Some thoughts on heterogeneous flowable systems

Morton Denn

Heterogeneous systems (suspensions, emulsions, etc.) that flow can exhibit both solid-like and liquid-like characteristics.

Unlike polymer solutions and melts, they need not exhibit memory.

From an engineering perspective, the ultimate goal is the development of invariant constitutive equations that are valid for flows in complex geometries and are, to the extent possible, physics-based.

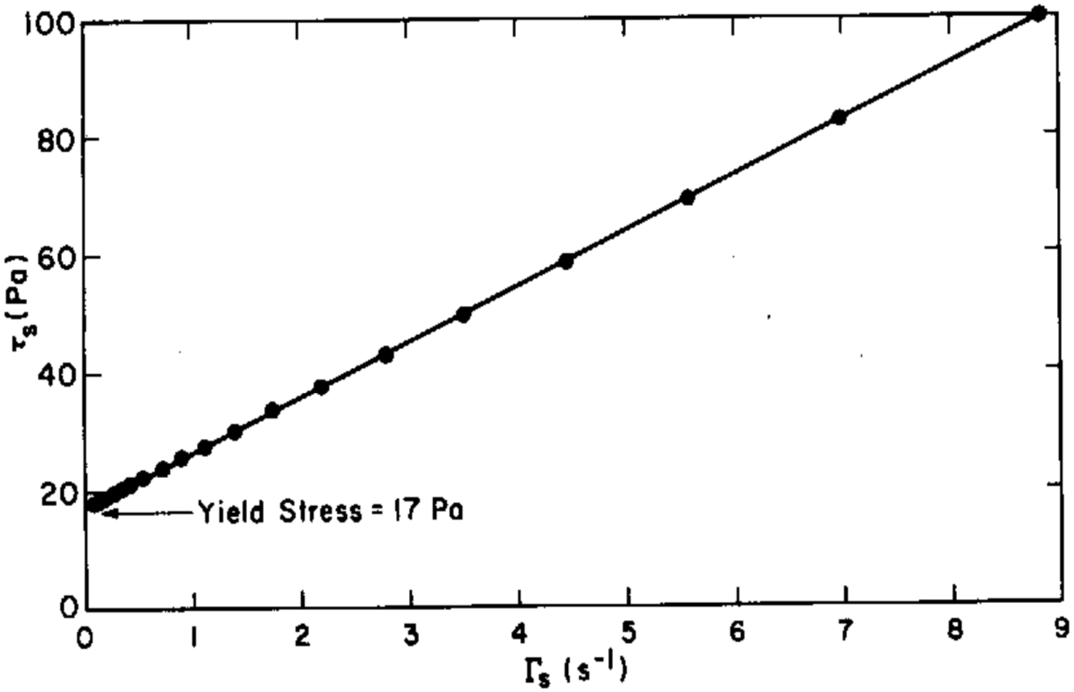

Figure 2-10. Shear stress as a function of shear rate for a meat extract at 77°C. (Data of D. V. Boger.)

Bingham fluid: $\tau = \tau_y + \eta_p \Gamma_s$

viscosity: $\eta = \tau/\Gamma_s = \eta_p + \tau_y/\Gamma_s$

Highly shear thinning!

Properly Invariant Bingham Fluid (Oldroyd, Prager)

$$\boldsymbol{\tau} = \left[\eta_p + \frac{\tau_y}{\sqrt{\tfrac{1}{2}\mathbf{D}:\mathbf{D}}} \right] \mathbf{D}, \quad \tfrac{1}{2}\boldsymbol{\tau}:\boldsymbol{\tau} \geq \tau_y^2$$

$$\boldsymbol{\tau} = 3G\mathbf{E}, \quad \tfrac{1}{2}\boldsymbol{\tau}:\boldsymbol{\tau} < \tau_y^2$$

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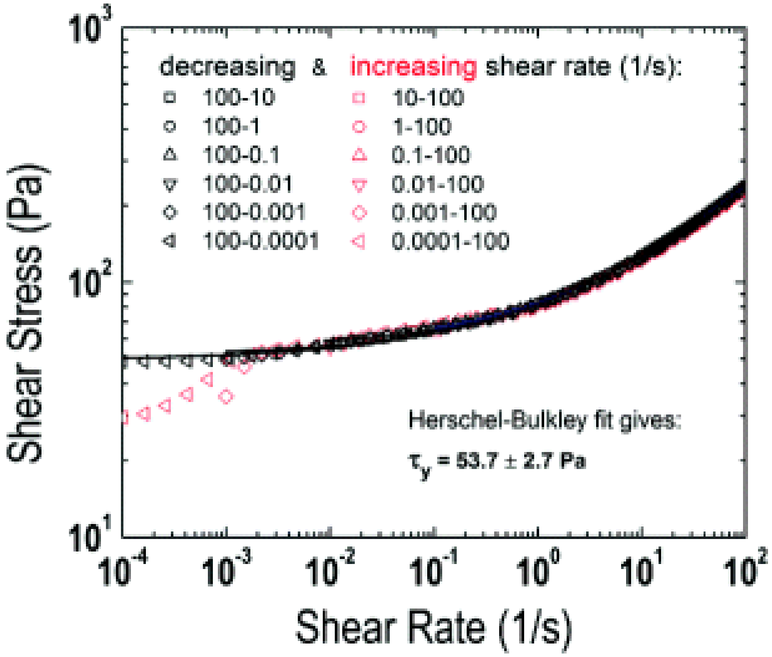
$$\boldsymbol{\tau} = 3G\mathbf{E}, \quad \tfrac{1}{2}\boldsymbol{\tau}:\boldsymbol{\tau} < \tau_y^2$$

