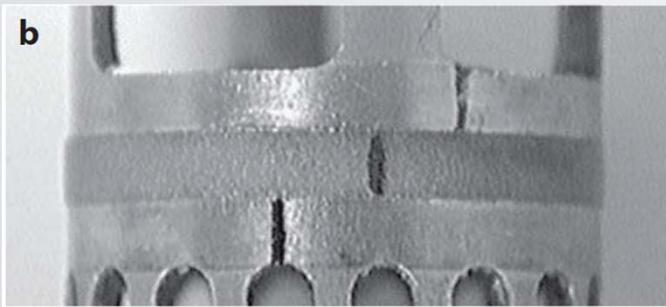
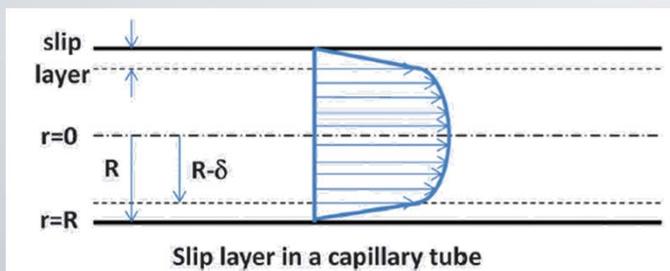


Review of Wall Slip for Concentrated Dispersed Systems



Kalyon & Aktas *Annu Rev Chem Biomol Eng* 2014



Hatzikiriakos *Soft Matter* 2015

Roger T. Bonnecaze

McKetta Dept. of Chemical Engineering

Texas Materials Institute

The University of Texas at Austin

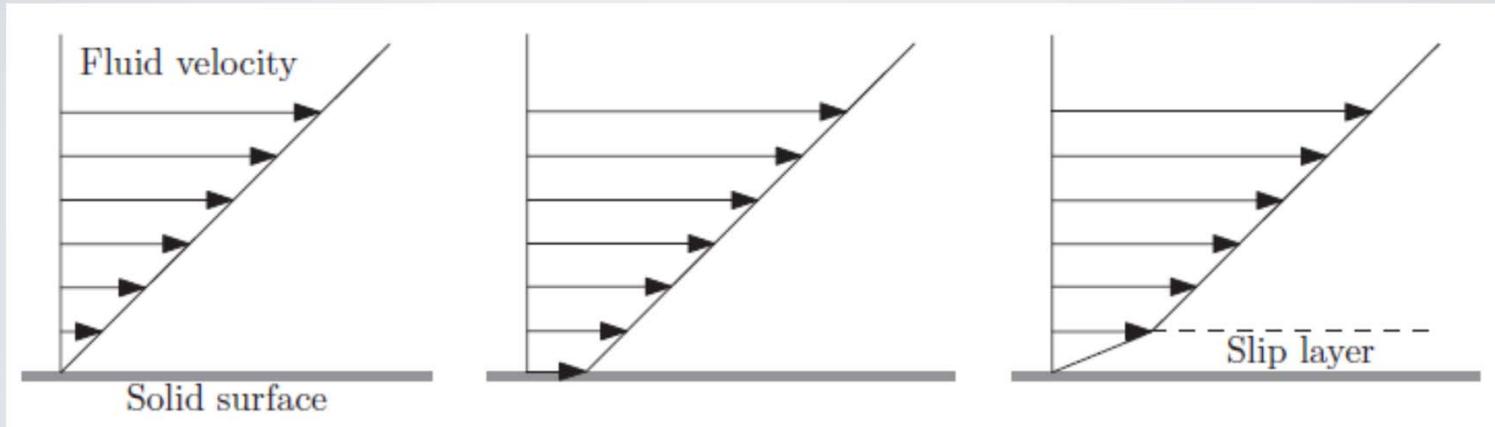
Outline

- What is wall slip?
- Is it useful or detrimental?
- What affects the magnitude of wall slip?
- How to model multiphase flows with wall slip?
- Is wall slip fundamentally different in extrusion versus injection molding?
- What are the research and practical opportunities?

WHAT IS WALL SLIP?

No-Slip, True Slip, Apparent Slip

Sochi Polymer Reviews 2011



No-slip: Fluid moves at same speed as surface

At stationary surface

$$\mathbf{u} = 0$$

$$\mathbf{u} \cdot \mathbf{t} = 0$$

True slip: Fluid moves tangentially relative to surface

(e.g., high mw polymers)

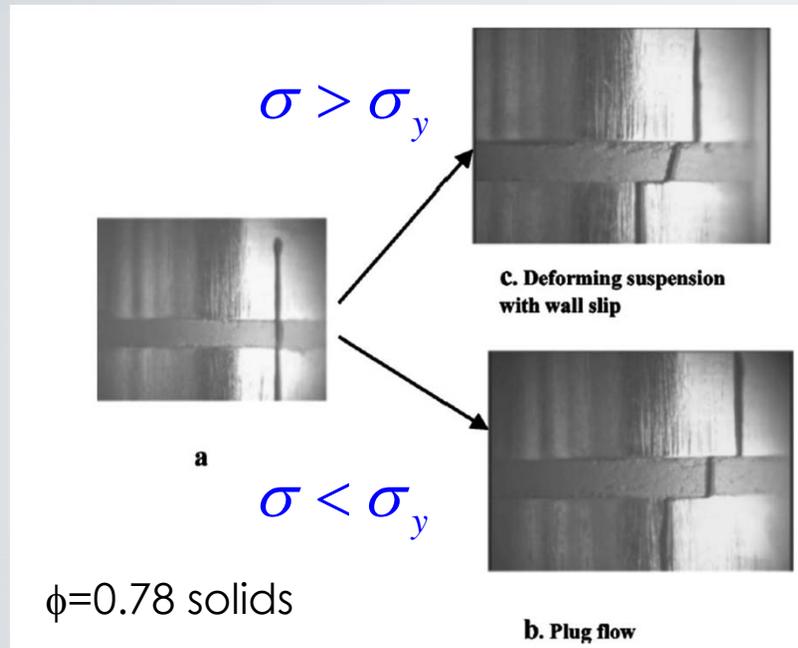
$$\mathbf{u} \cdot \mathbf{t} = U_s \longleftarrow \text{Slip velocity}$$

Apparent slip: Rapid variation of shear rate over small distance near the surface (e.g., dispersions)

Slip occurs in practice for complex fluids, e.g., polymer solutions, melts, suspensions, emulsions foams, due to physical or chemical interactions with the surface

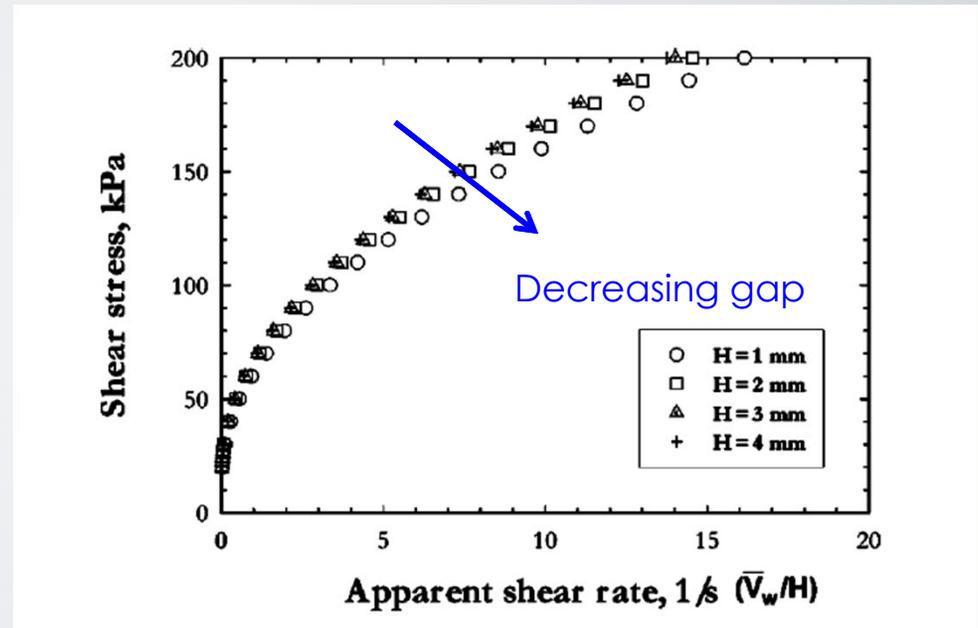
Observations of Wall Slip (Shear Flow Hard Particles)

Direct Observation



- Plug flow of suspension in gap when $\sigma < \sigma_y$
- Shear flow of suspension in gap when $\sigma > \sigma_y$

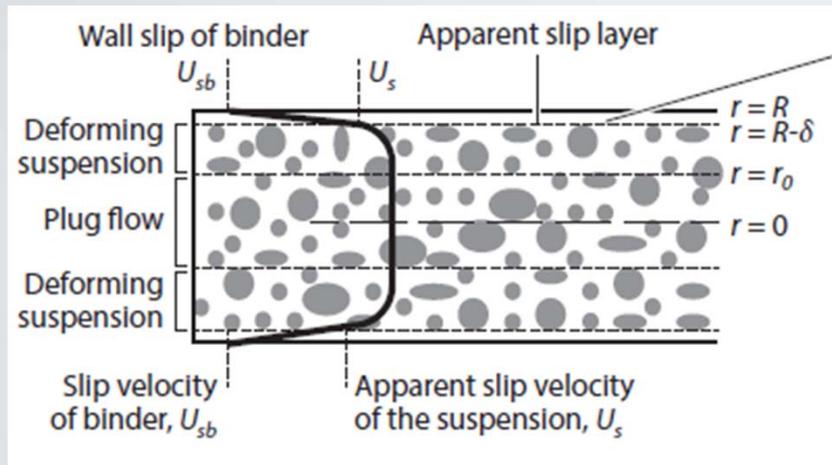
Rheometric Signature



- Flow curves depend on gap between rheometer surfaces
- Deviation (wall slip) largest for smallest gaps

Observations of Wall Slip (Pressure Driven Flow Hard Particles)

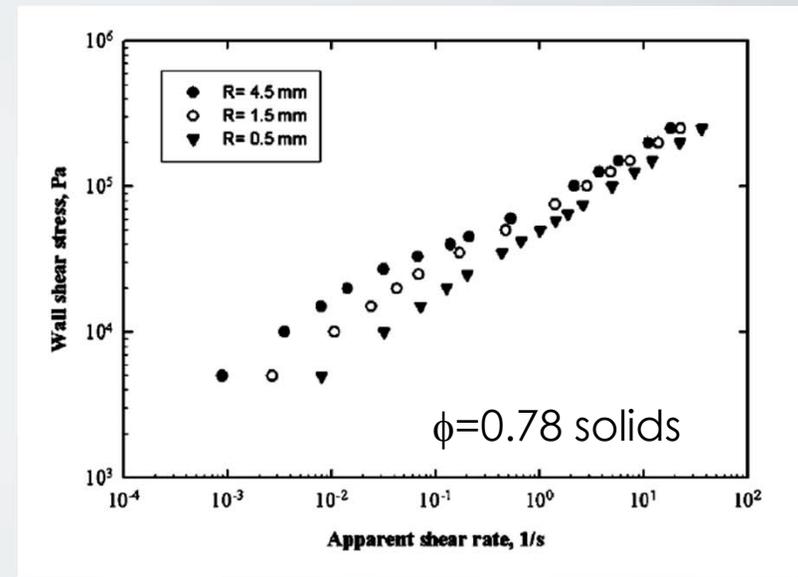
Flow Field



Kalyon & Aktas *Annu Rev Chem Biomol Eng* 2014

- Plug flow of suspension when $\sigma_w < \sigma_y$
- Regions of shear flow of suspension when $\sigma_w > \sigma_y$

Rheometric Signature



- Flow curves depend on gap between rheometer surfaces
- Deviation (wall slip) largest for smallest gaps

