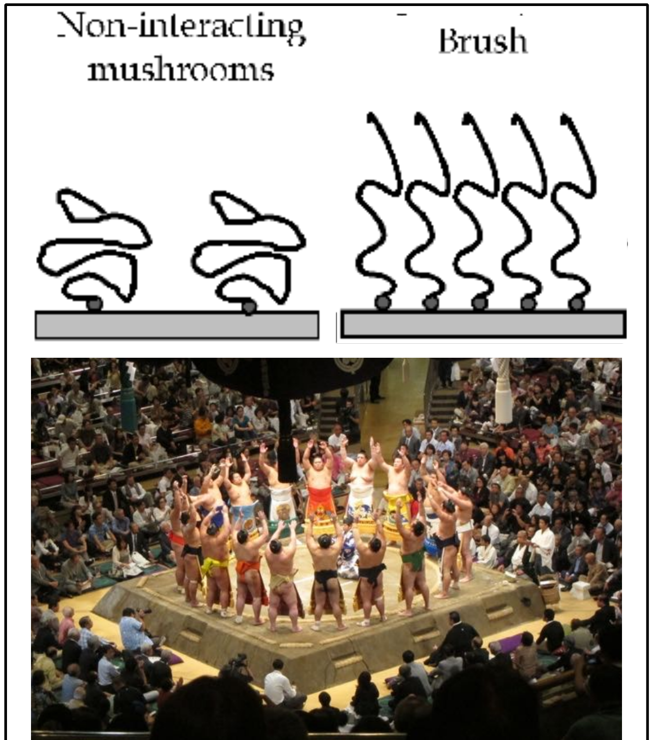
Modes of Lubrication



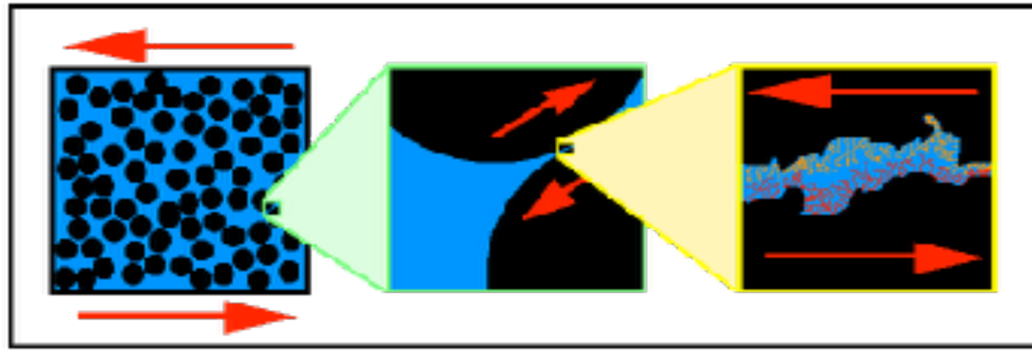
Enforced Fluid-Film Lubrication



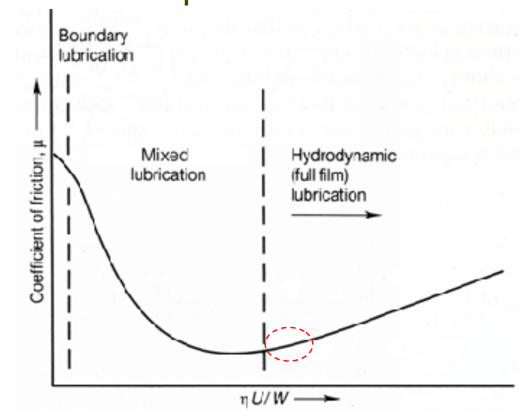
Brushy Stribeck Curve!