Usually assume $G \to \infty$, so $\mathbf{D} = \mathbf{0}, \quad \tfrac{1}{2}\boldsymbol{\tau}:\boldsymbol{\tau} < \tau_y^2$

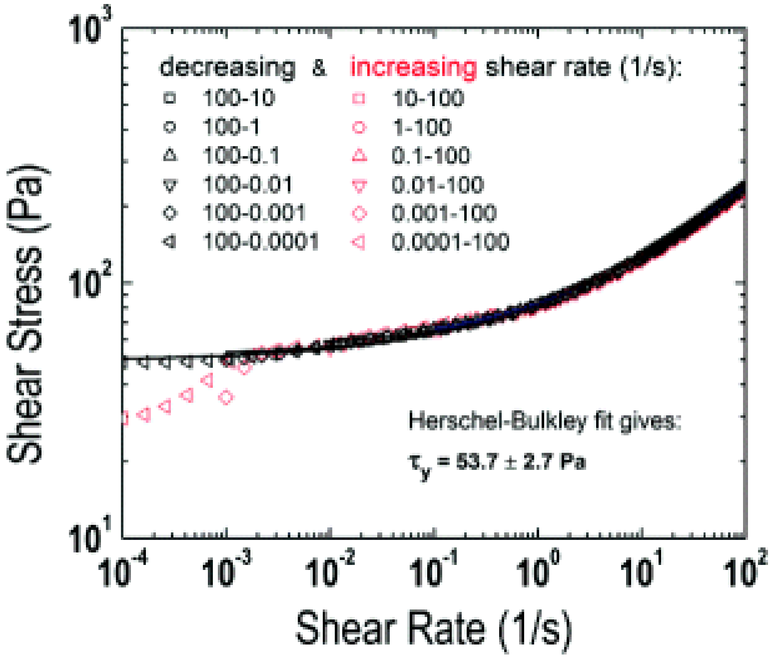
More interesting yield-stress materials

Example: Carbopol Ultrez U10 gel in water at pH7



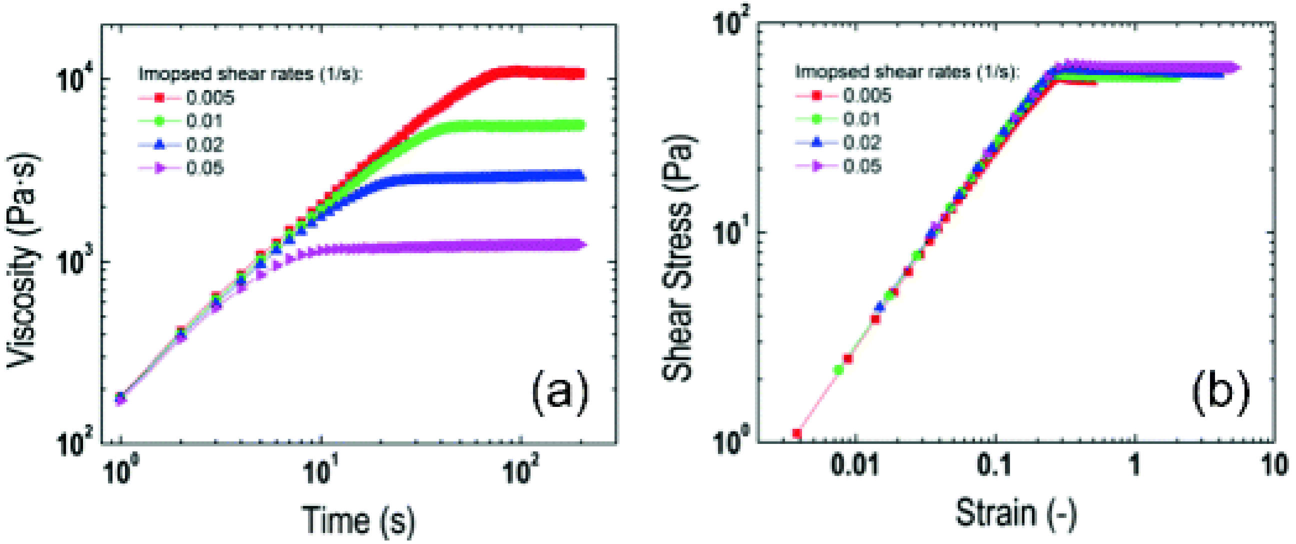
$$\tau = \tau_y + K\dot{\gamma}^n$$

This is a *simple* yield-stress fluid (no hysteresis)