Kalyon *J Rheol* 2005

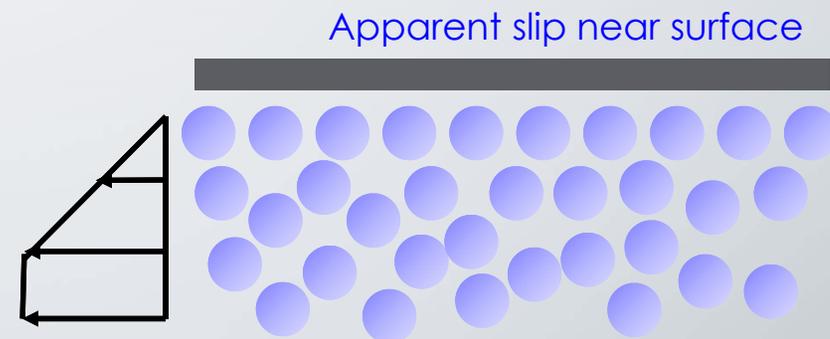
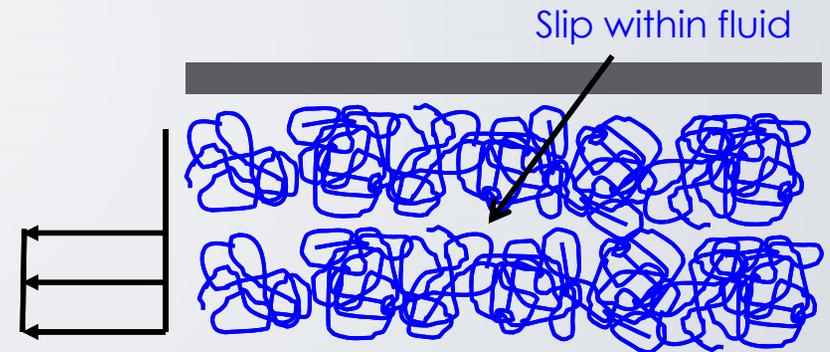
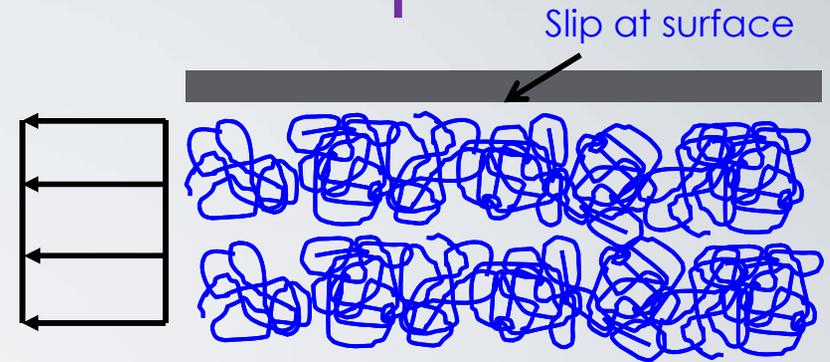
Observations of Wall Slip (Measurement Techniques)

Method	Spatial Resolution (μm)	Temporal Resolution (s)
Laser Doppler Velocimetry	50-100	10-100
Digital Imaging / Particle Tracking Methods	1-10	0.001-10
Ultrasonic Velocimetry	~ 40	0.02 - 2
Magnetic Resonance Imaging	~ 50	~ 10
Near-Field Optical Methods (Total Internal Reflection)	~ 0.050	0.01-1

Ultrasonic and MRI suited for opaque systems

Causes of Wall Slip

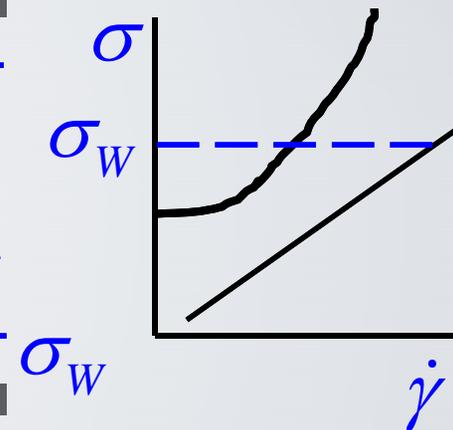
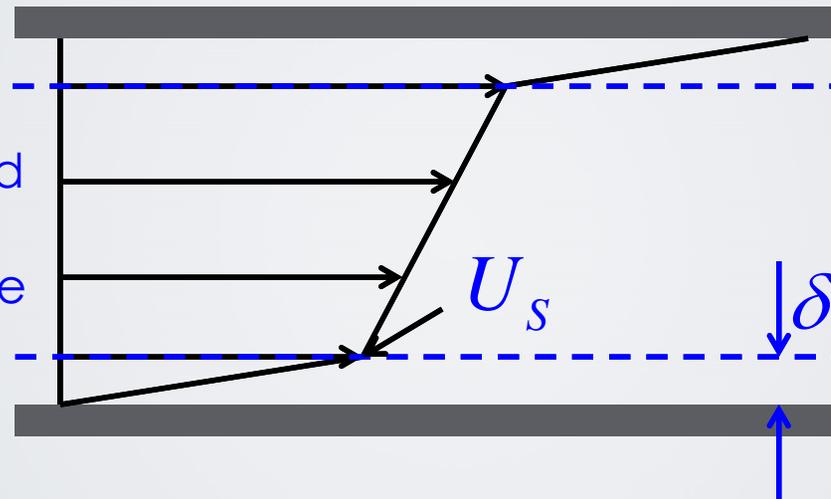
- Adhesive failure with wall surface
- Cohesive failure with the material
- Near wall variation of fluid microstructure and rheology



Wall Slip as an Extreme Form of Shear Banding

Different microstructure and flow curve \rightarrow different shear rate

Structure near wall different from bulk



For a Newtonian suspending fluid or binder, for example:

$$\sigma_w = \frac{\eta}{\delta} U_s \quad U_s = \frac{\delta}{\eta} \sigma_w$$

Constant shear stress σ across gap for steady shear

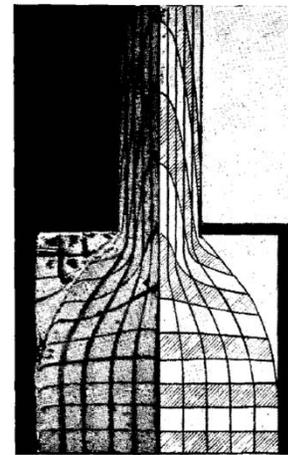
**IS WALL SLIP USEFUL OR
DETRIMENTAL?**

Benefits of Wall Slip

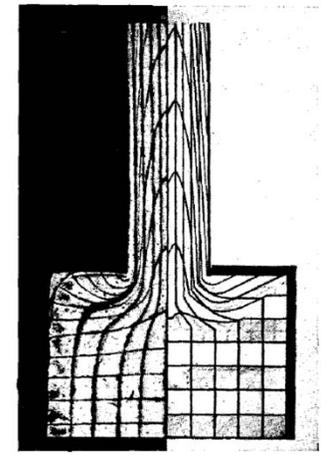
- Reduced energy for conveyance
- Reduced dead zones
- Lower pressure drops
- Faster mold filling
- Smoother extrudates
- Reduced particle-binder separation due to less differential shear rates and particle migration

Rough/No-Slip

Smooth/Slip

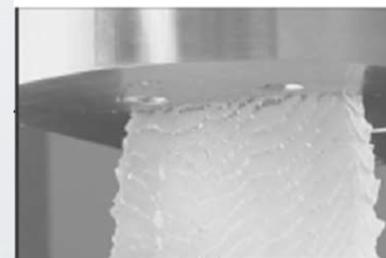


(a)



(b)

Green *Phil. Mag.* 1951



PDMS

$\phi = 0$



$\phi = 0.4$

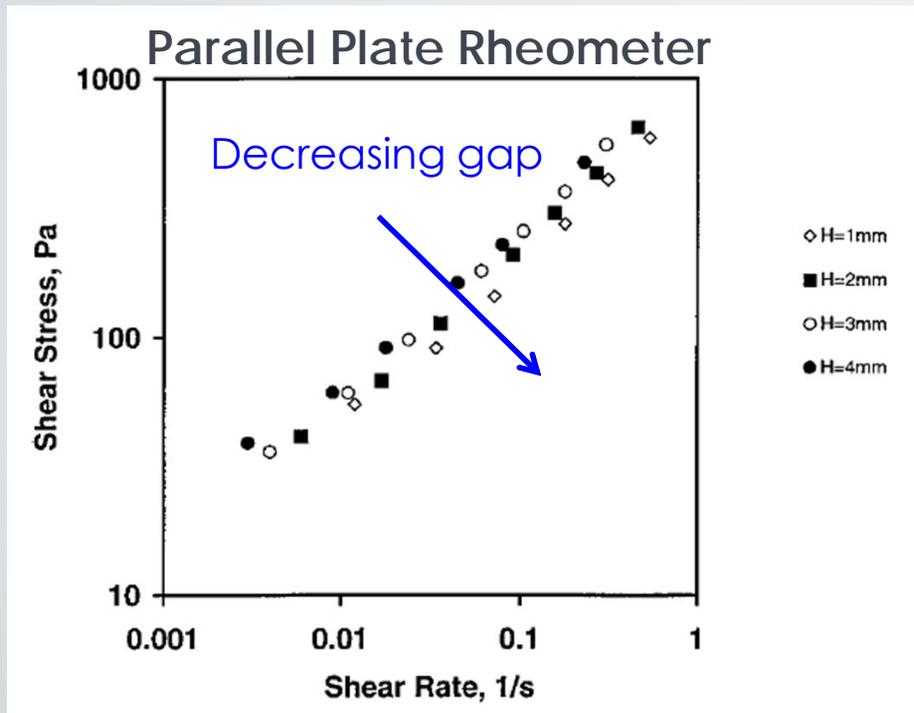
Glass beads

Birinci & Kalyon

J. Rheol 2016

Rheology Exhibits Gap or Capillary Radius Dependency

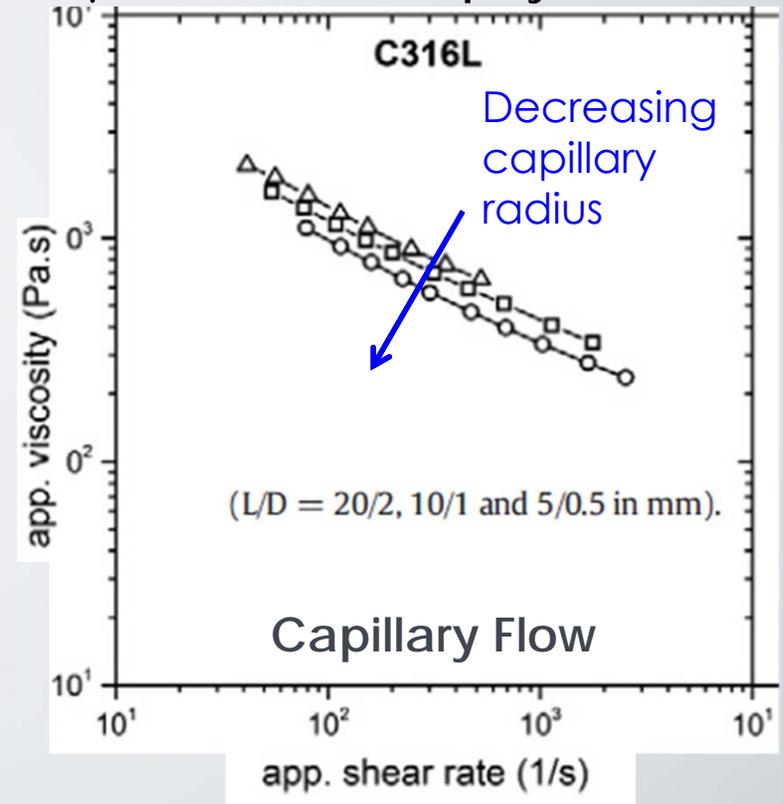
$\phi = 0.63$ 50 μm glass beads in polybutadiene



Flow curve decreases with decreasing gap due to wall slip

Soltani & Yilmazer *J App Poly Sci* 1998

5 μm steel beads in polymer binder



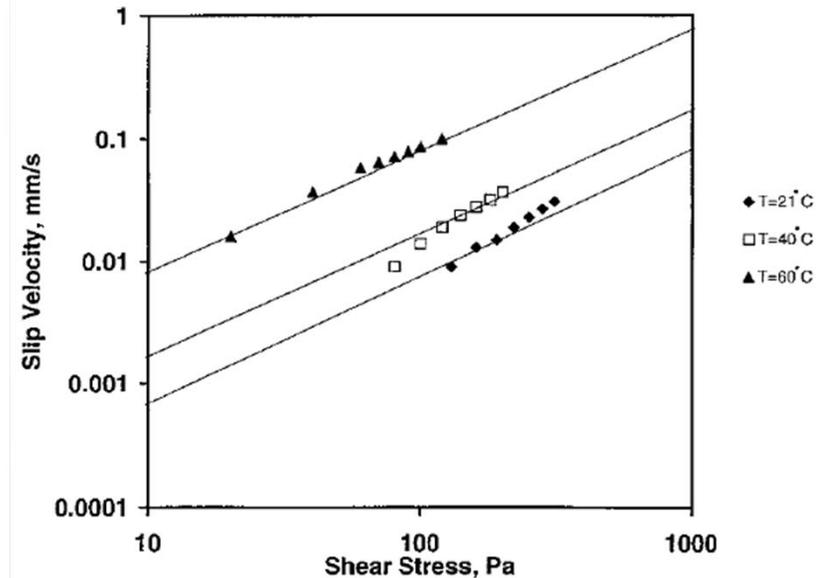
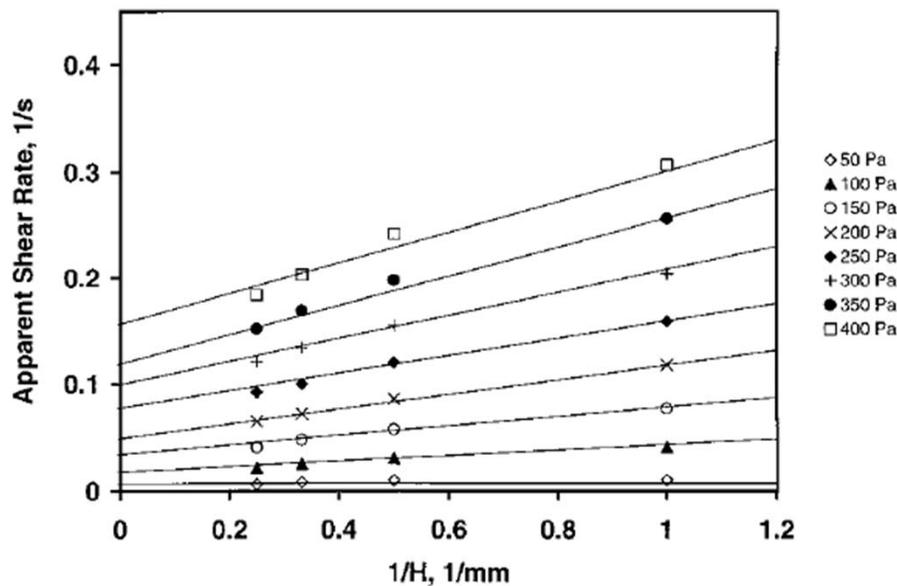
Apparent viscosity decreases with decreasing radius due to wall slip

