Change of title & topic

~~Sedimentation: progress and prospects~~

The mechanisms of slip and flow in weakly flocculated suspensions

Richard Buscall

MSACT Research & Consulting, Exeter, U.K.

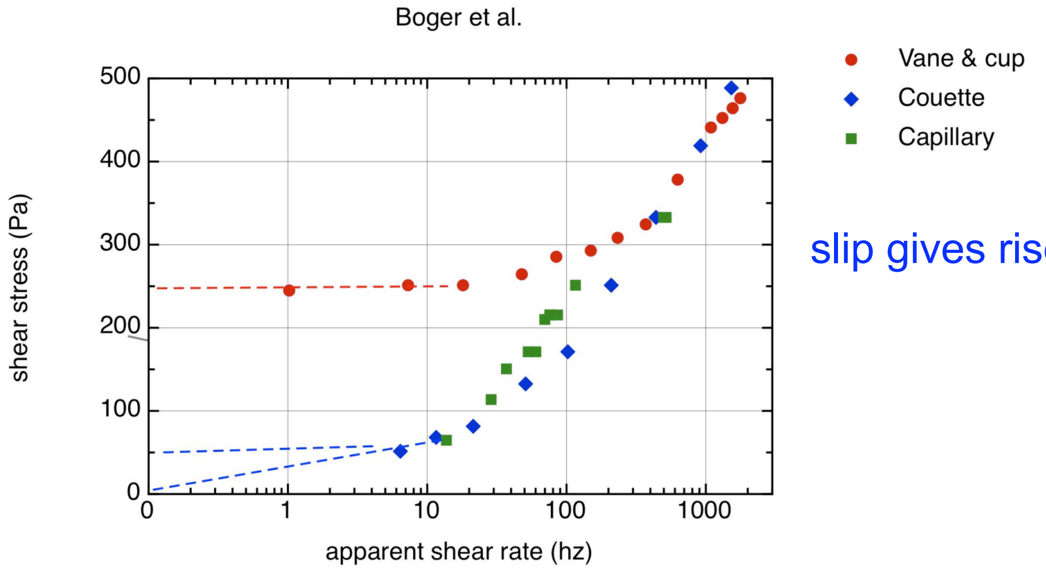
Slip & the rheology of disperse systems

• Dispersions, suspensions, emulsions, microgel solutions etc. are lazy…

… many will flow like true liquids* if made to, although most will also slip at boundaries given half a chance.

* Not all, some yield stress liquids seem to behave more like gels that rupture and heal, others like fractured solids.

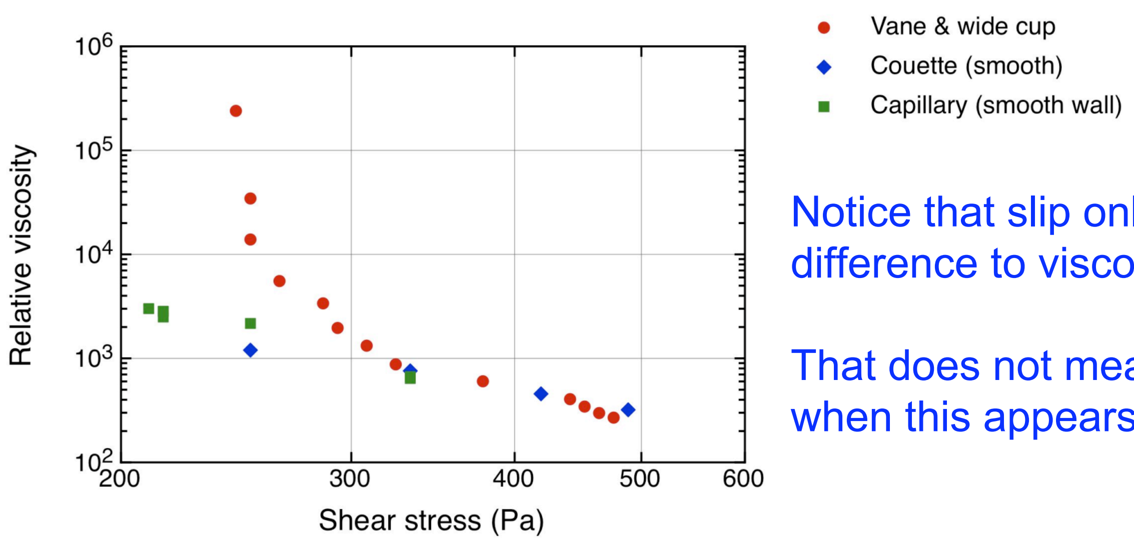
An arbitrary example of a yield stress liquid from the literature



slip gives rise to a > 80 % error in yield stress.

Data Stolen from

D BOGER, P SCALES, F SOFRA, "Rheological Concepts"in Paste and Thickened Tailings - A Guide Ed(s): RJ Jewell, AB Fourie (2006). UWA Press (Nedlands) 2006.



Notice that slip only makes a significant difference to viscosity values for RV >> 100.

That does not mean that it can be ignored when this appears to be so, though.

There is a problem though

- A substantial proportion of papers published on the rheology of such systems seem to ignore this fact.

This is true even in the specialist rheology journals, to this day …

This is true even in the specialist rheology journals, to this day …

Three recent examples:

Haleem, B. A. and P. R. Nott, "Rheology of particle-loaded semi-dilute polymer solutions", **J. Rheol**. 53, 383-400 (2009).

Grillet, A.M., R. R. Rao, D. B. Adolf, S. Kawaguchi, and L. A. Mondy, "Practical application of thixotropic suspension models", **J. Rheol**. 53, 169–189 (2009).