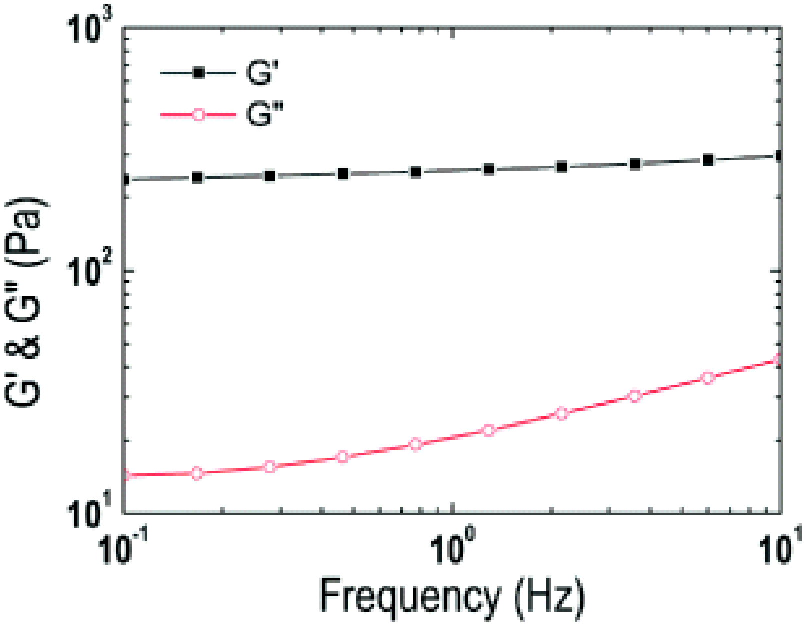


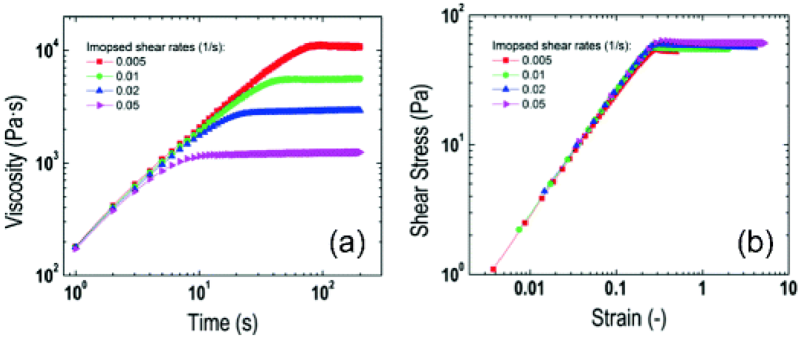
$$\tau = \tau_y + K\dot{\gamma}^n$$

Startup: Elastic response followed by transition to a fluid



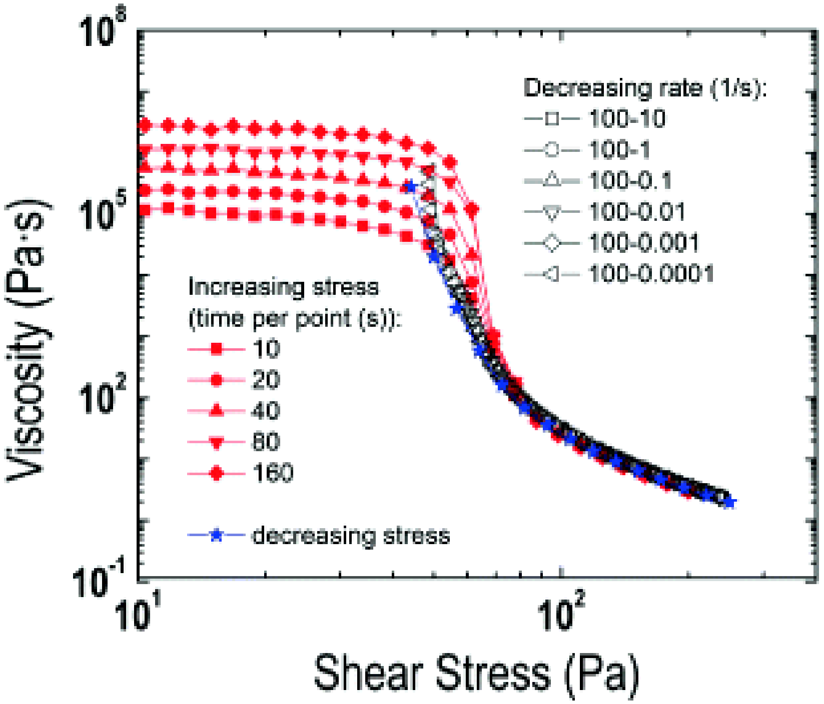
(Clearly $G \neq 0$)

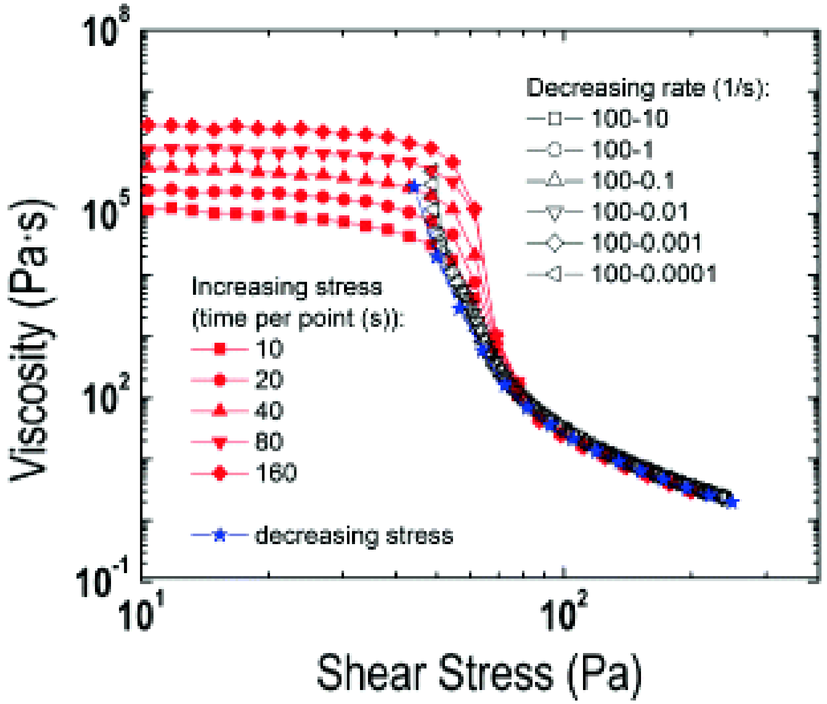




Indeed, G’ & G” ≠ 0 with small strain. This is a viscoelastic solid.

Not so simple. What is going on at low rates?