Sanetrik et al *Powder Tech* 2018

Correction to Parallel Plate Measurements

$$\left[\frac{\partial \dot{\gamma}_{aR}}{\partial (1/H)} \right]_{\sigma} = 2U_s \quad \dot{\gamma}_{aR} = \frac{\Omega R}{H} \quad \sigma_R = \frac{T}{2\pi R^3} \left(3 + \frac{d \ln T}{d \ln \dot{\gamma}_{aR}} \right)$$

Measurements of shear rate at different wall shear stress at edge R with different gap heights

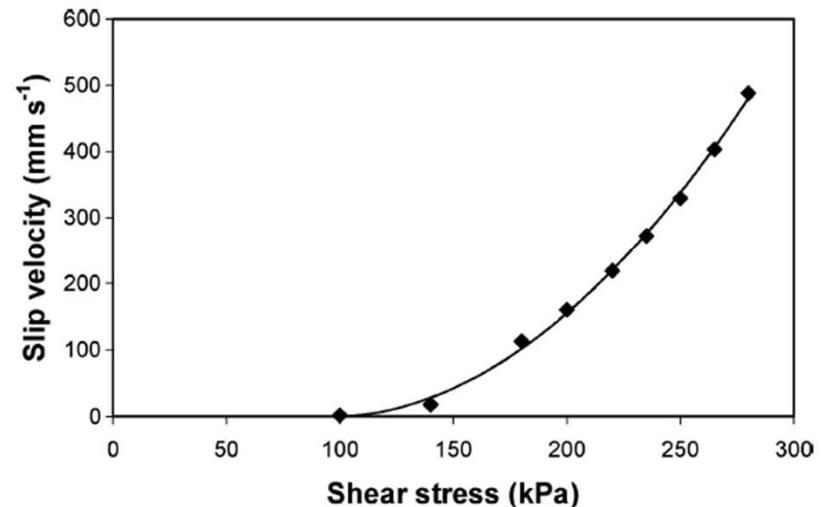
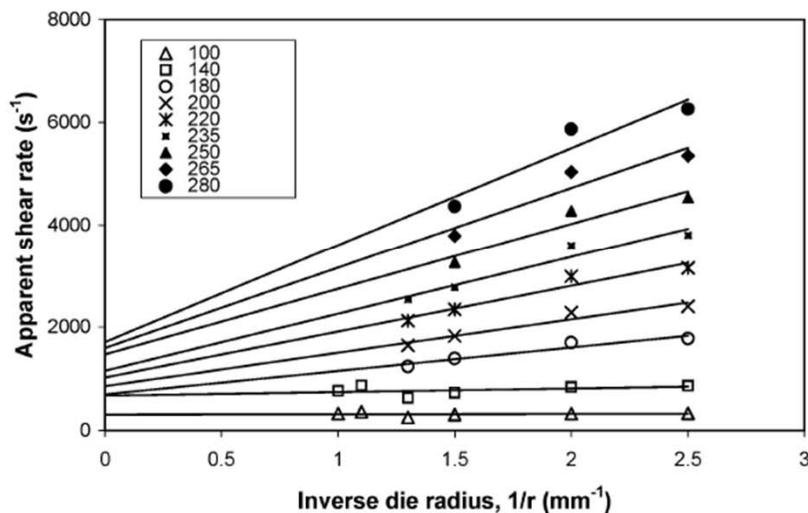


Soltani & Yilmazer *J App Poly Sci* 1998

Correction to Capillary Measurements

$$\left[\frac{\partial \dot{\gamma}_{app}}{\partial (1/R)} \right]_{\sigma} = U_s \quad \dot{\gamma}_{app} = \frac{Q}{\pi R^3}$$

Measurements of flow rate at different wall shear stress/pressure drop with different capillary radii



Haworth & Khan *J Mat Sci* 2005

THE UNIVERSITY OF TEXAS AT AUSTIN

Need to Identify Constitutive Equations for Slip Velocity

$$U_S = U^* \left(\frac{\sigma_W - \sigma_S}{\sigma_y - \sigma_S} \right)^m \quad \sigma_W < \sigma_y \quad \text{Below the yield stress}$$

$$U_S = B (\sigma_W - \sigma_y)^m \quad \sigma_W > \sigma_y \quad \text{Above the yield stress}$$

$$U_S = B \sigma_W^m \quad \sigma_W \gg \sigma_y$$

If binder slips, one form of correction

$$U_{sb} = \frac{B_b \sigma_W^{m_b}}{2} \left[1 + \tanh \left[\alpha (\sigma_W - \sigma_C) \right] \right] \quad B, B_b, m, m_b, \sigma_y, \sigma_S, \sigma_C$$

$$U_S = B \sigma_W^m + U_{sb}$$

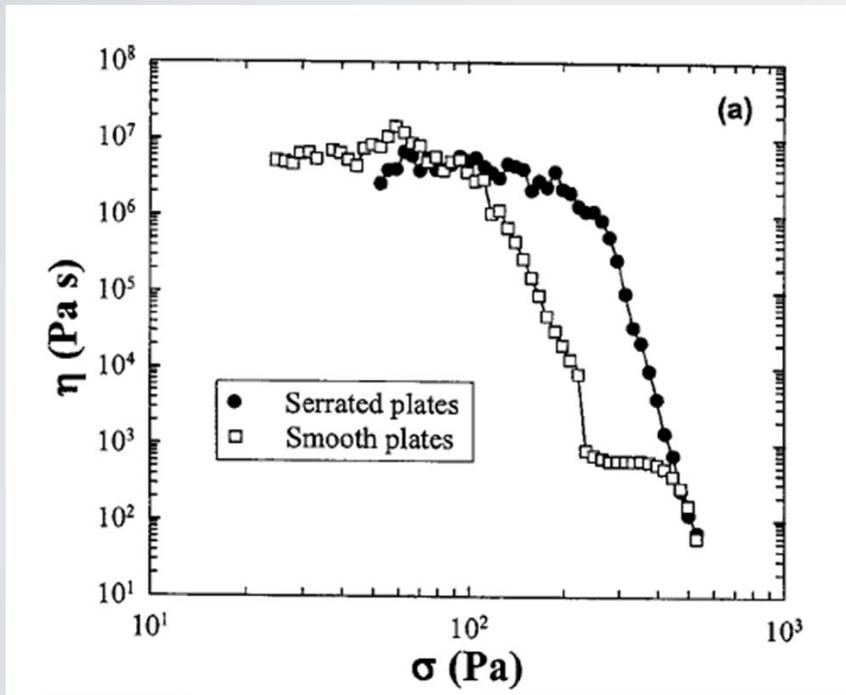
must be determined
and related to
material properties

WHAT EFFECTS THE MAGNITUDE OF WALL SLIP?

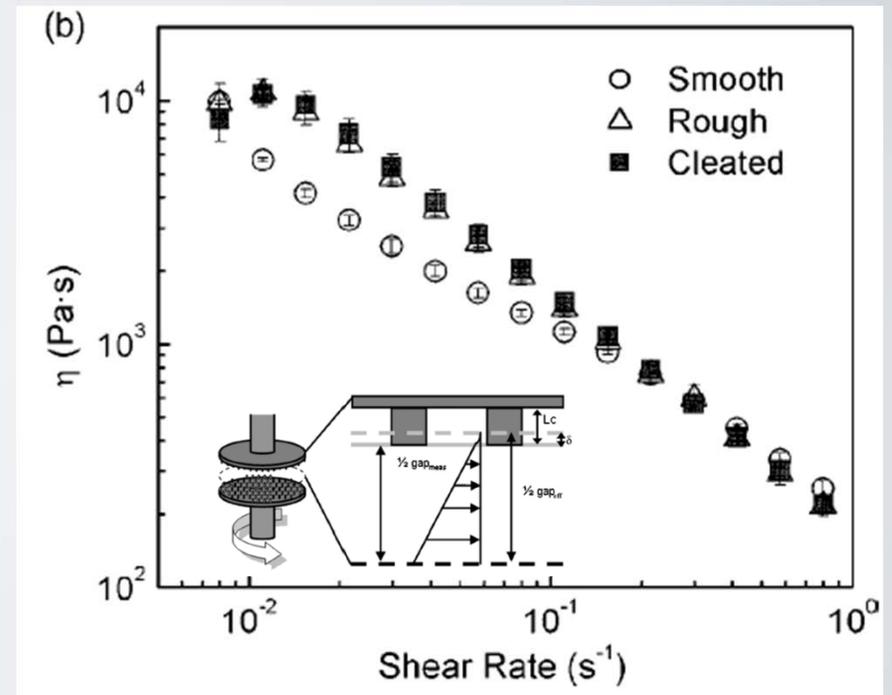
Surface Roughness

Silica gel $\phi = 0.045$

Mayonnaise



Walls et al. *J Rheol* 2003

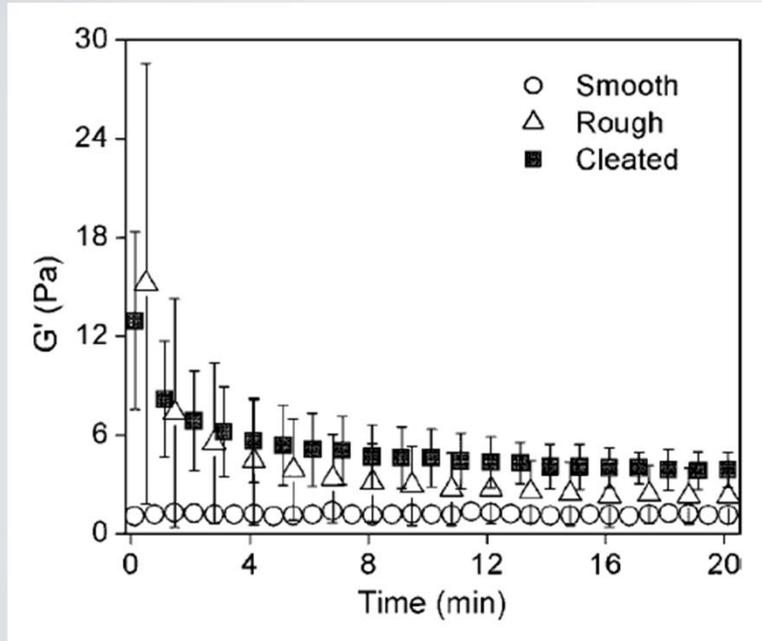


Nickerson & Kornfield *J Rheol* 2005

- Wall slip is minimized for rough surfaces
- Sufficiently roughened surfaces allow direct measurement of bulk rheology
- Rough surfaces prevent extraction of wall slip behavior

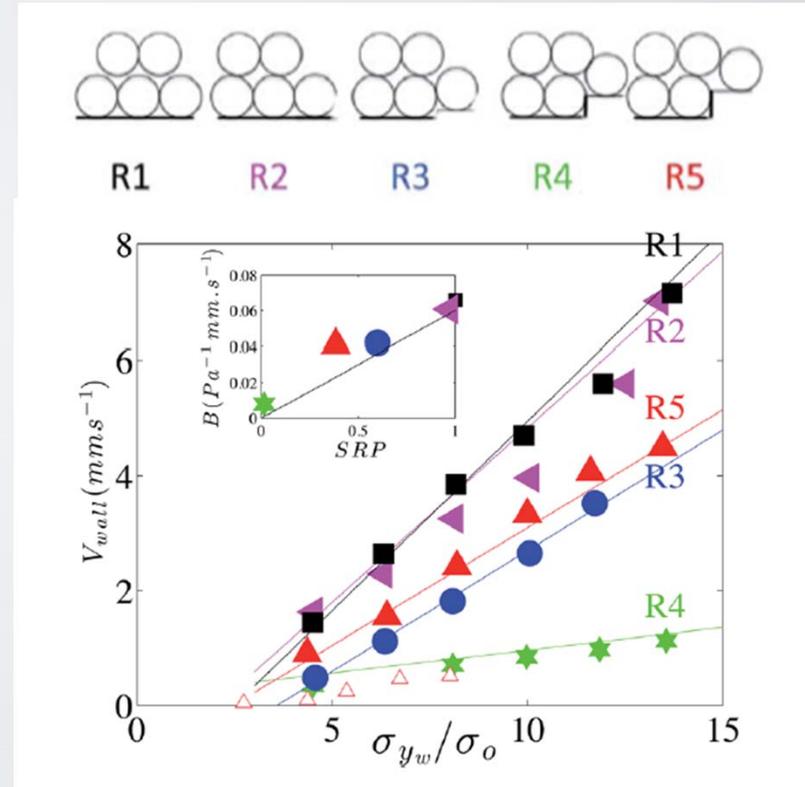
How Much Roughness?