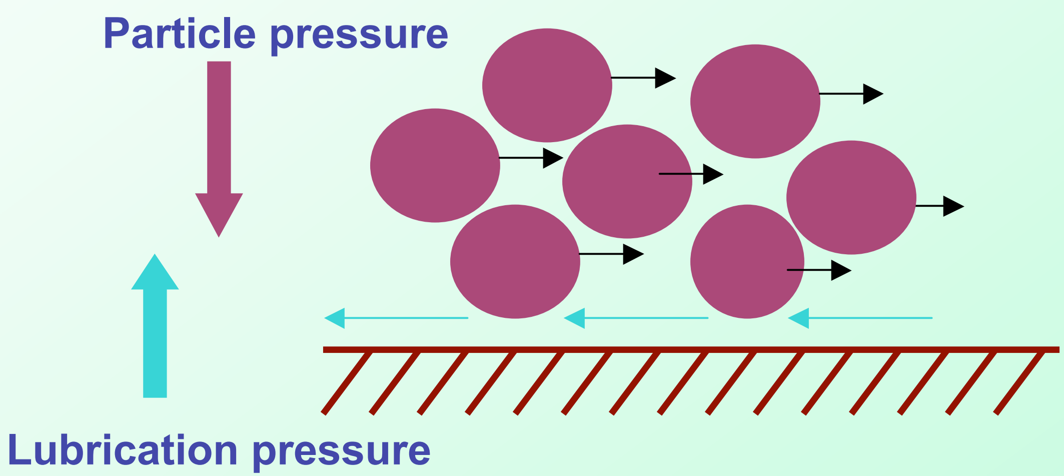
S. Mueller, E. W. Llewellin and H. M. Mader, The rheology of suspensions of solid particles, **Proc. R. Soc. A,** December 2009, doi: 10.1098/rspa.2009.0445.

(Don't mean to imply that Proc. Roy. Soc. Is a specialist rheology journal).

Elastohydrodynamic model of wall slip (MSBC)

Meeker, Seth Bonnecaze & Cloitre

Seth, J.R., Cloitre, M. & Bonnecaze, R.T. 2008 Influence of short-range forces on wall-slip in microgel pastes, J. Rheol., 52(5), 1241-1268;
Meeker, S., Bonnecaze, R.T. & Cloitre, M. Slip and flow in soft particles pastes, 2004 Phys. Rev. Lett., **92**, 198302; **Meeker, S., Bonnecaze, R.T. & Cloitre, M**. Slip and flow in pastes of soft particles: Direct observation and rheology, J. Rheol. 48-6, 1295-1320, 2004.



a) Colloidally stable

Slip at all stresses.

b) Flocculated

Slip above a critical stress associated with adhesion.

the "wall" yield stress.

Scaling expected from EH Model of MSBC

Predicts *inter alia* a dependence of slip layer thickness **δ** on the elastic modulus ***G*** of the particulate network like,

$$\delta \propto G^{-2/3}$$

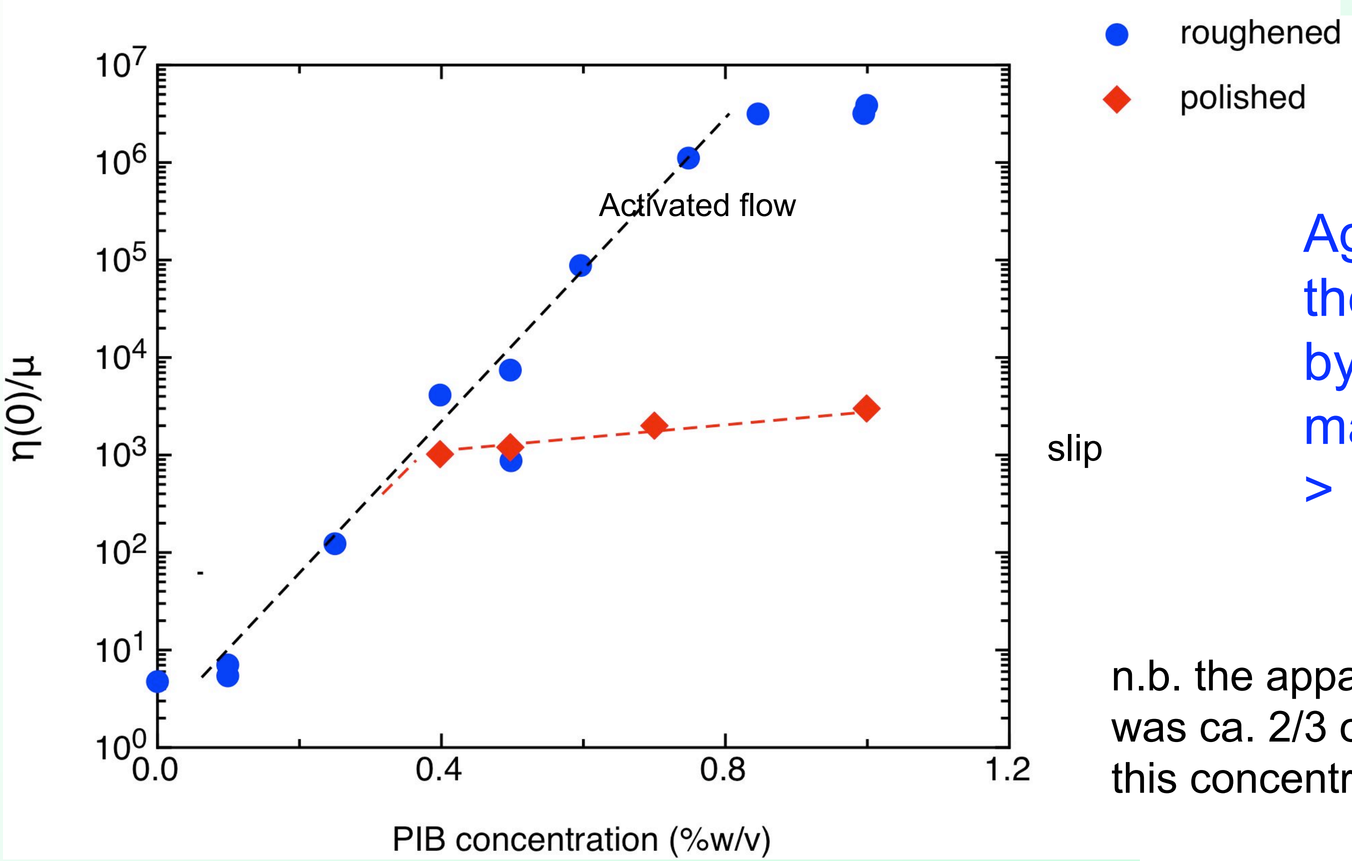
everything else being equal. Something to test exp'tally.

N.b. MSBC use the shear modulus G as a proxy for the compressional modulus

Meeker, S., Bonnecaze, R.T. & Cloitre, M. Slip and flow in soft particles pastes, 2004 Phys. Rev. Lett., **92**, 198302

Slip in weakly-flocculated dispersions

Zero shear viscosity of a depletion flocculated system



Again, you can see the error growing by orders of magnitude for RV > 1000

n.b. the apparent slip layer thickness was ca. 2/3 of a particle diameter at this concentration (φ = 0.4).