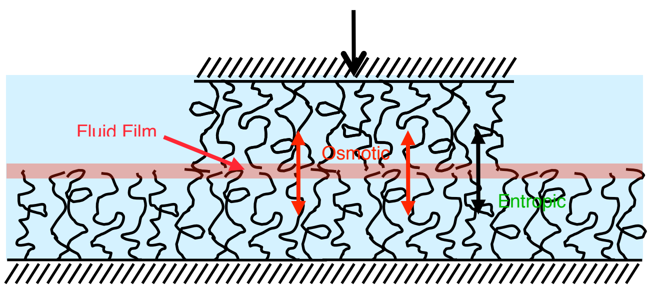
Polymer Brushes



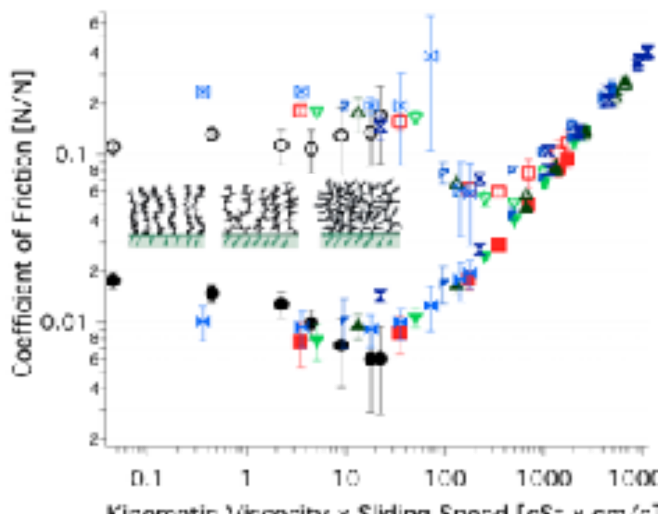
Brushes and Granular Suspensions



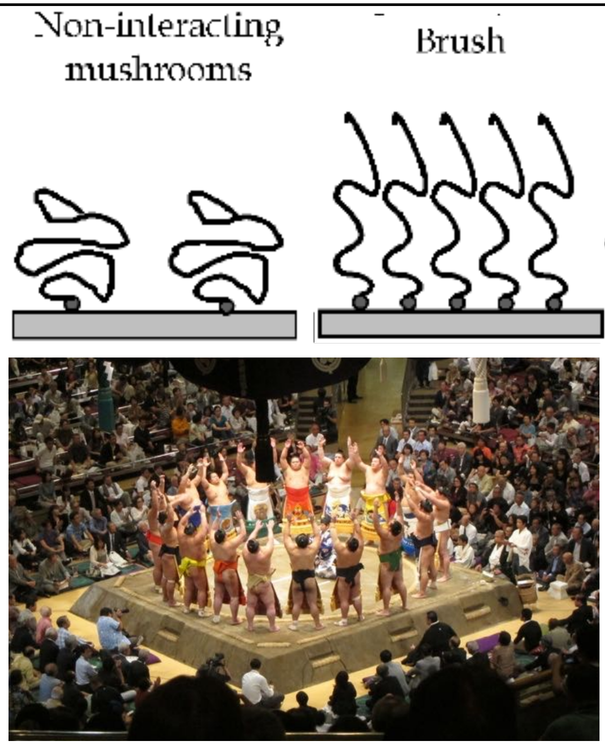
Modes of Lubrication



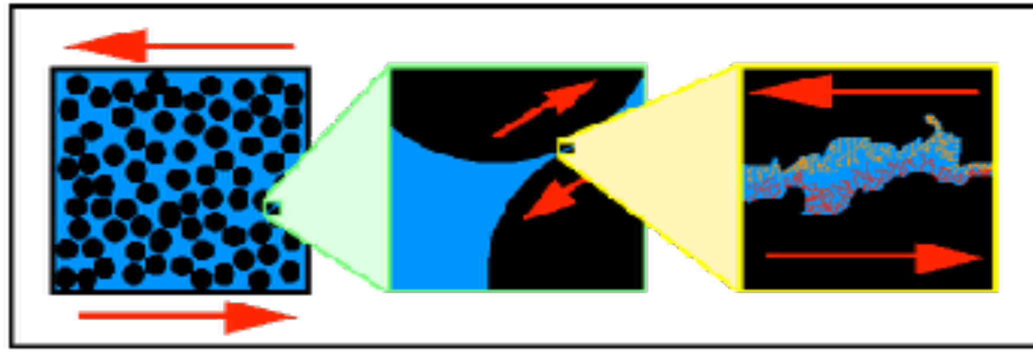
Enforced Fluid-Film Lubrication

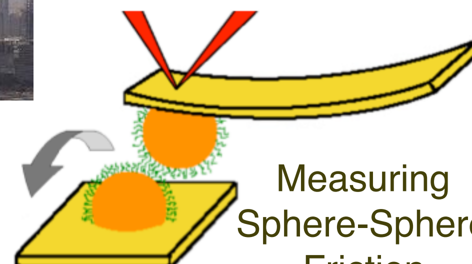


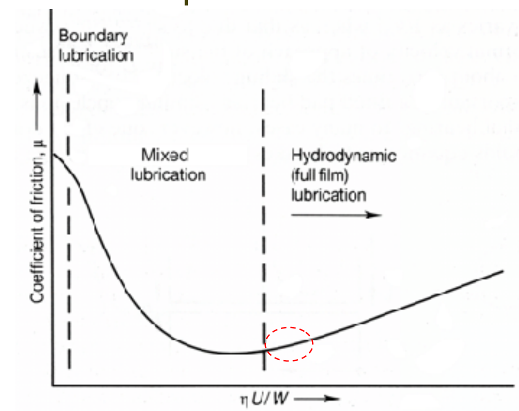
Brushy Stribeck Curve!