Vitreous Humor



Nickerson & Kornfield *J Rheol* 2005

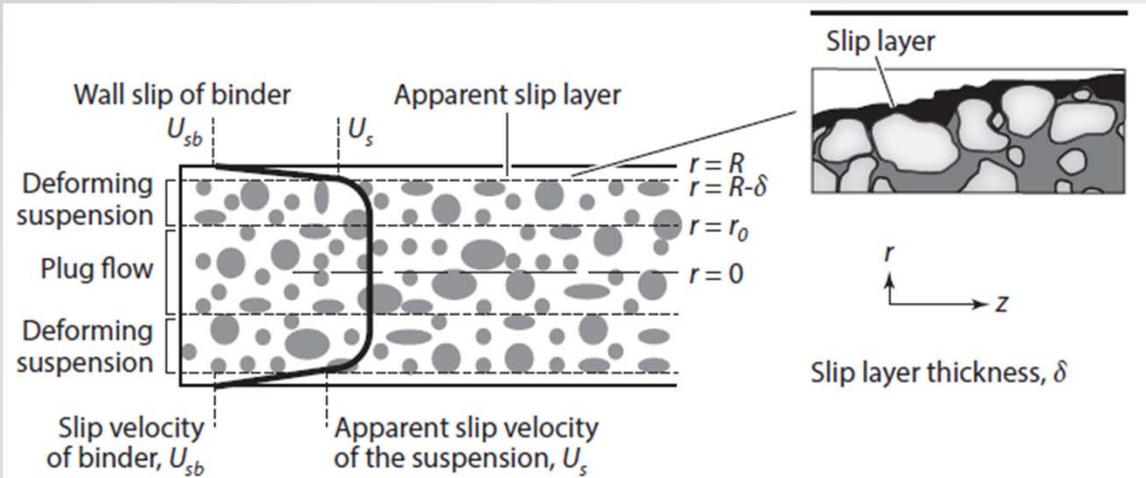
Emulsion



Mansard et al. *Soft Matter* 2014

- Nature of roughness matters: height, period relative to the particle size, ordered vs disordered, polydispersity

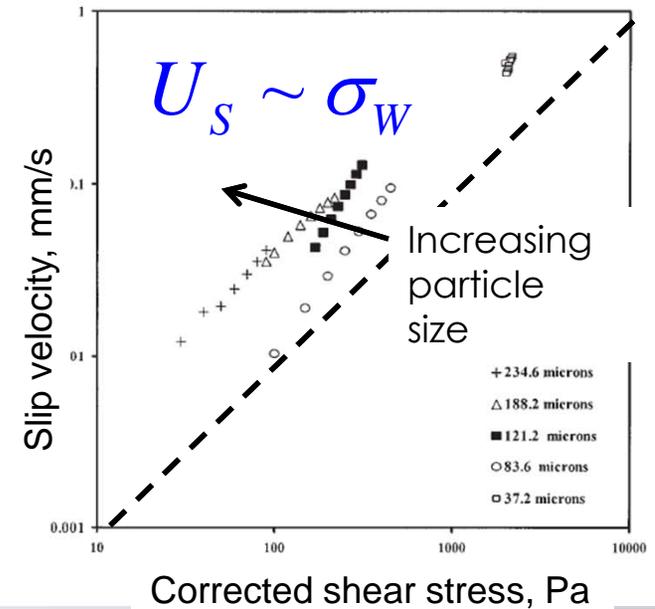
Wall Slip with Hard Particles



Slip due to particle depletion near the wall due to volume exclusion

Kalyon & Aktas *Annu Rev Chem Biomol Eng* 2014

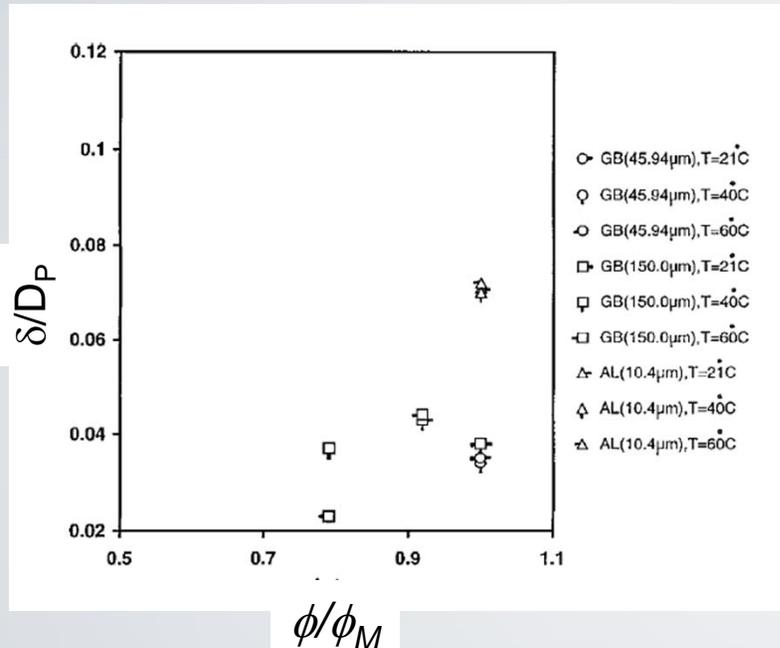
Slip increases with increasing particle size



Gulmus & Yilmazer *J Appl Poly* 2005
THE UNIVERSITY OF TEXAS AT AUSTIN

Correlation for Wall Slip with Hard Particles

Non-Brownian suspensions



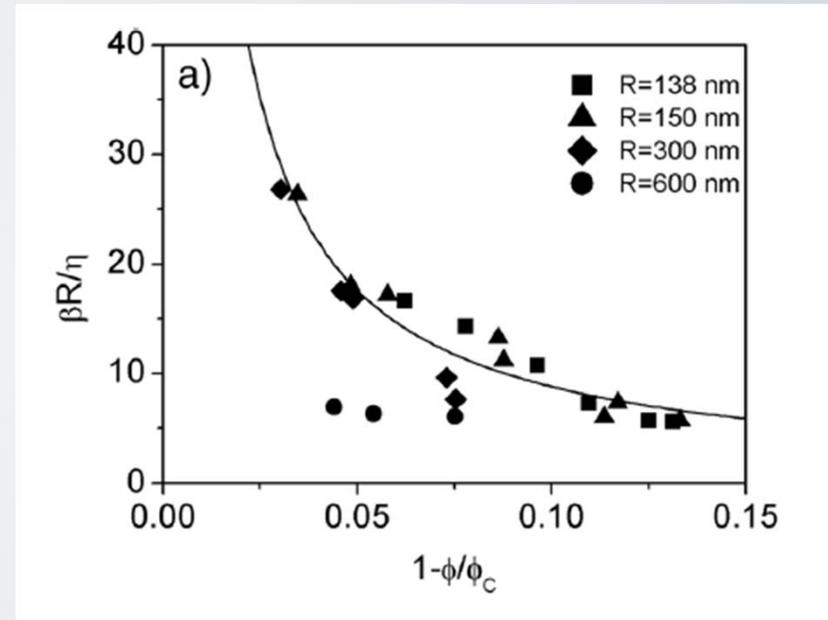
Soltani & Yilmazer *J App Poly Sci* 1998

$$\sigma_w = \frac{\eta(T)}{\delta} U_s$$

$$U_s = \frac{1}{\beta(T)} \sigma_w = \frac{\delta}{\eta(T)} \sigma_w \quad \text{Newtonian Fluid}$$

$$U_s = \frac{\delta}{\eta(T)^{1/m}} \sigma_w^{1/m} \quad \text{Power Law Fluid}$$

Brownian suspensions

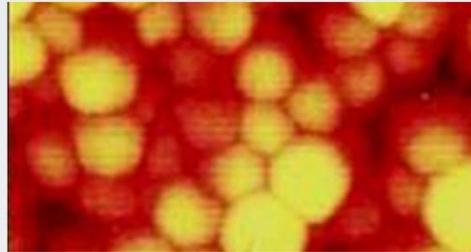


Ballesta et al *Phys Rev E* 2012

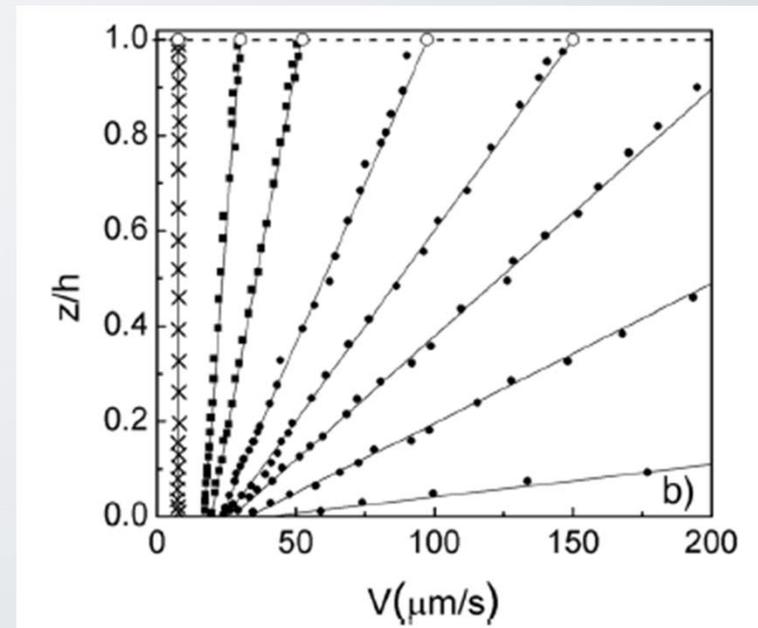
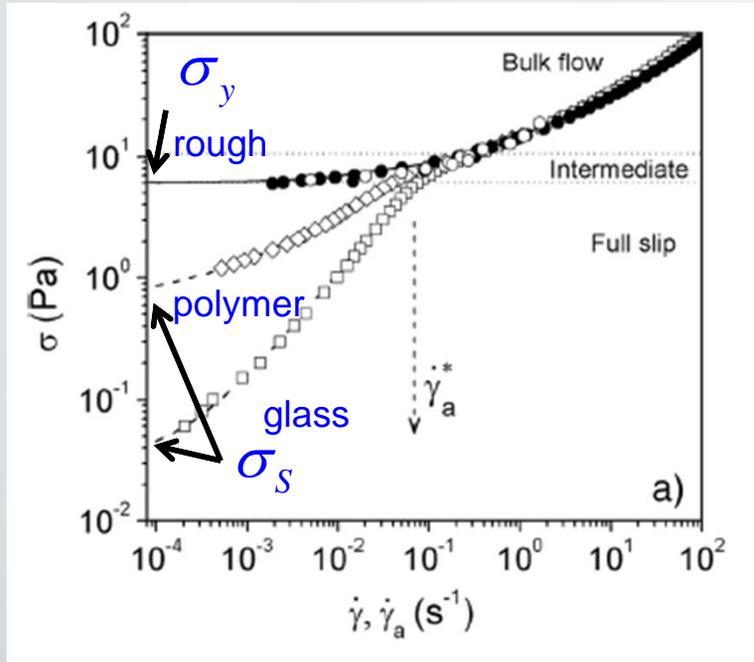
- Gap δ is independent of velocity/stress and correlated with relative volume fractions ϕ/ϕ_m
- Temperature effect embodied in interstitial fluid viscosity