Buscall, R., J. I. McGowan, and A. J. Morton-Jones,' J. Rheol. 37, 621–641 (1993).
Buscall, R., Wall slip in dispersion rheometry, arXiv:0903.0265v1 [cond-mat.soft] (2009); submitted to J. Rheol..

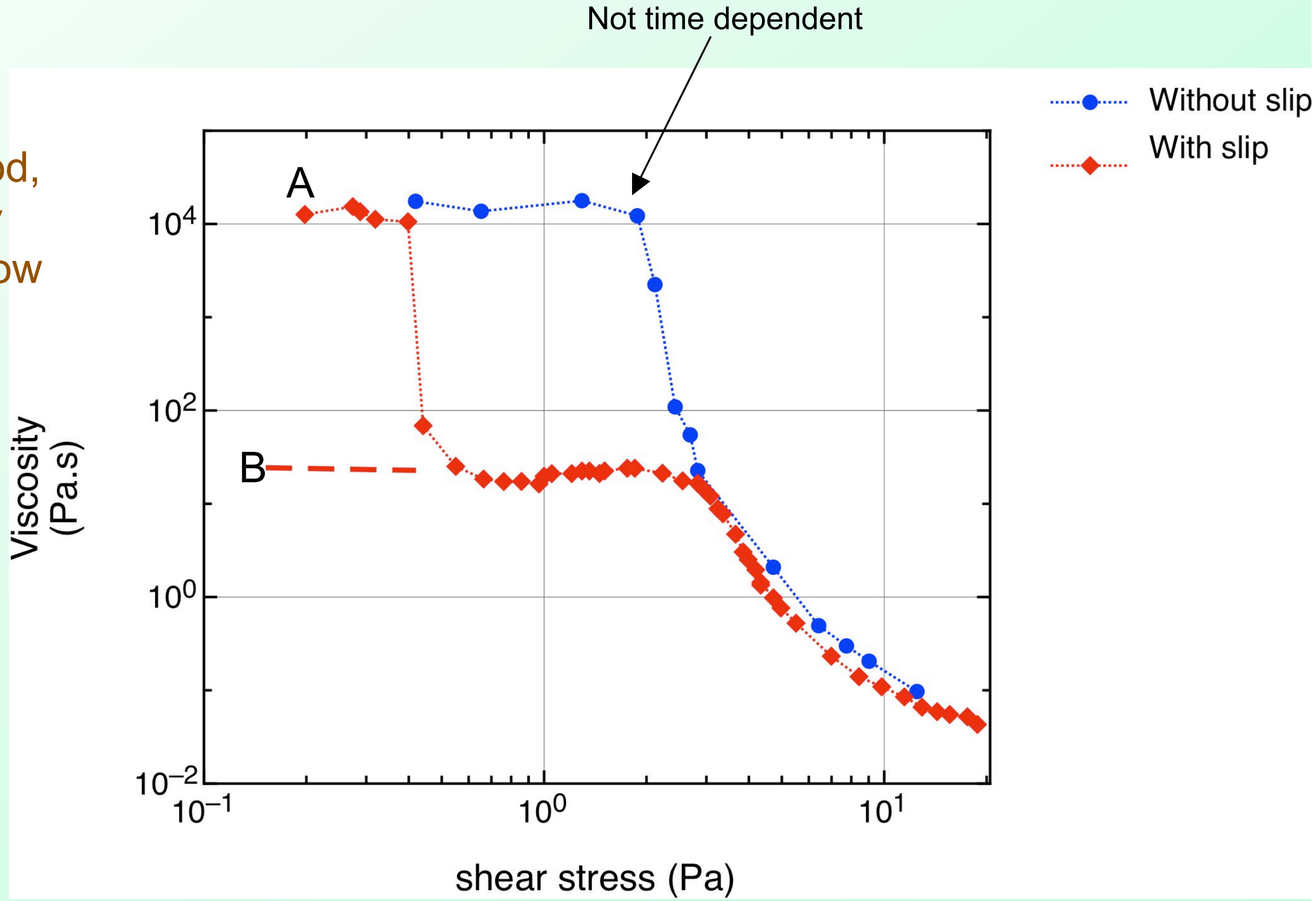
Wall versus bulk yielding & false thixotropy

Depletion flocculated latex φ = 0.4

• Yielding at the wall (**curve A**) was only seen if the dispersion was allowed time to bond - this took an hour or more.