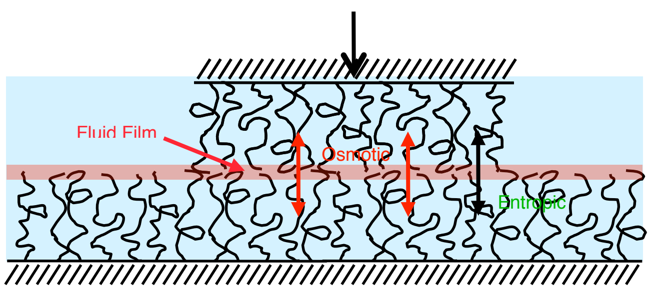
Polymer Brushes


Brushes and Granular Suspensions

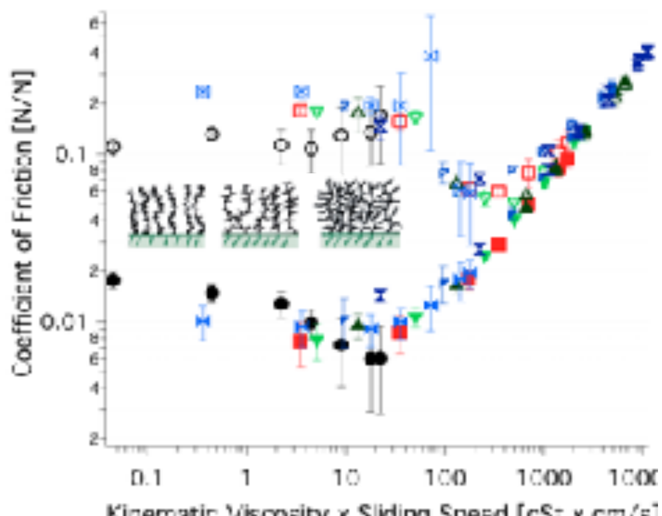

Measuring Sphere-Sphere Friction



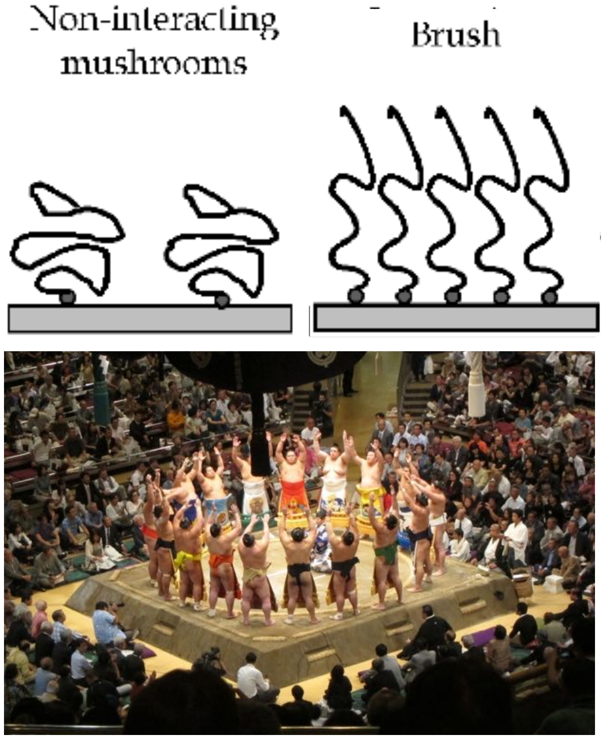
Modes of Lubrication



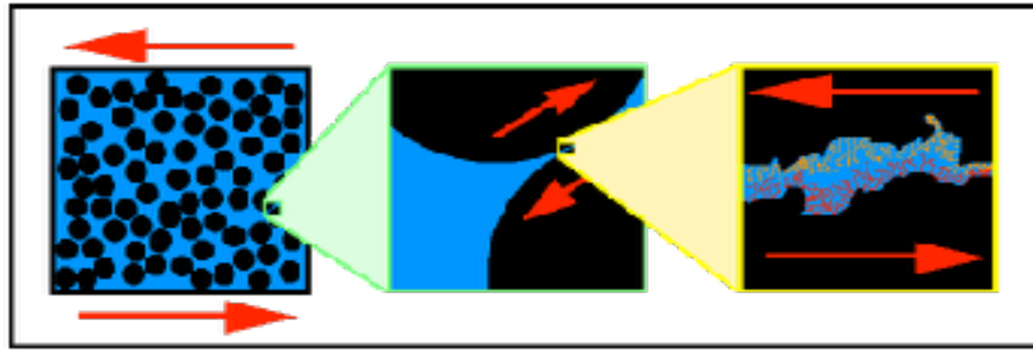
Enforced Fluid-Film Lubrication



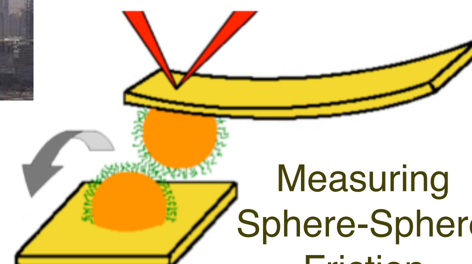
Brushy Stribeck Curve!