Wall Slip with Concentrated Suspensions of Soft Particles

Microgel suspension
~200 nm radii soft particles



- Rough, no-slip upper wall
- Smooth, slippery lower wall

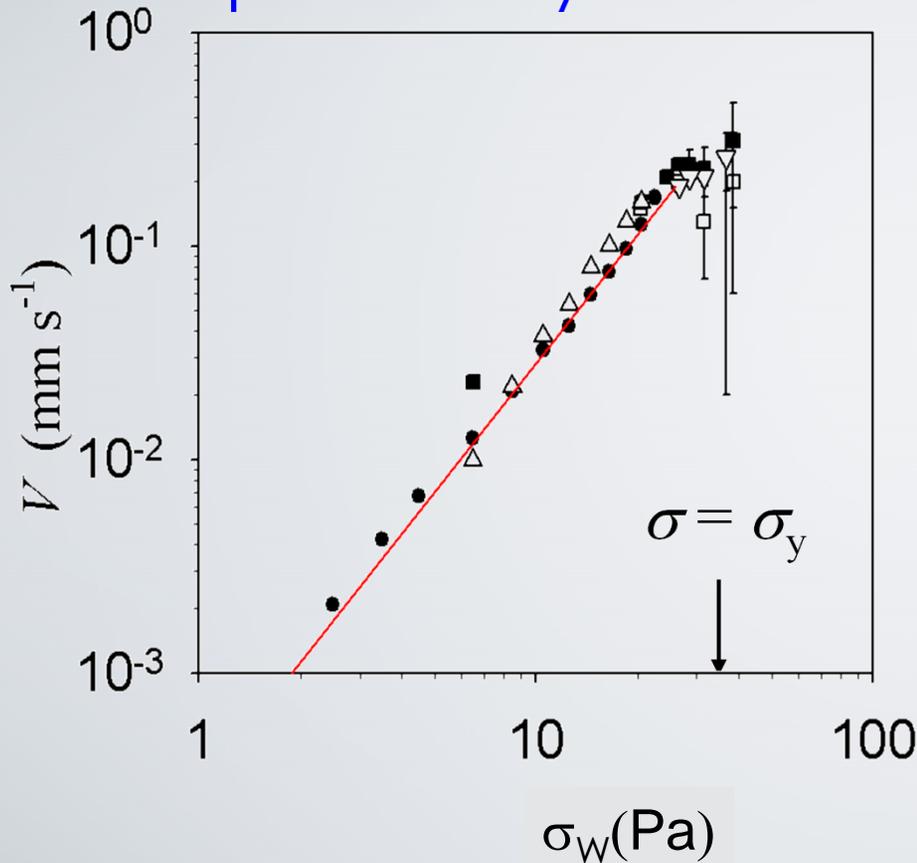


Soft particle suspensions slip is significant below the yield stress on smooth surfaces

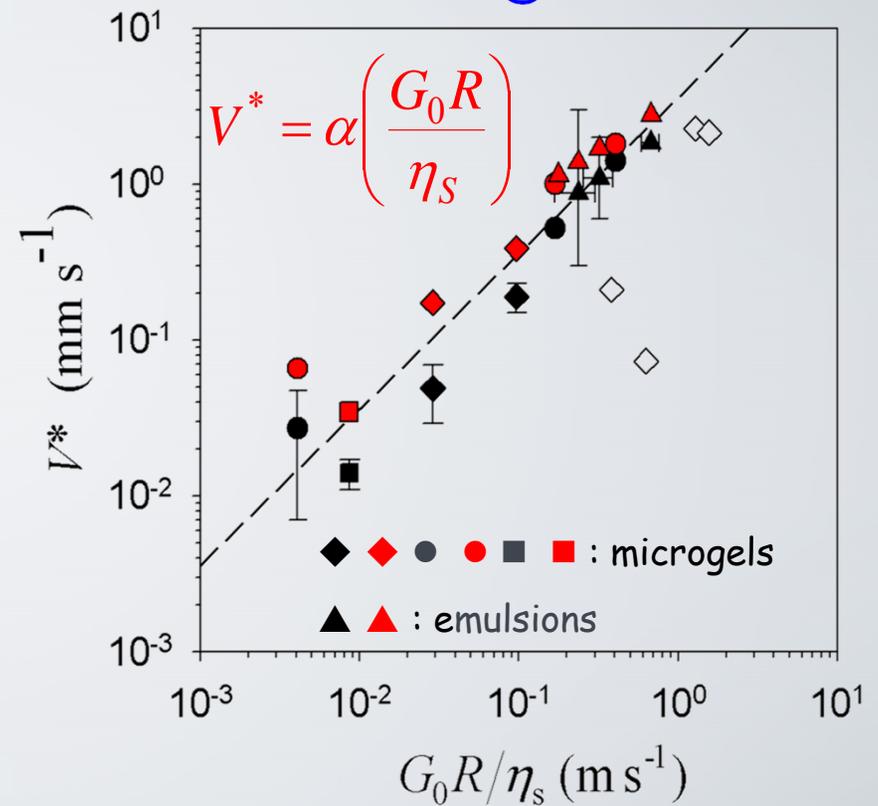
Seth et al. *Soft Matter* 2012

Wall Slip with Concentrated Suspensions of Soft Particles

Slip Velocity vs Stress



Scaling of V^*

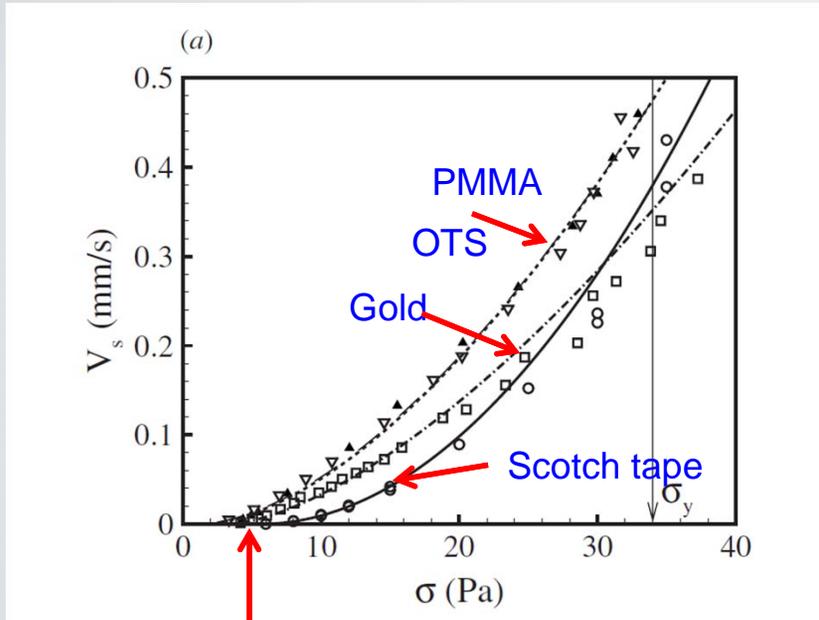


$$V_S = V^* \left(\frac{\sigma_W - \sigma_S}{\sigma_y - \sigma_S} \right)^2 \approx V^* \left(\frac{\sigma_W}{\sigma_y} \right)^2 \quad \sigma_W, \sigma_y \gg \sigma_S$$

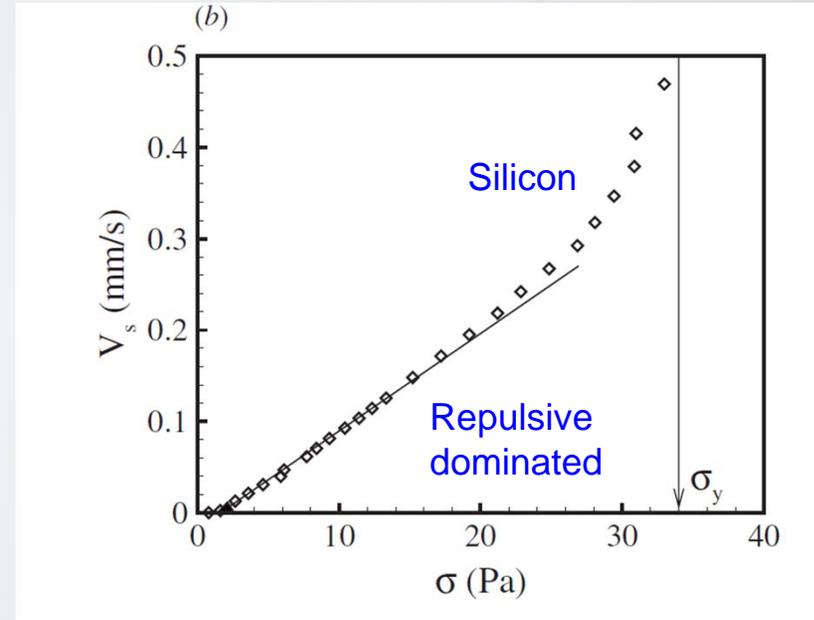
Meeker et al. *J Rheol* 2004

Chemical Influence of Smooth Surfaces

Microgels on Varying Attractive Surfaces



Microgels on Repulsive Silicon Surface



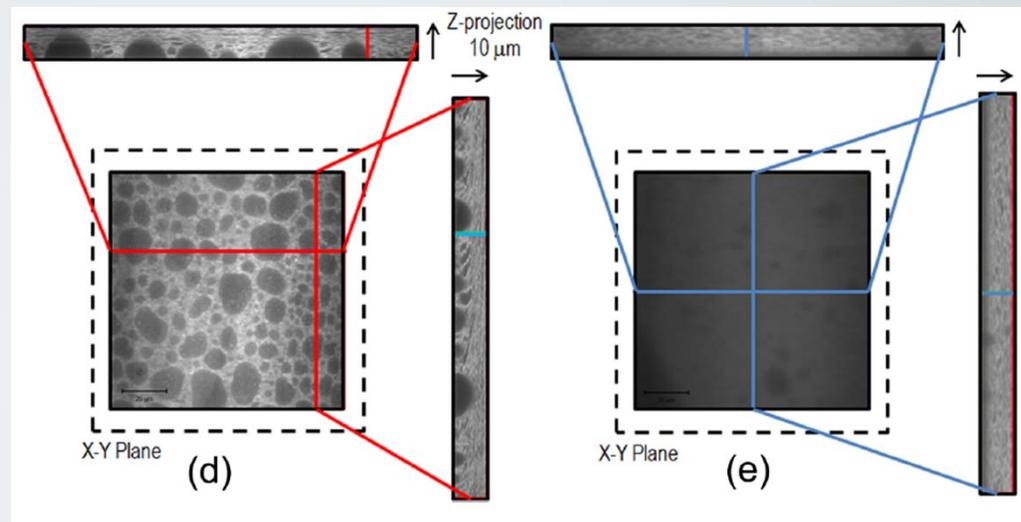
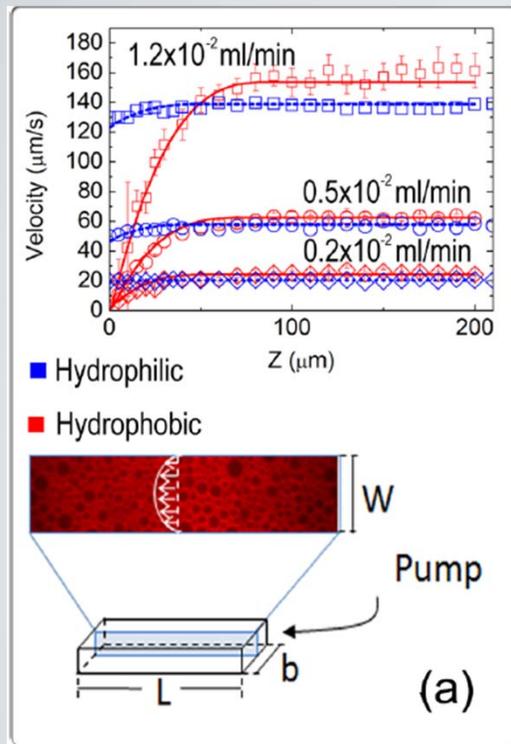
σ_s varies with attractive strength

$$U_s \sim \left(\frac{\sigma_w - \sigma_s}{\sigma_y - \sigma_s} \right)^2$$

$$U_s \sim \left(\frac{\sigma_w}{\sigma_y} \right) \quad \text{in repulsive dominated regime}$$

Seth et al *J Rheol* (2008)

Highly Attractive Surface Can Suppress Wall Slip



Hydrophobic Surface

Hydrophilic Surface

- Silicone oil-in-water emulsion, $\phi = 0.8$, $D_p = 5 \mu\text{m}$
- Confocal microscopy imaging

Hydrophobic surface attracts silicone drops to surface, roughening it and suppressing wall slip

HOW TO MODEL MULTIPHASE FLOWS WITH WALL SLIP?