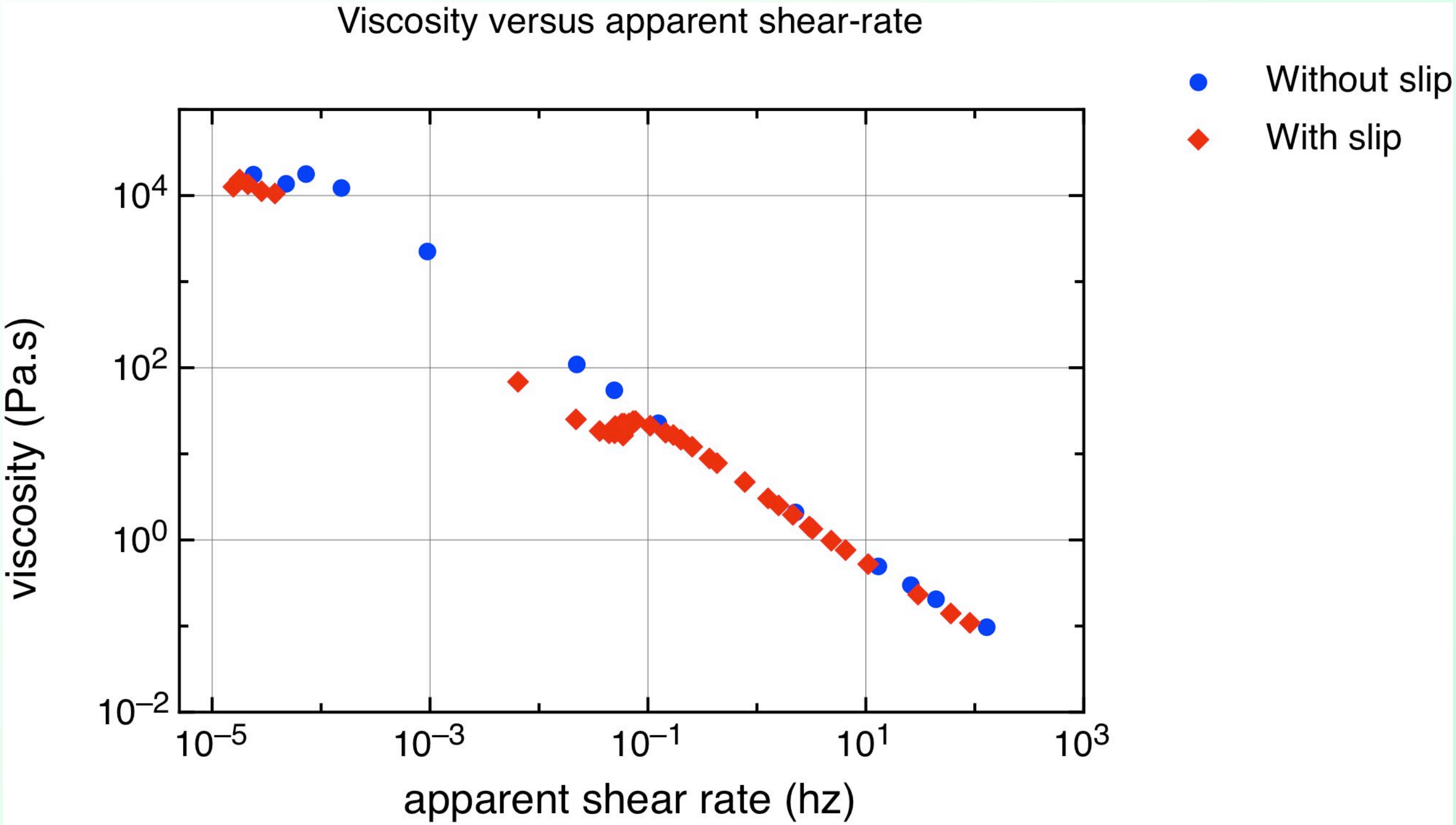
• Without such a rest period, slow "thixotropic" recovery from **B** to **A** was seen below the wall yield stress.

Why does wall adhesion take ~ 100 minutes to develop?



Buscall, R., J. I. McGowan, and A. J. Morton-Jones,' J. Rheol. 37, 621–641 (1993).

Same data plotted as viscosity vs shear rate



Common though it is, this is a very unhelpful way of plotting data - it suppresses features & differences.

Scaling expected from EH Model of MSBC

Predicts dependence of slip layer thickness δ on the elastic modulus G of the particulate network like,

$$\boxed{\delta \propto G^{-2/3}}$$

Everything else being equal.

N.b. MSBC use the shear modulus G as a proxy for the compressional modulus

Meeker, S., Bonnecaze, R.T. & Cloitre, M. Slip and flow in soft particles pastes, 2004 Phys. Rev. Lett., **92**, 198302