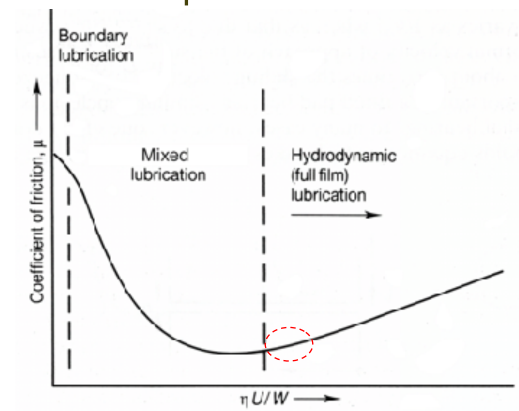
Polymer Brushes



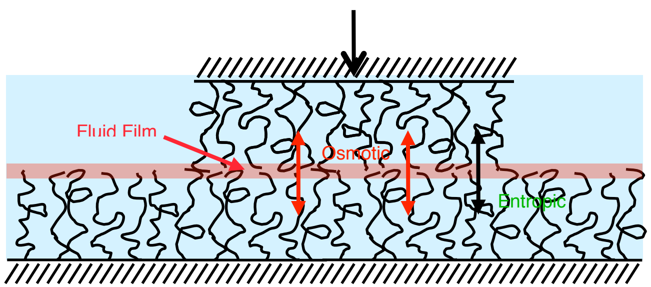
Brushes and Granular Suspensions



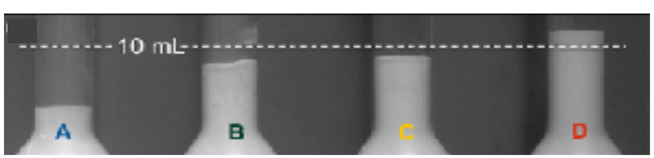
Measuring Sphere-Sphere Friction



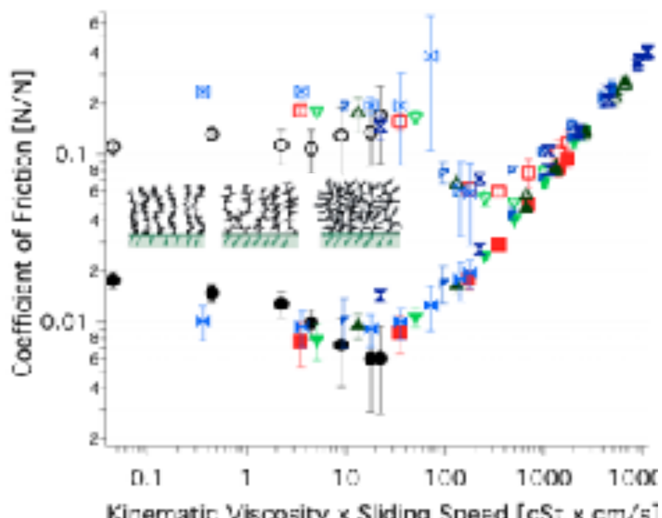