Particle-Surface Models (e.g. Soft Particles)

Hydrodynamics

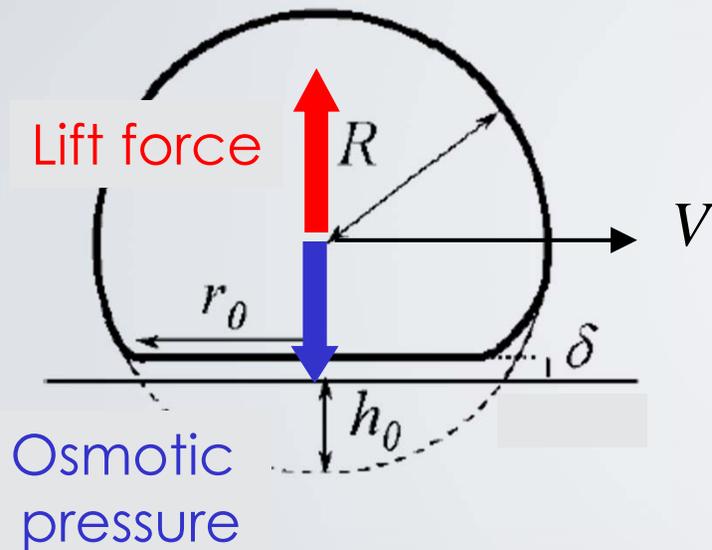
$$\nabla \cdot (\delta^3 \nabla p) = -\frac{\partial \delta}{\partial x}$$

Geometry

$$\delta(x, y) = -1 + \frac{r^2}{R} + w(x, y)$$

Elasticity

$$w(x, y) = \lambda \iint_A \frac{p(\xi, \eta) d\xi d\eta}{\left[(x - \xi)^2 + (y - \eta)^2 \right]^{1/2}}$$

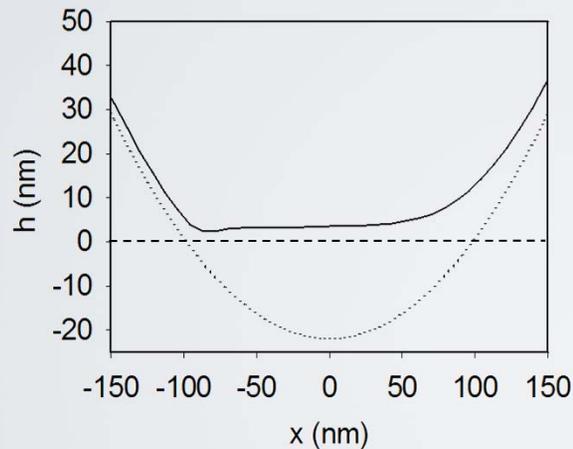


$$\lambda = \frac{6\eta_s VR}{E^* h_0^2} \sim \mathcal{O}(10^{-3} - 10^{-1}) \rightarrow \delta \ll 1$$

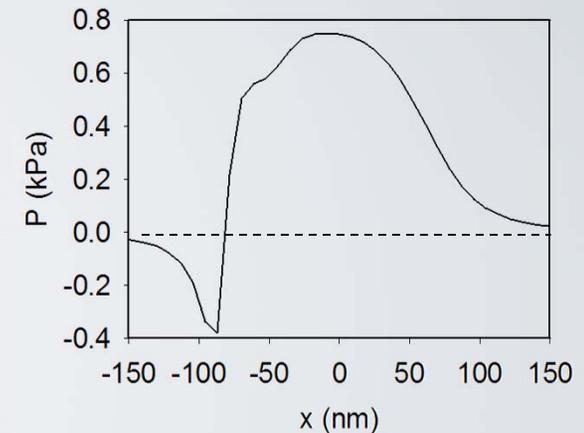
$$r_0 = (Rh_0)^{1/2}$$

Particle Shape and Pressure Near Wall

Film thickness



Pressure field



Side
view

$$E^* = 10^4 \text{ Pa}$$

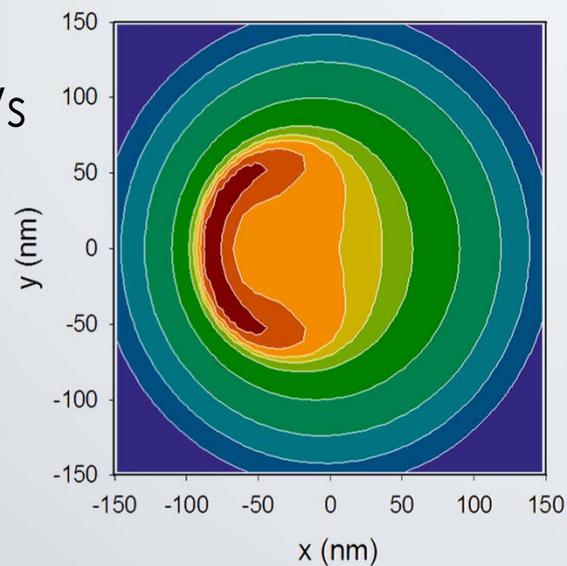
$$R = 220 \text{ nm}$$

$$h_0 = 22 \text{ nm}$$

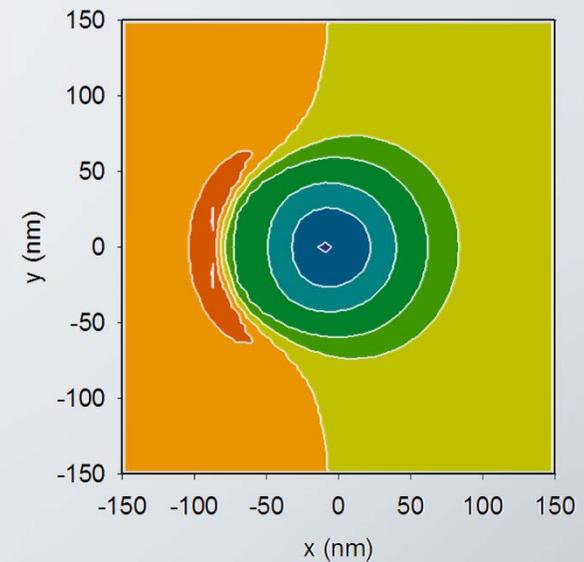
$$\eta_s = 1 \text{ mPa}\cdot\text{s}$$

$$V = 0.2 \text{ mm/s}$$

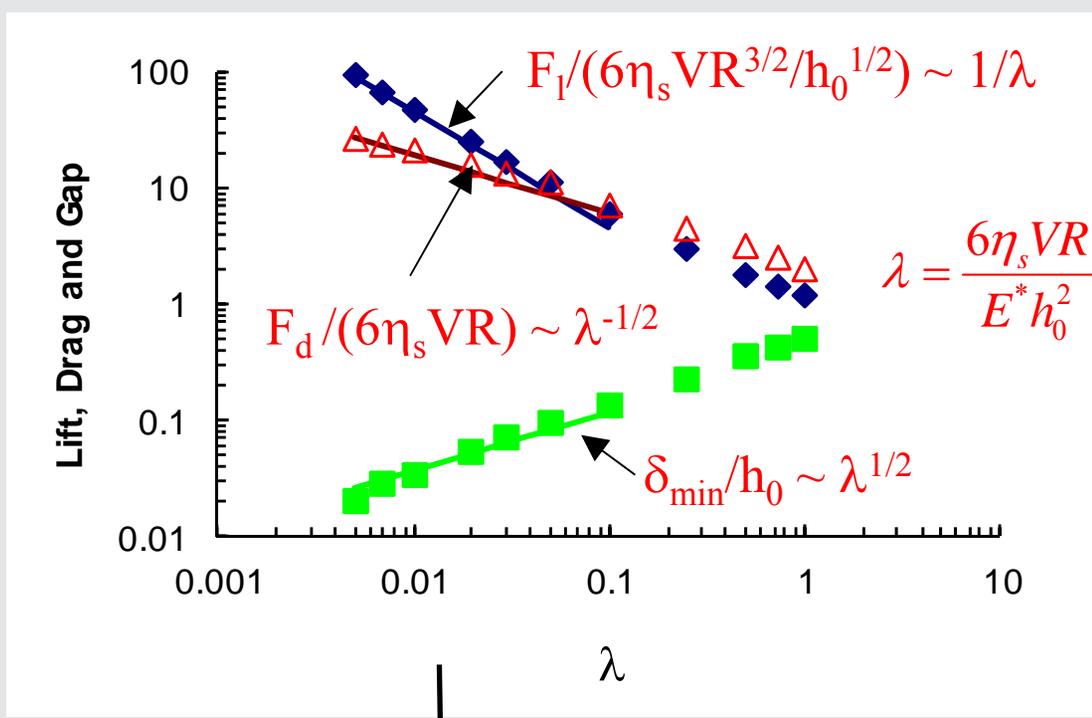
$$\lambda = 0.05$$



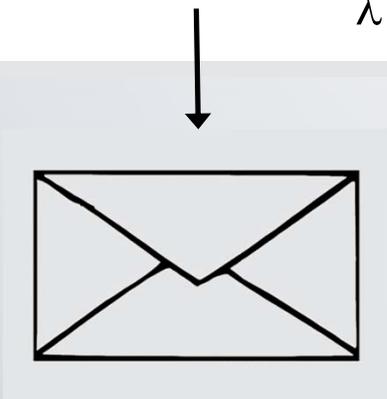
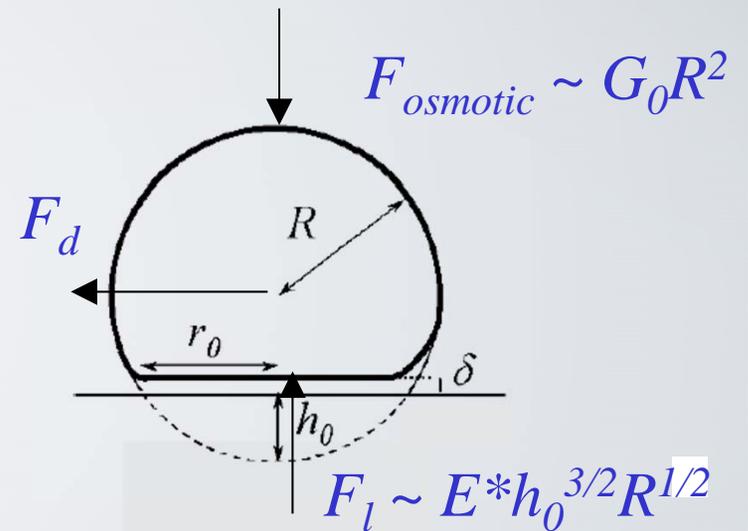
Bottom
view



Shear Stress and Slip Velocity Scalings



Balance elastohydrodynamic lift force with osmotic force



$$\frac{V}{V_s} = \left(\frac{\sigma}{\sigma_y} \right)^2$$

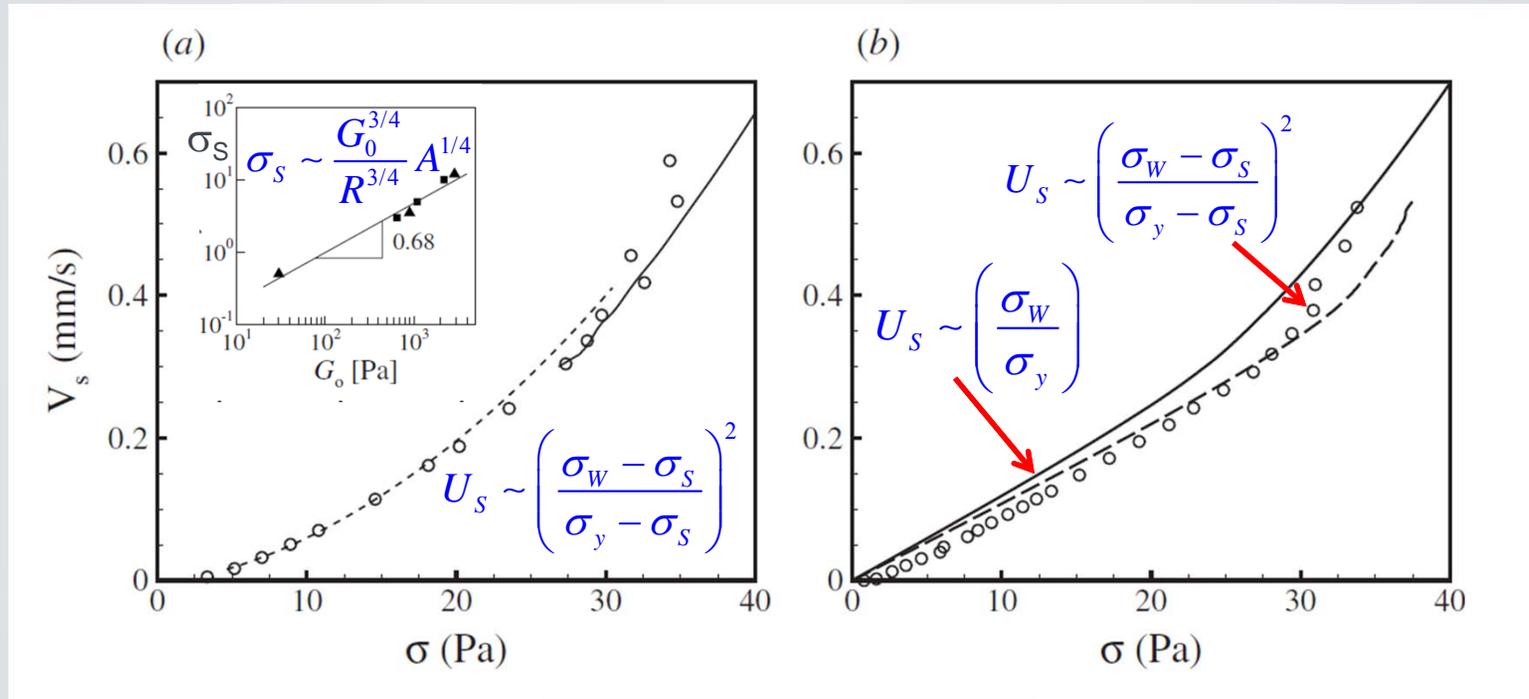
$$V^* \sim \left(\frac{G_0 R}{\eta_s} \right)^{1/2}$$

$$\frac{\sigma}{\sigma_y} \sim \left(\frac{\eta_s V}{G_0 R} \right)^{1/2} (f(\phi))^{1/6}$$