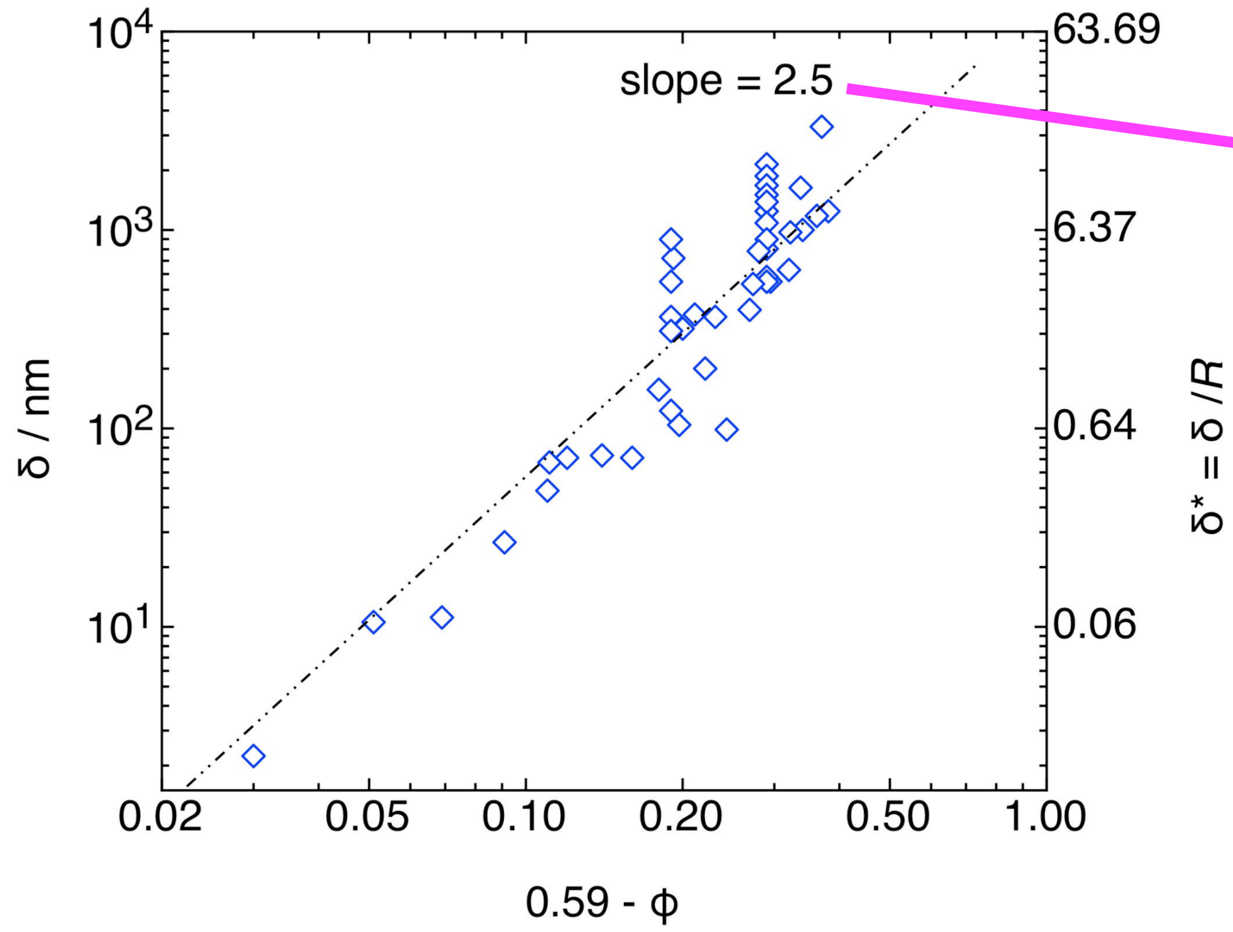
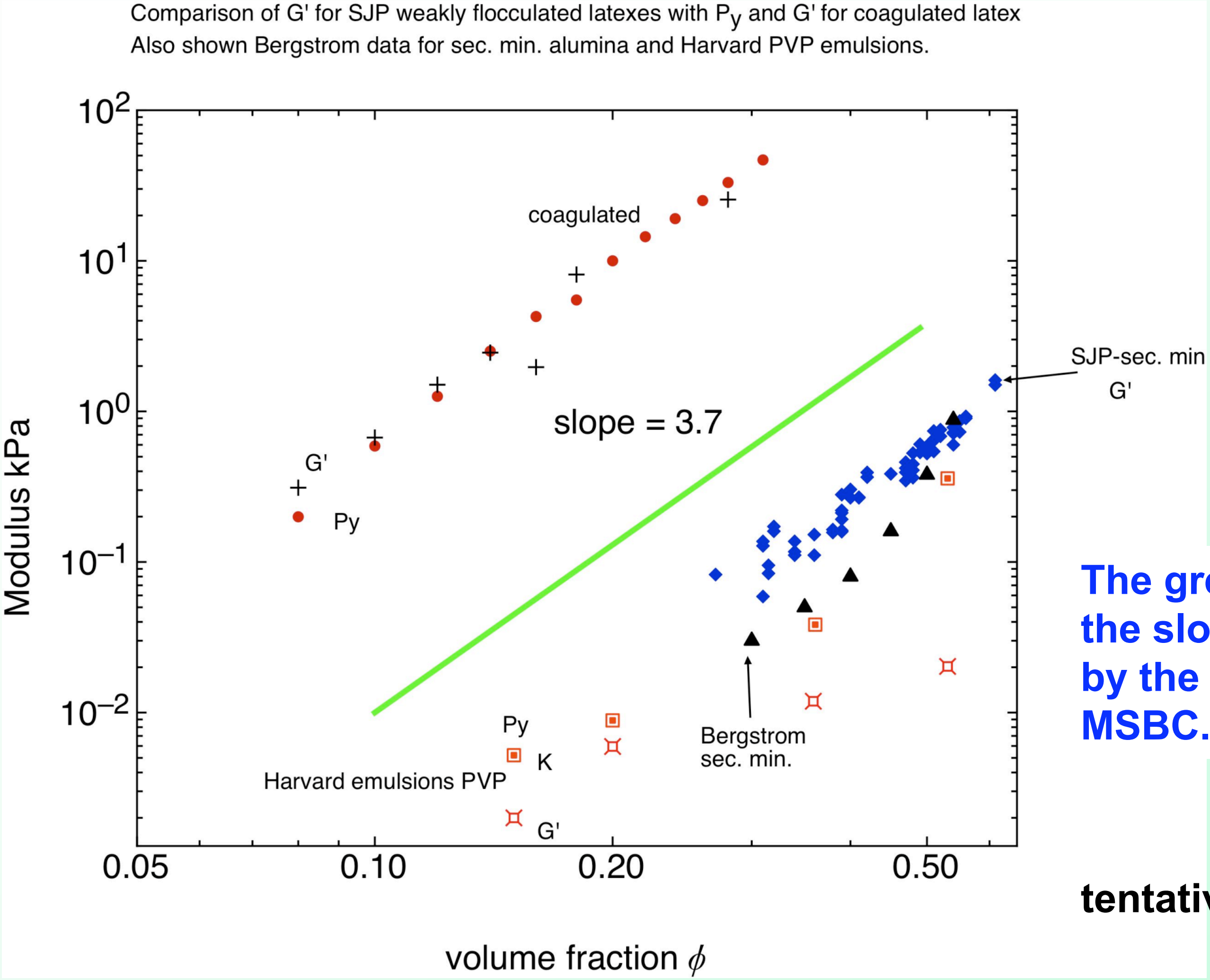


Fig.1 Apparent slip layer thickness δ (left) and scaled thickness δ/R (right) versus volume-fraction for depletion flocculated latex of mean particle radius $R = 157$nm. Data taken from Buscall *et al.* (1993). A concentration exponent of ca. 2.5 is indicated.

MSBC Model

Implied exponent for modulus = 3.7

Compare with ex'tal data.



Don't have data for the the particular system in question, it is however found more generally that both strongly & weakly flocculated systems show a modulus, concentration exponent of ca. 4.

Some examples are shown.

The green line indicates the slope deduced from by the slip data using MSBC. (Its position is arbitrary).

tentative, but, looks promising

Bergstrom, L., C. H. Schilling, and I. A. Aksay, "Consolidation behaviour of flocculated alumina suspensions", J. Am. Ceram. Soc. 75 3305-3314 (1992).

Buscall, R., J. W. Goodwin, M. W. Hawkins & R. H. Ottewill, "The viscoelastic properties of concentrated latices, part I, methods of examination", JCS Faraday Trans. I, 78 2873 (1982).

Buscall, R., P. D. A. Mills, J. W. Goodwin, D. W. Lawson, Scaling behaviour of the rheology of aggregate networks formed from colloidal particles, J. Chem. Soc. Faraday Trans. I, 84(12) 4249-4260 (1988).