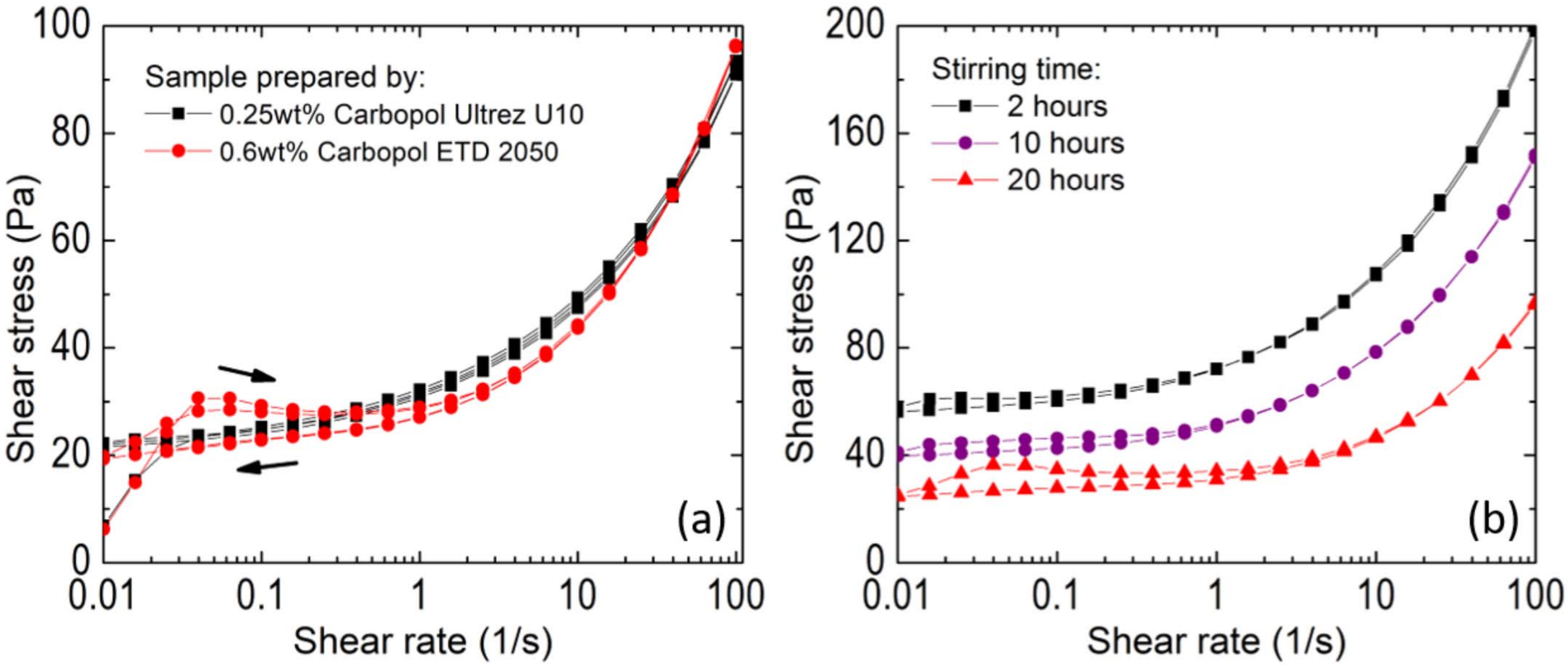
This behavior is qualitatively that of a Kelvin-Voigt solid prior to yielding: $\tau = G\gamma + \eta\dot{\gamma}$

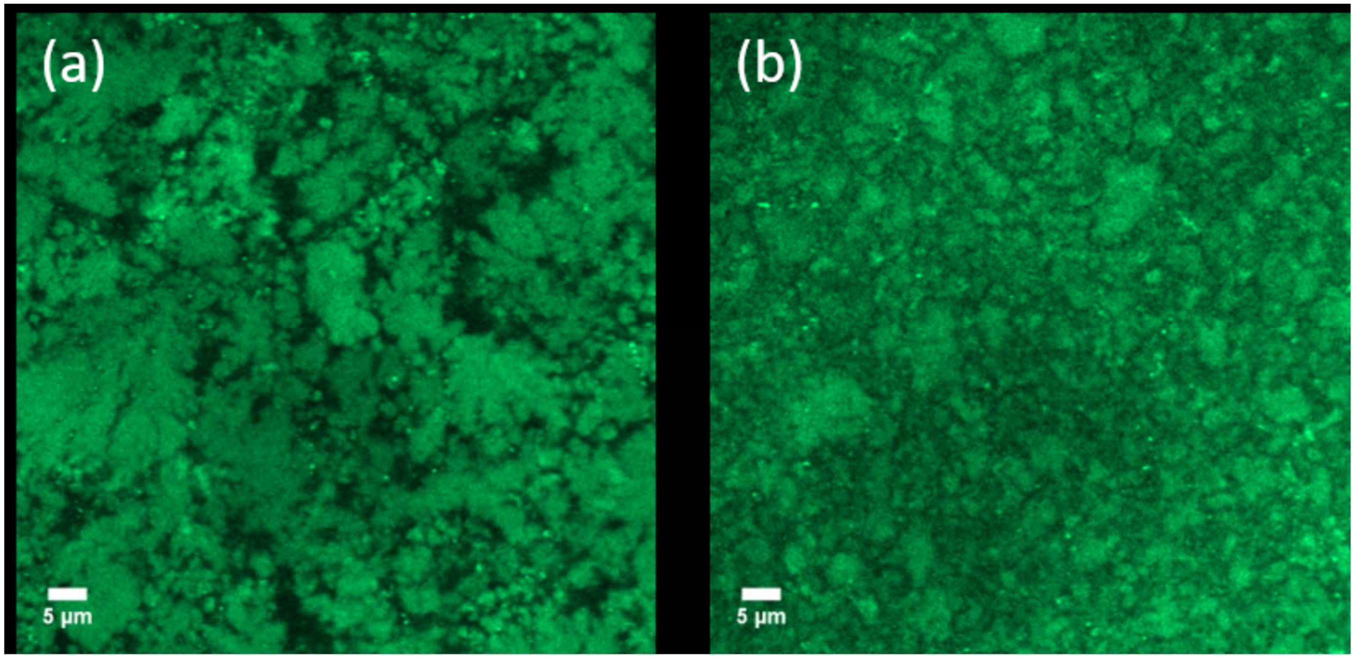
$$\frac{\tau}{\dot{\gamma}} = \eta_{app} = \eta e^{Gt/\eta}$$