Modes of Lubrication



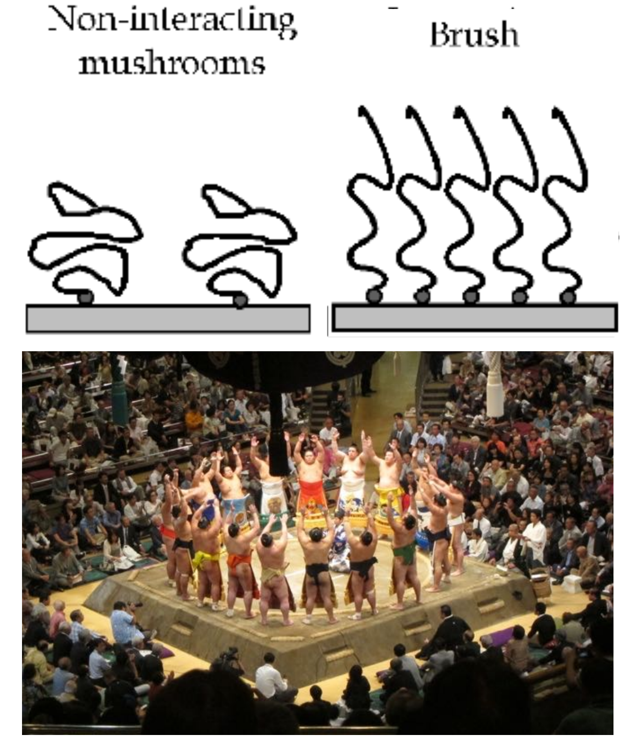
Enforced Fluid-Film Lubrication



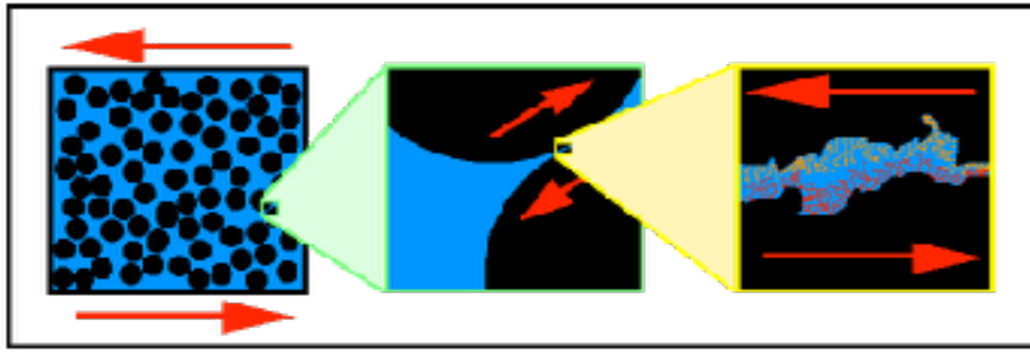
Centrifuge Measurements of Φ_{max}^{BL}



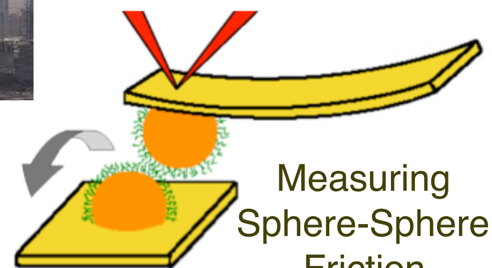
Brushy Stribeck Curve!