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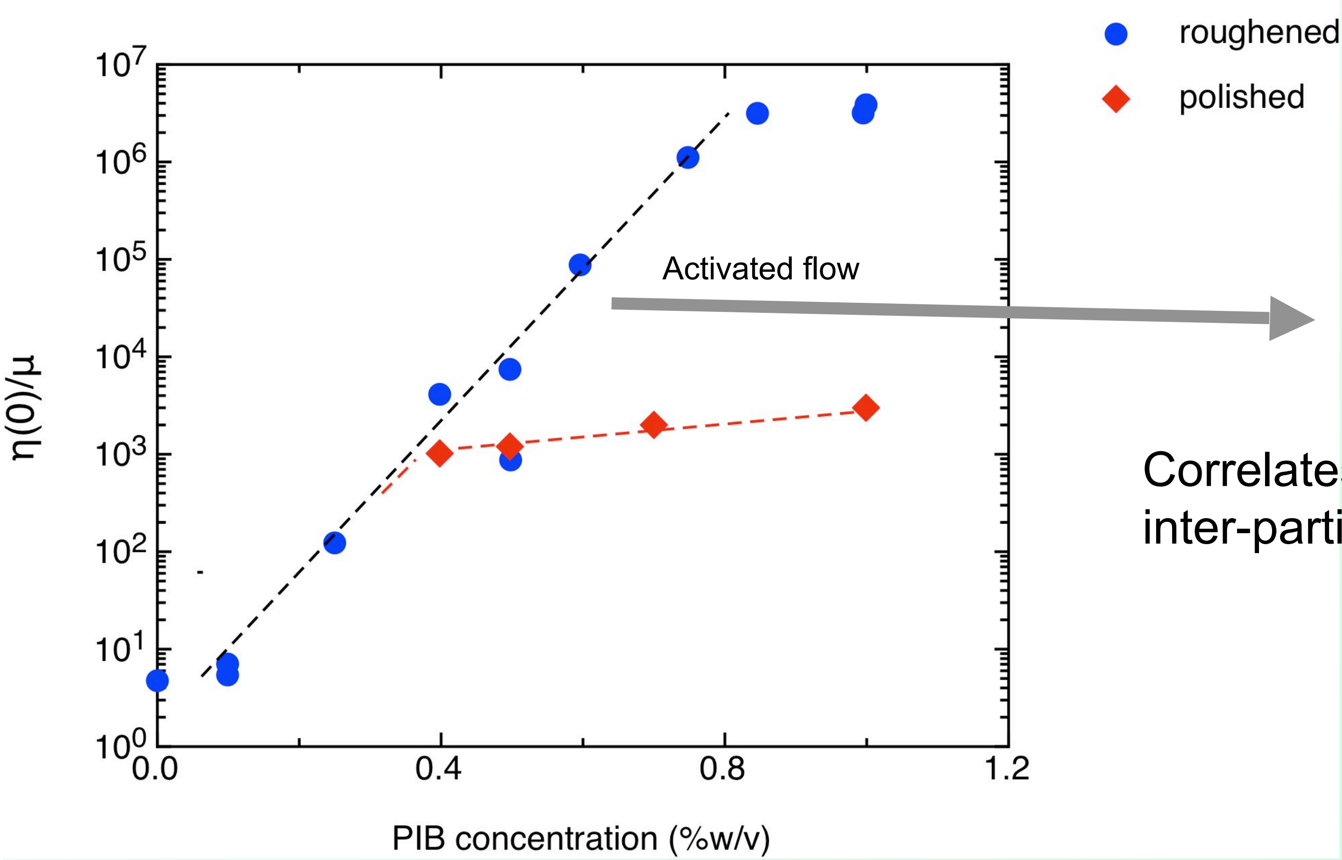
Partridge, S. J., "The rheology of cohesive sediments", Ph.D. thesis, School of Chemistry, University of Bristol (1985).

Let us return to the zero-shear viscosity

Zero shear viscosity of a depletion flocculated system



$$\eta \propto \exp\left(\frac{U_{\min}}{k_B T}\right)$$

Correlates with well-depth of inter-particle potential

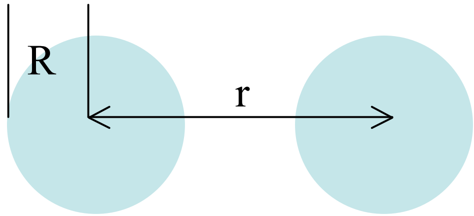
??

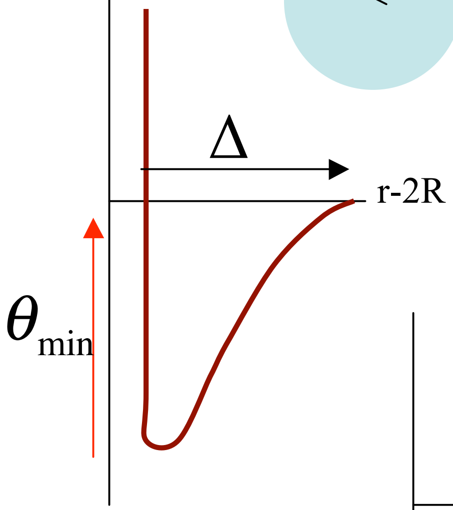
Buscall, R., J. I. McGowan, and A. J. Morton-Jones,’ J. Rheol. 37, 621–641 (1993).
Buscall, R., Wall slip in dispersion rheometry, arXiv:0903.0265v1 [cond-mat.soft] (2009); submitted to J. Rheol..

Mean escape time (Kramers' time)

H.A. Kramers, *Physica* **7** (1940), p. 284

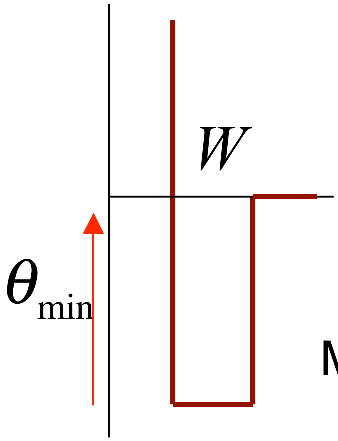
$$\theta(r) = \frac{U(r)}{k_B T}$$





Can be calculated numerically for any potential, e.g. depletion potential, from theory of diffusion-controlled reactions*.