More physics-based models can fit this behavior quantitatively.

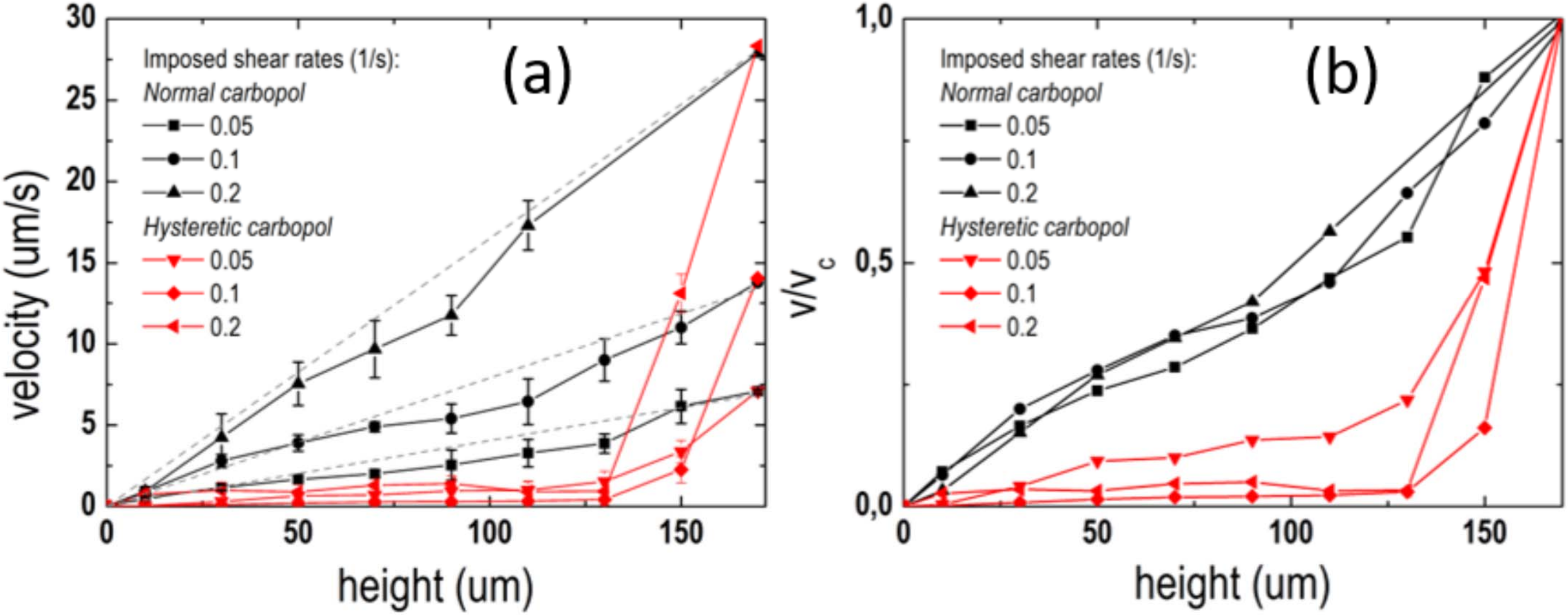
But not everything is “simple.” In fact, few yield-stress fluids *are* simple.

Hysteresis, or *thixotropy*.