Modeling Effect of Surface Forces

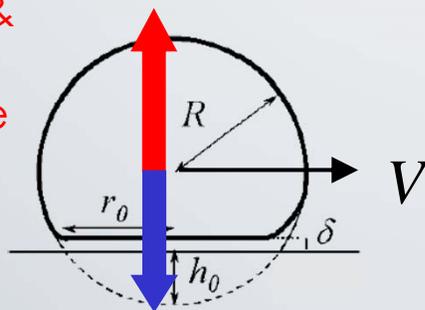
Microgels on Attractive PMMA Surface

Microgels on Repulsive Silica Surface



Lift Force &
Repulsive
Wall Force

Osmotic
Pressure &
Attractive
Wall Force



Modified Elasticity

$$w(x, y) = \lambda \iint_A \frac{(p + p_{vdW} + p_R) d\xi d\eta}{\left[(x - \xi)^2 + (y - \eta)^2 \right]^{1/2}}$$

Application of Slip Boundary Conditions in Transport Models

Generalized Boundary Condition

$$U_s = \mathbf{t} \cdot (\mathbf{u} - \mathbf{U}_w) = B(\phi, T, P) (\text{sgn}(\mathbf{nt} : \boldsymbol{\sigma})) \left[|(\mathbf{nt} : \boldsymbol{\sigma})| - \sigma_y \right]^m$$

Transport Equations

$$\nabla \cdot \mathbf{u}, \quad \rho \frac{D\mathbf{u}}{Dt} = \nabla \cdot \mathbf{T}(\mathbf{u}) + \rho \mathbf{g}$$

Single Phase Model

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot (\phi_i \mathbf{u}_i) = 0$$

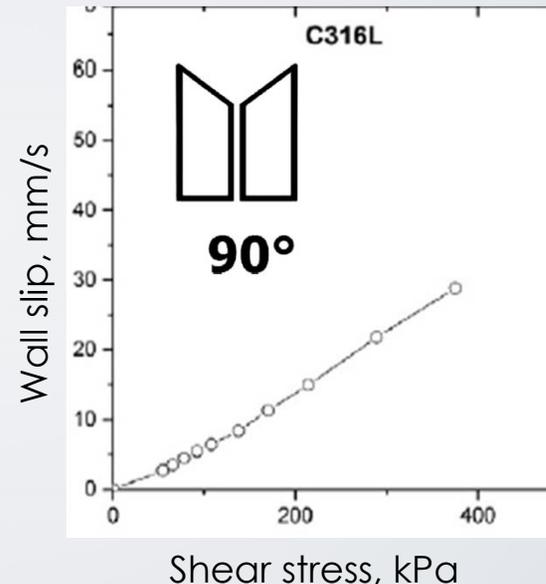
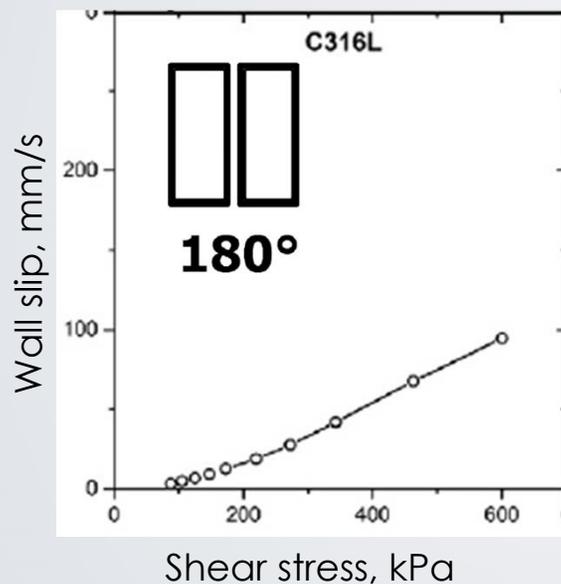
Two-Phase Model

$$\rho \phi_i \frac{D\mathbf{u}_i}{Dt} = \nabla \cdot \mathbf{T}_i(\langle \mathbf{u} \rangle, \phi_i, \phi) - \mathbf{F}_i(\mathbf{u}_i - \langle \mathbf{u} \rangle) + \rho \phi_i \mathbf{g}$$

**IS WALL SLIP FUNDAMENTALLY
DIFFERENT IN EXTRUSION VERSUS
INJECTION MOLDING?**

Measured Wall Slip Affected by Angled Surfaces

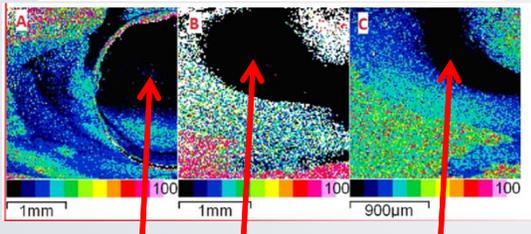
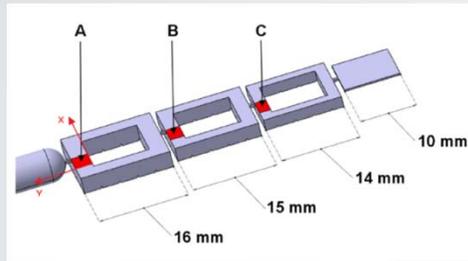
5 μm steel beads in polymer binder



- Very different wall slip relationships depending on inlet conditions
- Particle distribution uneven due to the sharp transition

Sanetrik et al *Powder Tech* 2018

Particle-Binder Separation Will Affect Wall Slip

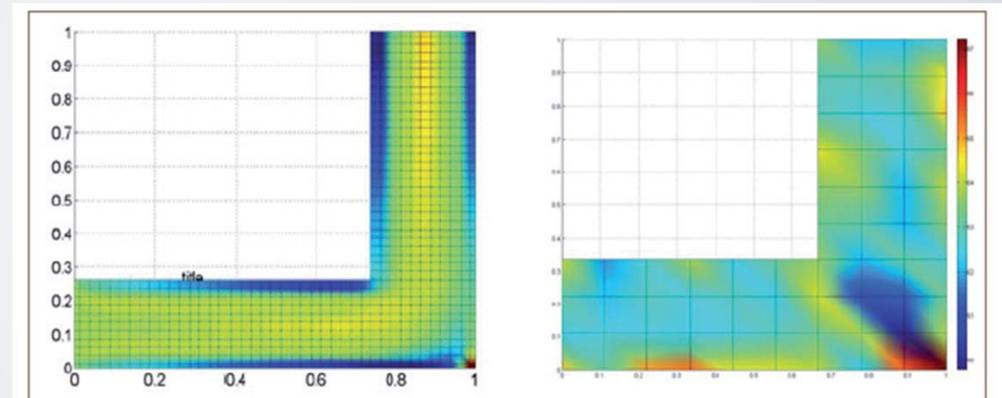


Particle separation near entrance

Particle Distribution

Simulation

Expt.



Jenni et al Pow Inj Mould 2008

Hausnerova 10.2417/spepro.005097 2013

Particle migration and separation from binder changes concentration, possibly size distribution, and local microstructure near the wall and hence wall slip

WHAT ARE THE RESEARCH AND PRACTICAL OPPORTUNITIES FOR WALL SLIP?

Knowledge Gaps for Wall Slip

Prediction and Control of Wall Slip for

- Polydispersity of particle size and shape
- Different surface morphologies and chemistries
 - influences near field and contact forces

Lack of Experimentally Validated Models and Simulation Tools

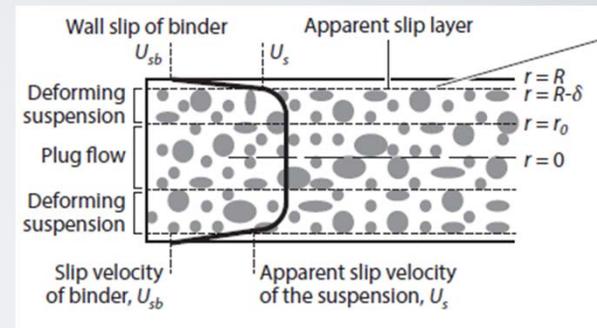
- Particle scale
- Continuum scale

Prediction of Particle Microstructure Near Surfaces

$$\text{Slip BC } U_s = \beta(\phi_i, T, P) [\sigma - \sigma_y]^m$$

Local rheology and slip layer thickness

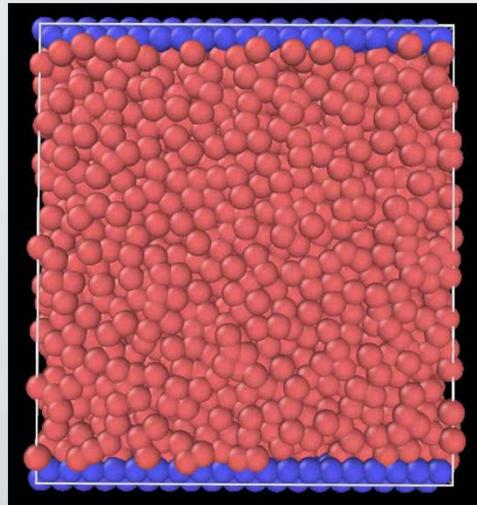
Particle size and shape distribution and surface morphology and chemistry



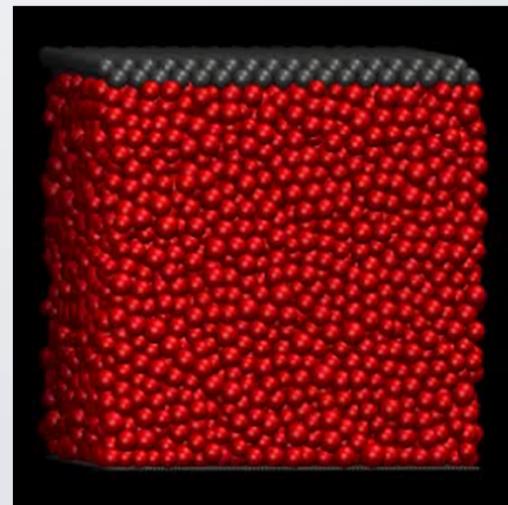
Kalyon & Aktas *Annu Rev Chem Biomol Eng* 2014

Develop Particle Simulations and Continuum Models

Rough Walls,
No Wall Slip
 $\sigma > \sigma_w$ Linear
Shear Flow



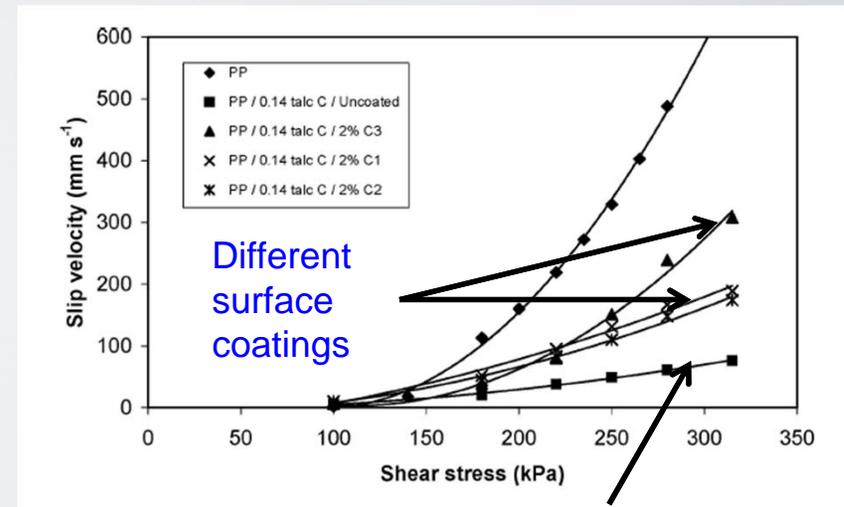
Smooth
Lower Wall,
Wall Slip
 $\sigma < \sigma_w$ Plug
Flow



Exploration of Surface Treatments for Walls and Particles to Control Wall Slip

- Understanding and design of surface treatments (processing aids) to control wall slip
 - Surface treatment for walls
 - Surface treatment of particles
- Choose molecules to minimize adhesive/cohesive stress to promote wall slip, minimize deleterious effects of particle roughness

Haworth & Khan *J Mat Sci* 2004



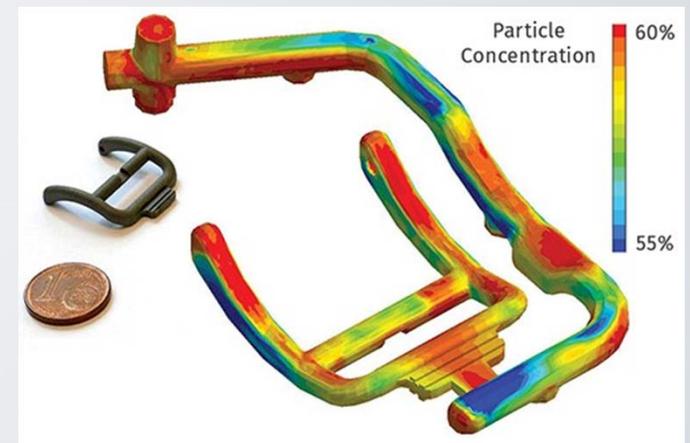
No coating



Self-compacting concrete with superplasticizer

Establish Benchmark Problems for Evaluation of Computational Simulations

- No quantitative measure of strengths and weaknesses of commercial and academic computational tools for disperse flow
- Establish benchmark systems (e.g., powder injection molding)
 - Test mold with key geometries (e.g., expansions, contractions, etc.)
 - Two or more powder/binder mixtures
 - Standardized rheological and slip characterization
 - Standardized injection conditions
 - In-situ and post-injection measurement of particle distribution