Analytical result: e.g square well* for $\theta_{\min}$ >>1



$$\boxed{\tau_{esc,sw} = \frac{W^2}{D} e^{\theta_{\min}} = \frac{6\pi W^2 R \mu}{k_B T} e^{\theta_{\min}}}$$

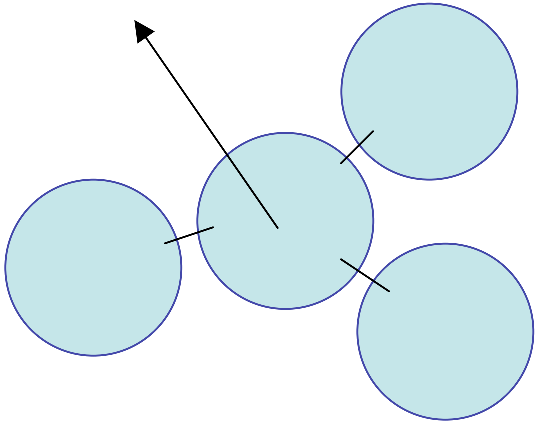
More generally, $\tau_{esc} \approx \tau_{esc,sw}(W_{eff});\ W_{eff} / \Delta \le 1$

**Escape by diffusion from a square well across a square barrier B.U. Felderhof, Physica A: Stat. Mech., Volume 387, 2008, Pages 39-5

*Reaction Rate Theory: Fifty Years After Kramers, P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. 62, 251–342 (1990)

Mean escape or Kramers' time

At φ=0.4 mean Z > 3



z nearest neighbours?

Assume that the activation energy is $z\theta_{min}$

i.e., that the mean escape time from an local environment z is

$$\tau_{esc}(z\ldots) \cong \frac{\Delta^2}{D} e^{z\theta_{\min}} = \frac{6\pi\Delta^2 R\mu}{k_B T} e^{z\theta_{\min}} = \boxed{\tau_0 \frac{\Delta^2}{R^2} e^{z\theta_{\min}}}$$

So, why don't we see more like $\eta \propto \exp\left(3\frac{U_{\min}}{k_B T}\right)$?

Particulate gels have a heterogeneous structure

Does

$$\eta \propto \exp\left(\frac{U_{\min}}{k_B T}\right)$$

Imply that escape of the minor fraction of singly-bonded particles facilitates creeping flow?

It looks like it. The test would be to vary volume-fraction and well-depth as we might then expect, something like,

$$\eta(\varphi) \propto \eta_{\mathrm{HS}}(\varphi) f(\varphi) \exp\left(\frac{U_{\min}}{k_B T}\right)$$

Hard-sphere viscosity

fraction of singly-bonded

Concluding remarks

Concerning slip in general

- Slip is what suspensions (etc.) do, if they can.

- It is not just as source of quantitative error, its effect can be qualitative. (cf. false thixotropy).

- The smooth tools supplied by default by some rheometer manufacturers and their agents are simply not suitable for testing suspensions (etc).

- Why is that so many papers appear which do not even mention testing for slip in the methods section?
    - vicious circle? Who is refereeing these papers? What can be done?

- The model of Seth et al. looks to be a very promising basis for rationalising slip and wall yielding.

Ab uno disce omnes

(from one example learn about all (Virgil)).

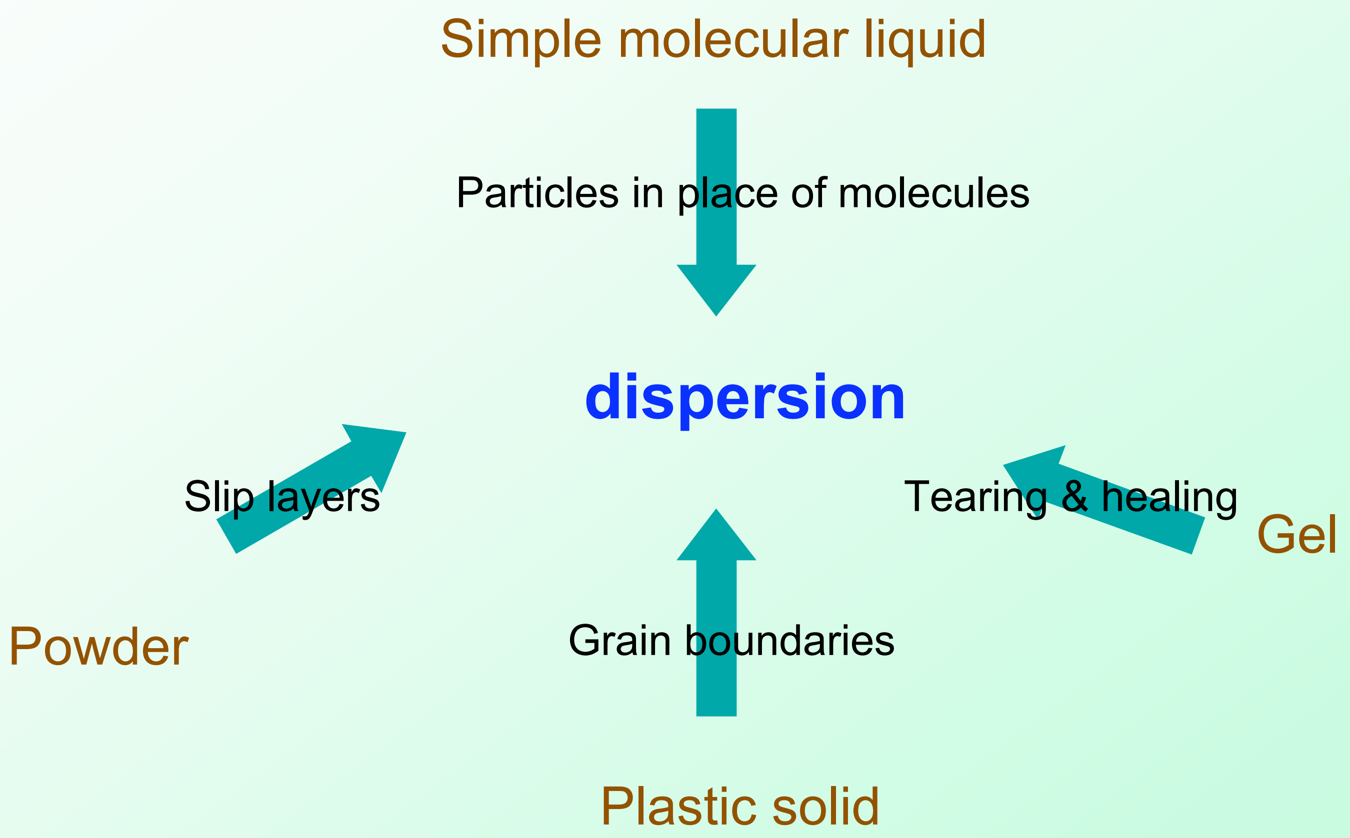
• Since disperse systems slip, the only sensible or logical way to approach suspension rheology is to assume that yours will until proved otherwise.