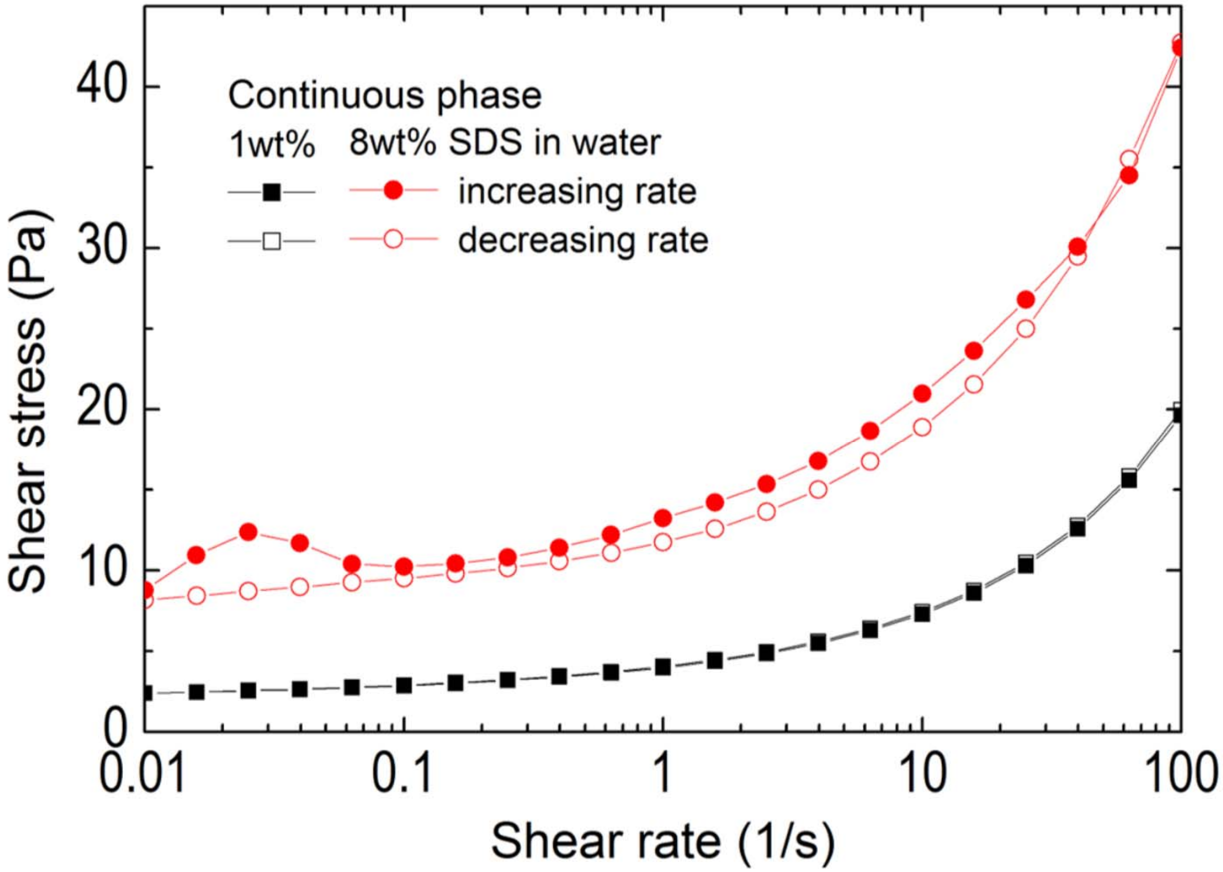




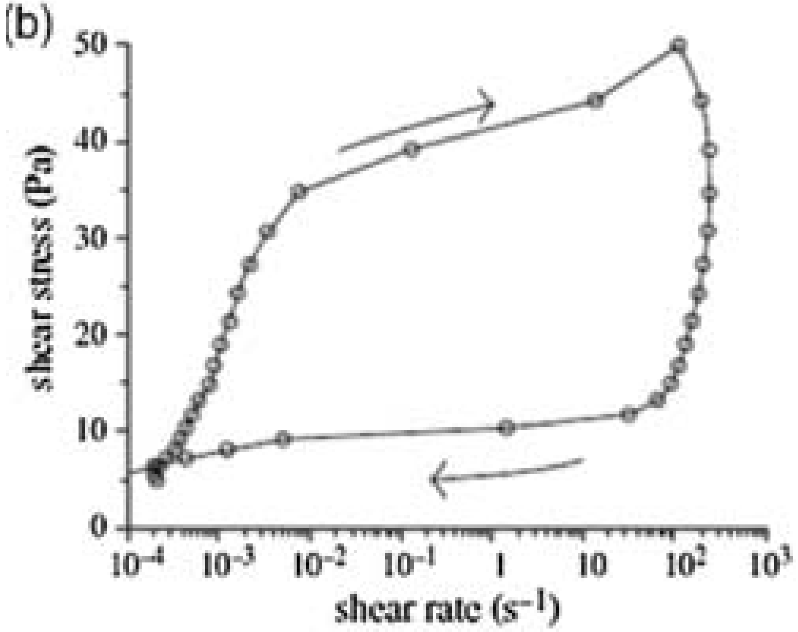
Confocal fluorescent microscope image of two initially identical samples of 0.5wt% Carbopol in water (Carbopol is dyed with Rhodamine 6g). In (a) simple yield stress sample and in (b) after heavy stirring the cross-linked structures are broken. The small thermal particles in the presence of larger ones cause a depletion interaction, creating an effective attractive force between the larger polymer sponges. The depletion interaction can then lead to the formation of a percolated network of the large Carbopol microgel particles that is sensitive to the shear, which leads to the observed thixotropy. (Maureen Dingreve)



Velocity profiles at different imposed shear rates for normal (black) and thixotropic (red) Carbopol.



Flow curves for 70% Castor oil-in-water emulsion for different SDS concentration in the continuous phase. This system has attractive depletion forces between droplets. Filled/empty symbols are increasing/decreasing imposed shear rate.

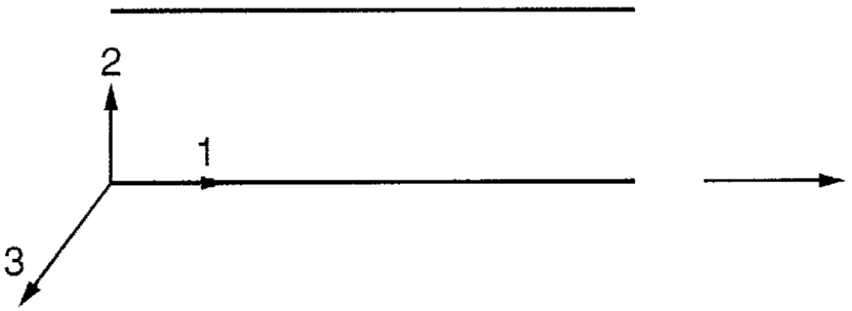


LAOS

10% bentonite exhibiting thixotropy

There is a lot of attention currently being paid to deriving material information from the shapes of various parts of the cycle.