From SIGMASOFT® Virtual Molding Software Website

CONCLUSIONS & PROSPECTS

Concluding Remarks

- Wall slip in dispersions occurs when a thin, relatively low viscosity microstructure can form near the wall
- Rheometric signature is geometry-dependent flow or viscosity curves
 - Data must be corrected or slip suppressed by roughening rheometer walls to determine true rheology
- Slip velocity can be extracted from rheometric data and correlated to system parameters

$$U_s = f(\sigma_w, \sigma_y, \sigma_s, \eta(T), D_p, \phi/\phi_M, \Pi(T) \text{ or } P(T))$$

- Slip velocity can be predicted for a few systems
 - Many other systems are poorly understood theoretically
- Opportunities to control and predict slip by
 - understanding dispersion microstructure and rheology near shearing surfaces
 - physically and chemically manipulating wall surfaces, surfaces of particles

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Eiffel Programme

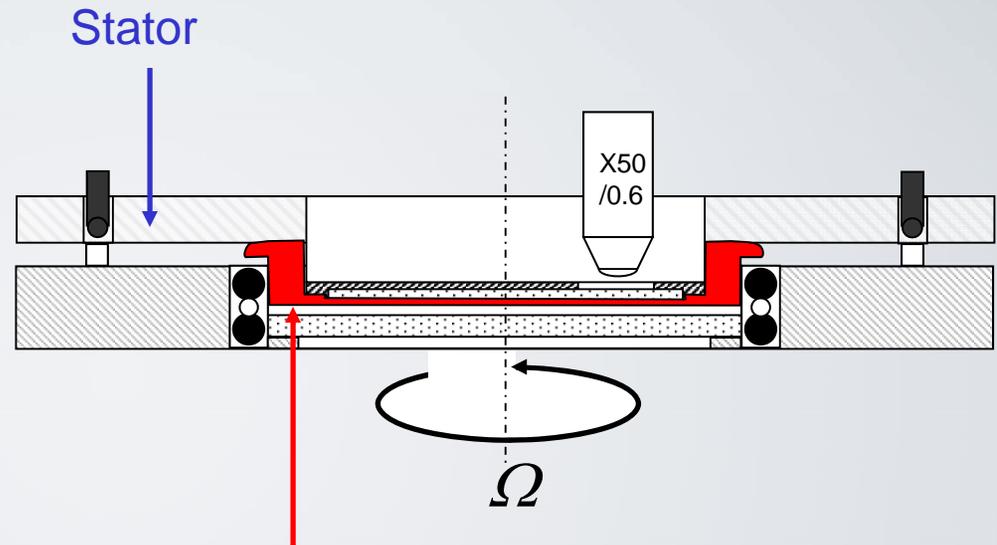
Questions ?

Back-Up Slides

Fluorescence Microscopy & PTV



Strain controlled set-up



Paste seeded with fluorescent beads ($d = 1 \mu\text{m}$)

Determination of trajectories

Δx and $\Delta y \cong 0.2 \mu\text{m}$;

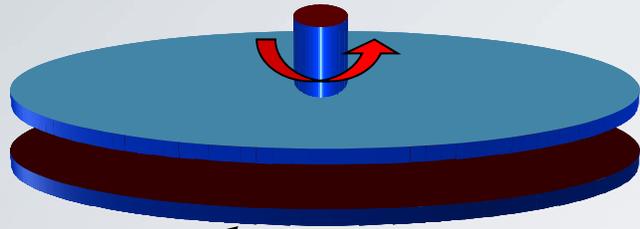
$\Delta z \cong 1 \mu\text{m}$

$10^{-2} \mu\text{m/s} < V < 10^3 \mu\text{m/s}$

IDL Software, Crocker and Grier (1996)

Gap thickness: 10^2 to $10^3 \mu\text{m}$

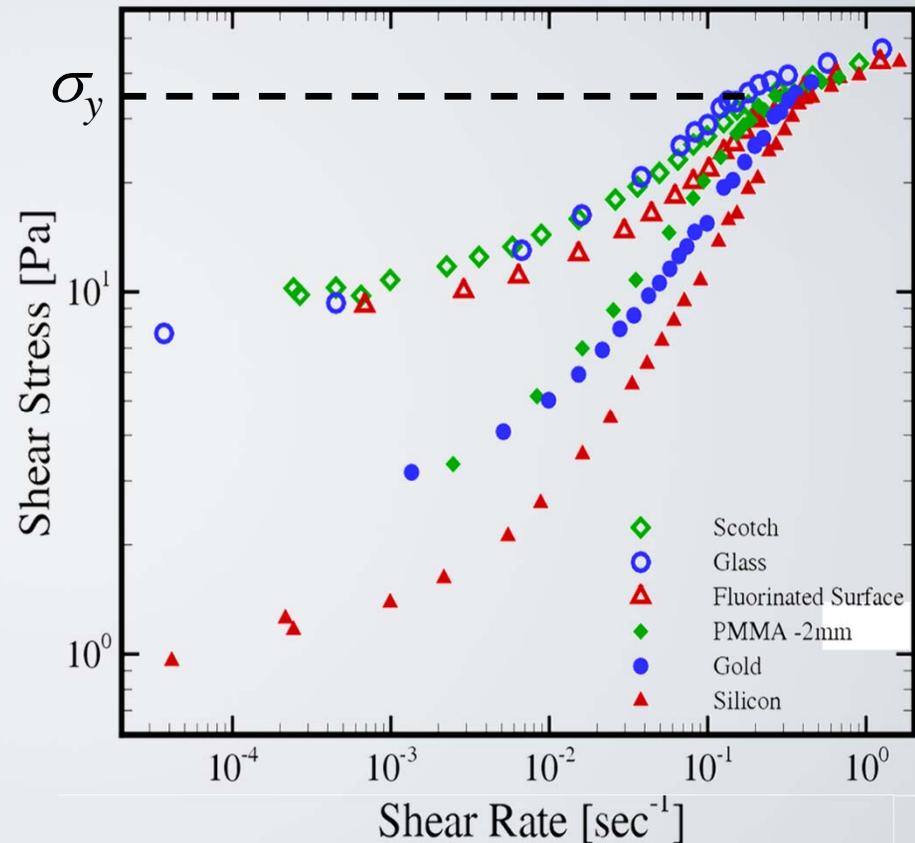
Wall Slip Varies with Particle-Wall Interaction Strength



Stationary Rough Surface
(roughness $\sim 30\mu\text{m}$)

Smooth Shearing Surface
(roughness $< 5\text{nm}$)

- Silicon
- Gold
- Fluorinated surface
- PMMA coated glass
- Glass
- Scotch Tape

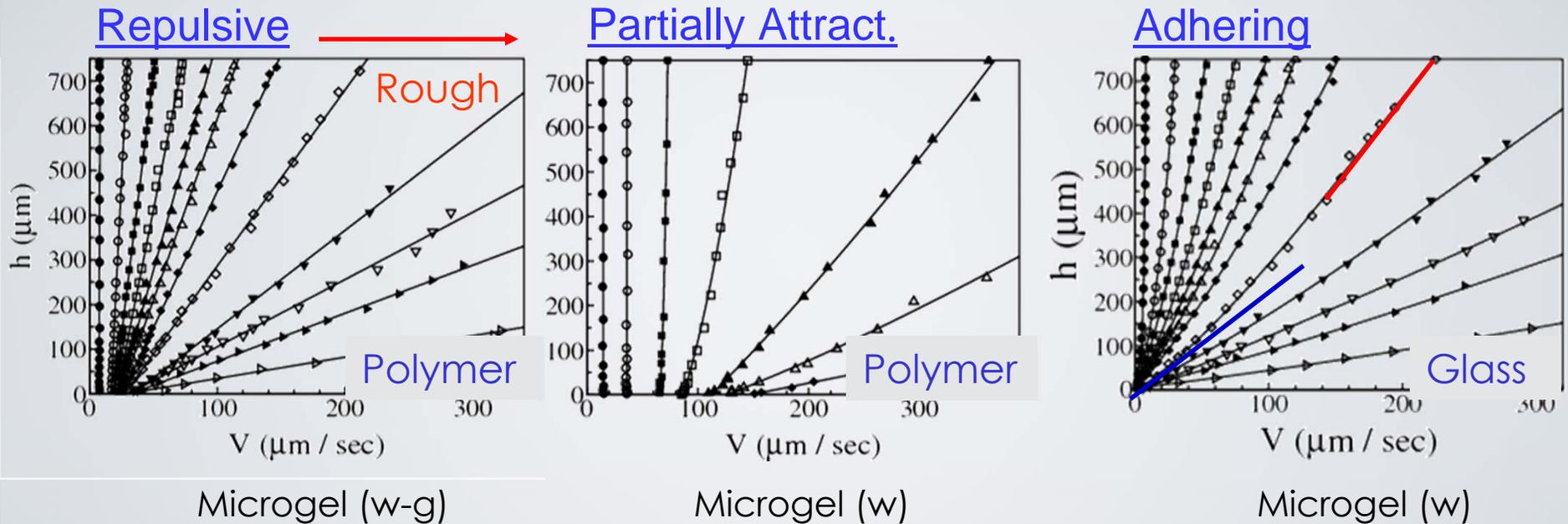


In the slip regime, flow is sensitive to the nature of the shearing surface

Seth, Cloitre & Bonnecaze *J. Rheology* (2008)

Slip and Shear Banding Can Occur

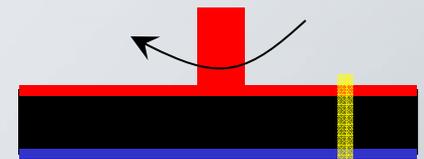
Rough-Rough \rightarrow no slip + linear flow



Solid motion (total slip) at low velocities/stresses
The layer of particles next to the wall is slipping

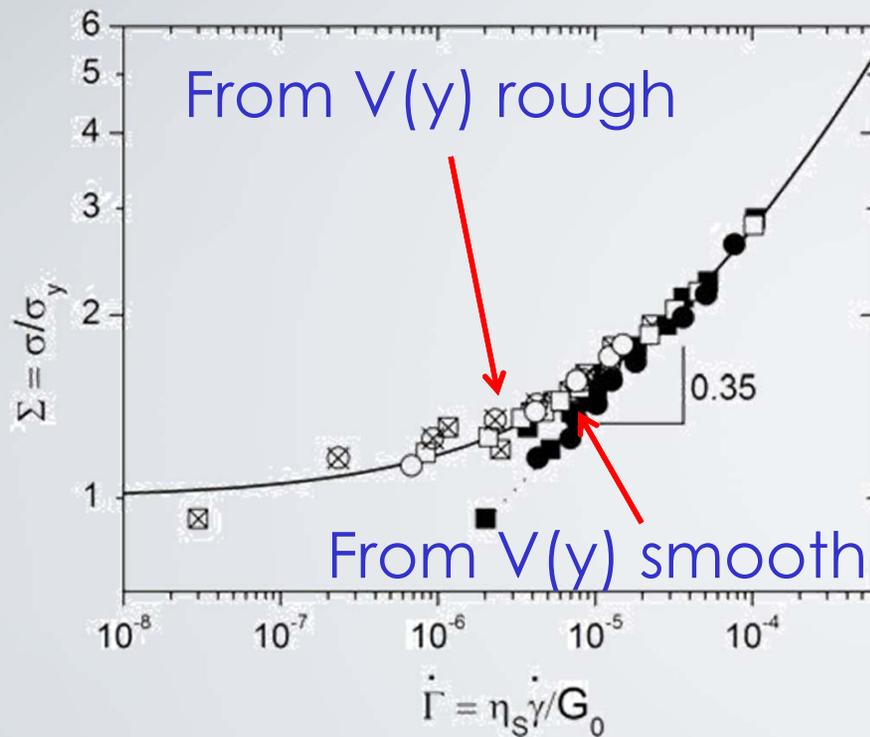
Yielding is sensitive to the nature of the surface

- Repulsive – large slip velocity + linear velocity profile
- Attractive – small slip velocity + inhomogenous flow



Seth et al. *Soft Matter* 2012

Multivalued Stress for Adhering Particles



Rheology near smooth wall
different from that near
rough wall

$$\tilde{V}_E(z) = \frac{[V_a - (h-z)\dot{\gamma}_R - V(z)]}{V_E(0)}$$

$$\tilde{V}_E(z) = e^{-z/\xi} \quad \xi \approx 70-150 \mu\text{m}$$

Smooth wall effects
velocity non-locally