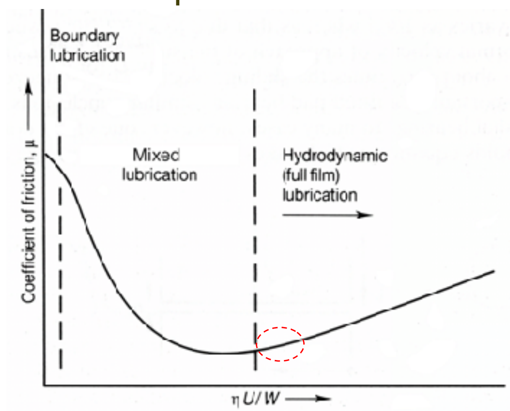
Polymer Brushes



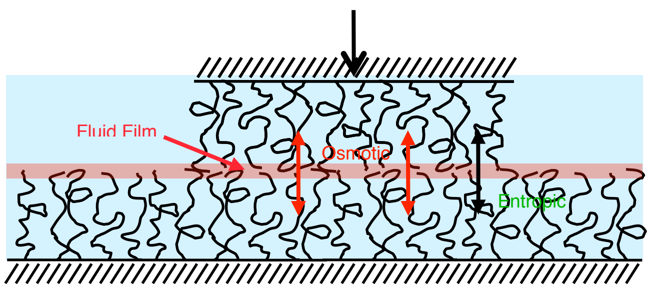
Brushes and Granular Suspensions



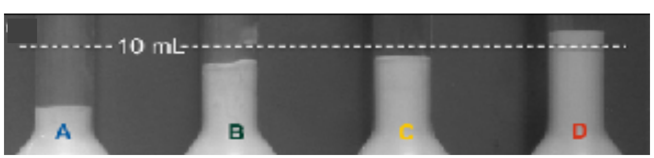
Measuring Sphere-Sphere Friction



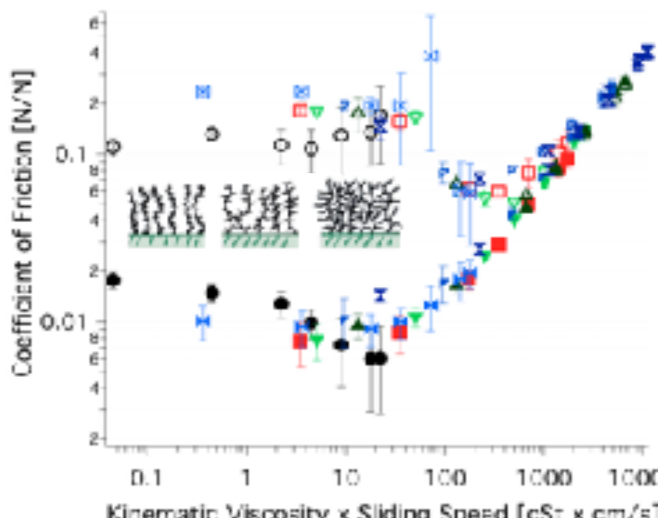
Modes of Lubrication



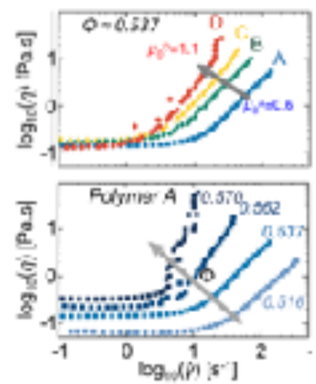
Enforced Fluid-Film Lubrication



Centrifuge Measurements of Φ_{max}^{BL}



Brushy Stribeck Curve!



Tribology Influences Rheology

LSST and ISA, Figueres, Spain, August, 2017