Shear rheometry



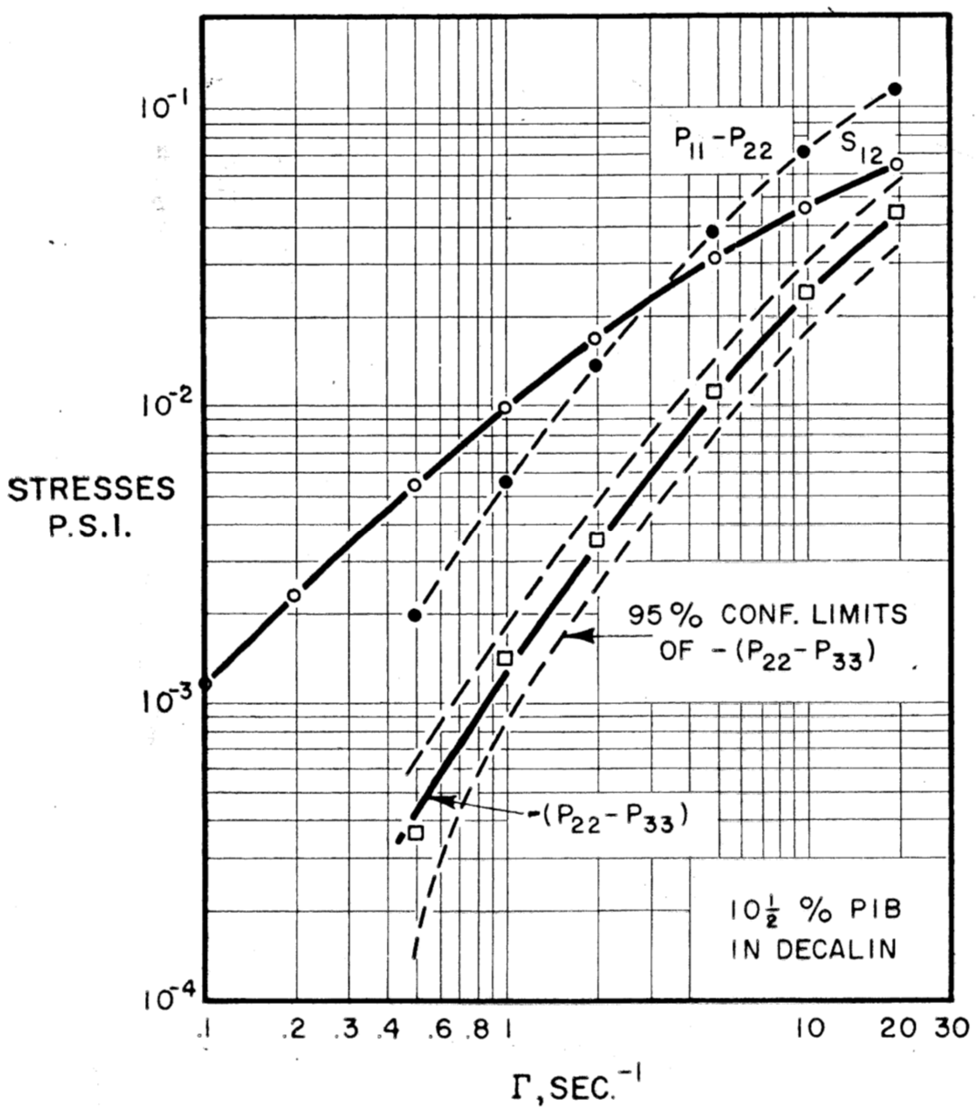
1 = shear direction
2 = gradient direction
3 = neutral (vorticity) direction

$$\eta = \tau_{12}/\dot{\gamma}$$

$$N_1 = \tau_{11} - \tau_{22} = \text{total normal stress in } \textit{gradient} \text{ direction}$$

$$N_2 = \tau_{22} - \tau_{33} = \text{total normal stress in } \textit{neutral} \text{ direction}$$

Flexible polymers: N_1 always positive. N_2 typically negative and much smaller in magnitude than N_1.



Ginn and Metzner, *Trans. Soc. Rheology*, **13**, 429-453 (1969)