• Whereas, the received message appears to be "If others can ignore slip so can I".

• And, one suspects, that there are too many people refereeing experimental papers who have little understanding of the subleties and difficulties of dispersion rheometry.

Buscall, R., J. I. McGowan, and A. J. Morton-Jones,' J. Rheol. 37, 621–641 (1993).
Buscall**, R.,** Wall slip in dispersion rheometry**,** arXiv:0903.0265v1 [cond-mat.soft] (2009); submitted to J. Rheol..
Buscall, R, T. H. Choudhury, M. A. Faers, J. W. Goodwin, P. A. Luckham & S. J. Partridge, Soft Matter (2009); DOI:10.1039/b805807e.

Paradigms or analogies



Weakly flocculated systems

• Viscous flow of weakly flocculated systems relies on the escape of singly bonded particles from the network*; this is an activated process.

• Delayed collapse (sedimentation) is an activated process likewise, albeit a somewhat more democratic one (not just singly bonded particles).

• Much (most?) thixotropy is "false", wall slip in disguise?(1,2).

• Slip may indeed correlate with the elasticity of the particulate network as suggested by MSBC (2).

(1) My experience suggests this.

(2) more data needed though - generated, preferably, by people who know what they are doing.

Buscall, R., J. I. McGowan, and A. J. Morton-Jones,' J. Rheol. 37, 621–641 (1993).
Buscall, R., Wall slip in dispersion rheometry, arXiv:0903.0265v1 [cond-mat.soft] (2009); submitted to J. Rheol..
Buscall, R, T. H. Choudhury, M. A. Faers, J. W. Goodwin, P. A. Luckham & S. J. Partridge, Soft Matter (2009); DOI:10.1039/b805807e.

Some references*

* Some which have been cited already but are included for completeness

Some papers on (or which make explicit mention of) slip

Ahuja, A. and Singh, A., 2009, Slip velocity of concentrated suspensions, J. Rheol. 53: 1461-1485.

Aral, B. K., and D. M. Kalyon, ''Effects of temperature and surface roughness on time-dependent development of wall slip in steady torsional flow of concentrated suspensions,'' J. Rheol. 38, 957–972 (1994).

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Meeker, S. P., R. T. Bonnecaze, and M. Cloitre, ''Slip and flow of soft particle pastes,'' Phys. Rev. Lett. 92, 198302/1–4 (2004).

Meeker, S. P., R. T. Bonnecaze, and M. Cloitre, "Slip and flow of pastes of soft particles: Direct observation and rheology," J.Rheol. 48, 1295–1320 (2004).

Møller, P. C. F., A. Fall and D. Bonn, Origin of apparent viscosity in yield stress fluids below yielding, EPL 87 No 3 (2009) 38004.

Mooney, M., ''Explicit formulas for slip and fluidity,'' J. Rheol. 2, 210–222 (1931).

Ovarlez, G., Q. Barral, P. Coussot Three-dimensional jamming and flows of soft glassy materials, Nature Materials 9, 115-119 (2010) doi:10.1038/nmat2615 Letter.

Pal, R., ''Slippage during the flow of emulsions in rheometers,'' Colloids Surf., A 162, 55–66 (2000).

Persello, J., A. Magnin, J. Chang, J.-M. Piau, and B. Cabane, ''Flow of colloidal aqueous silica dispersions,'' J.Rheol. 38, 1845–1869 (1994).

Pignon, F., A. Magnin, and J.-M. Piau, ''Thixotropic colloidal suspensions and flow curves with minimum: Identification of flow regimes and rheometric consequences,'' J. Rheol. 40, 573–587 (1996).

Plucinski, J., R. K. Gupta, and S. Chakrabarti, ''Wall slip of mayonnaises in viscometers,'' Rheol. Acta 37, 256–269 (1998).

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Princen, H. M., ''Rheology of foams and highly concentrated emulsions. II. Experimental study of the yield stress and wall effects for concentrated oil-in-water emulsions,'' J. Colloid Interface Sci. 105, 150–171 (1985).

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Seth, J. R., M. Cloitre and R.T. Bonnecaze, "elastic properties of soft particle pastes", J. Rheol. 50, 353-376 (2006).

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Tindley, A. L., "The effect of electrolytes on the properties of titanium dioxide dispersions", Ph.D. Thesis, Engineering Faculty, University of Leeds, (2007).

Walls, H. J., S. B. Caines, A. M. Sanchez, and S. A. Khan, "Yield stress and wall slip phenomena in colloidal silica gels", J. Rheol. 47, 847-867 (2003).

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Some late additions

Rheol Acta (2010) 49:305–314
DOI 10.1007/s00397-010-0430-4
Non-linear viscoelasticity and temporal behavior of typical yield stress fluids: Carbopol, Xanthan and Ketchup G. Benmouffok-Benbelkacem · F. Caton · C. Baravian · S. Skali-Lam

Rheol Acta (2008) 47:601–607 DOI 10.1007/s00397-008-0267-2
Plastic behavior of some yield stress fluids:from creep to long-time yield
Francois Caton � Christophe Baravia i

Some recent counter-examples (of many!) wherein the possibility of slip *appears* not to have been considered.

Haleem, B. A. and P. R. Nott, “Rheology of particle-loaded semi-dilute polymer solutions”, J. Rheol. 53, 383-400 (2009).

Grillet, A.M., R. R. Rao, D. B. Adolf, S. Kawaguchi, and L. A. Mondy, “Practical application of thixotropic suspension models”, J. Rheol. 53, 169–189 (2009).

S. Mueller, E. W. Llewellin and H. M. Mader, The rheology of suspensions of solid particles, Proc. R. Soc. A, December 2009, doi: 10.1098/rspa.2009.0445.

User's guide to data obtained using smooth tools

- If there is no yield stress, no apparent thixotropy or hysteresis and if the apparent relative viscosity is less than ca. 100 at ALL (1) stresses and shear rate…
- Then you can probably believe the viscosity values (1, 2).
- Otherwise…, they are likely be flawed.
- Should you happen to find a viscosity shear-rate exponent of unity, or close to it, then be very suspicious.
- Should you see thixotropy, likewise.

(1) Not just the measured range, you need to be sure that the zero-shear viscosity is << 1000.

- Even then, please address the issue in any publications, it is because people don't, arguably, that so much bad practice propagates.

A copy of my original talk on sedimentation is available on request