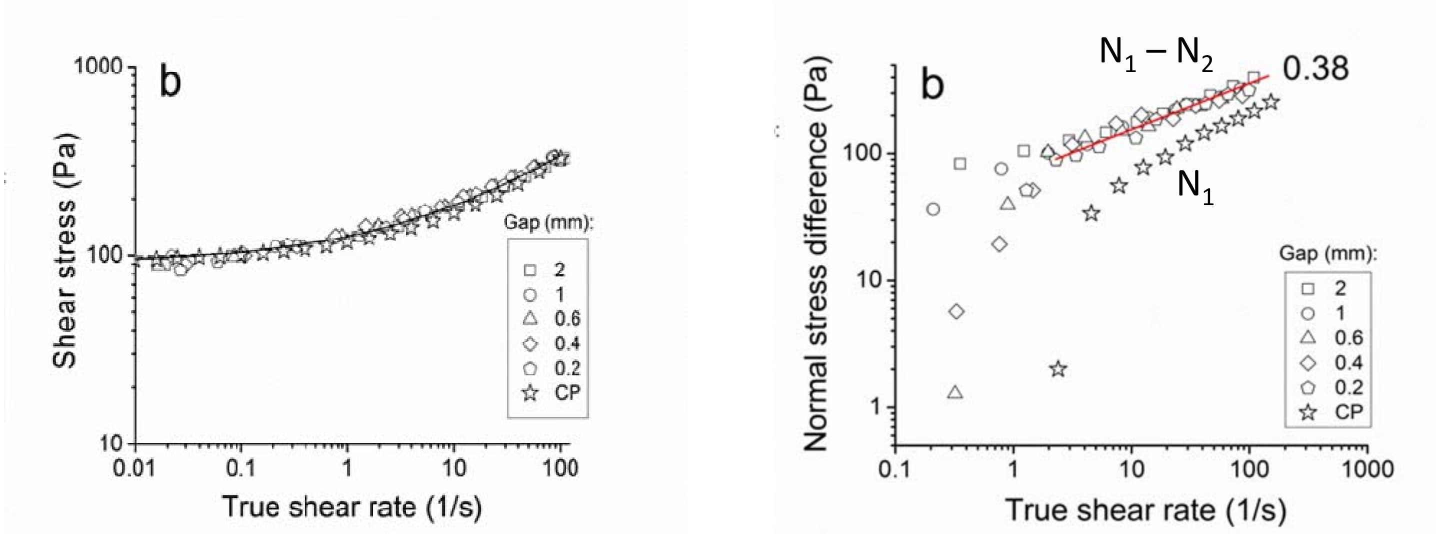
10-1/2% PIB in decalin

N_1 from cone-and-plate total force

$N_1 – N_2$ from parallel plate total force

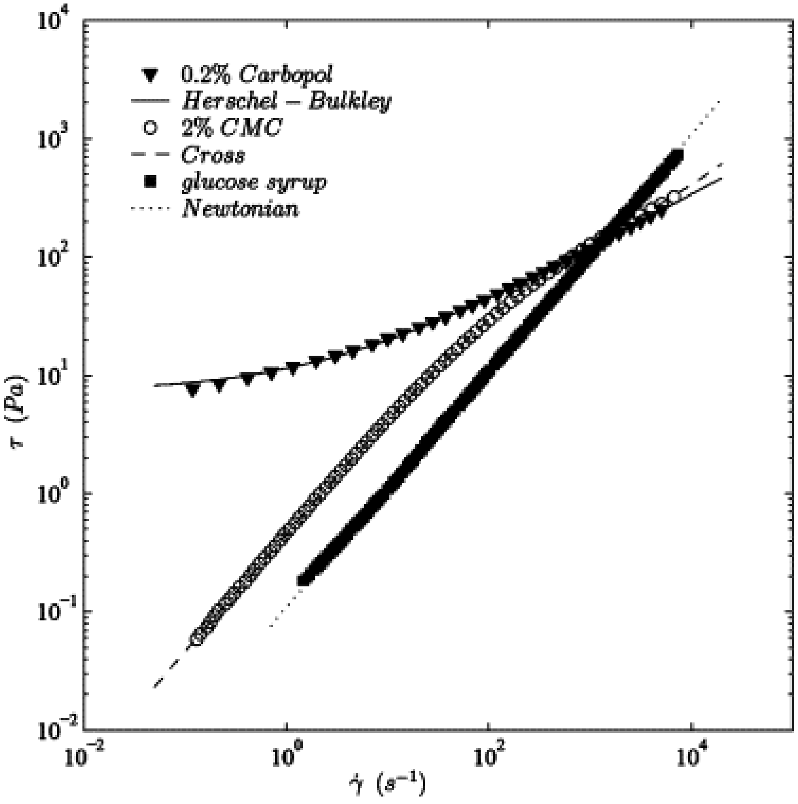
$N_2 < 0$, obtained by difference

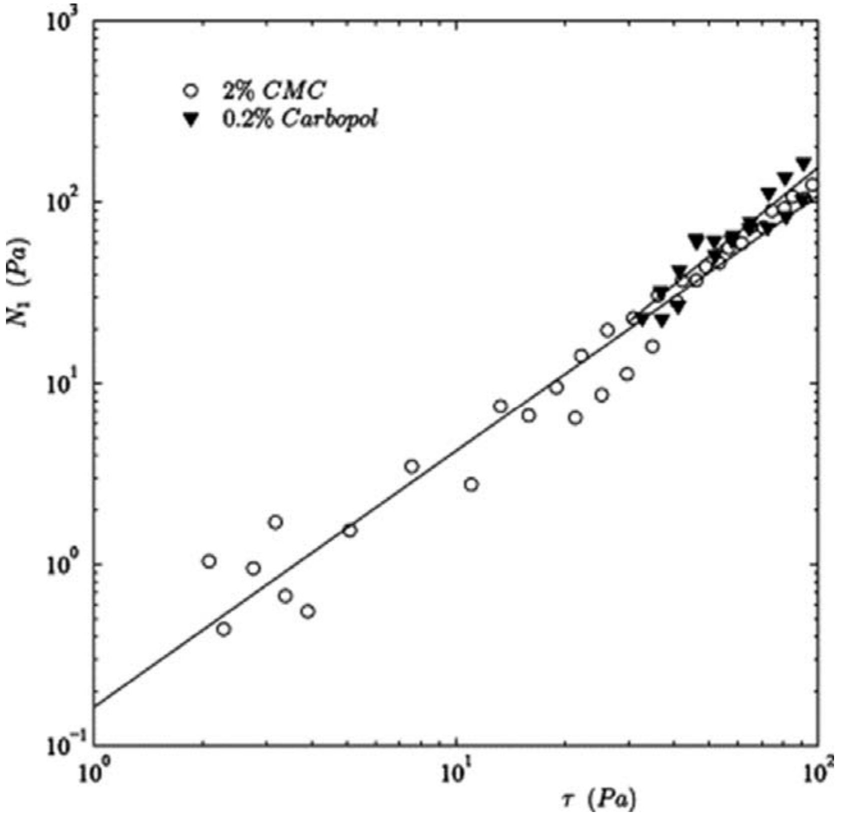
Normal stresses are observed for yield-stress fluids, but few measurements.



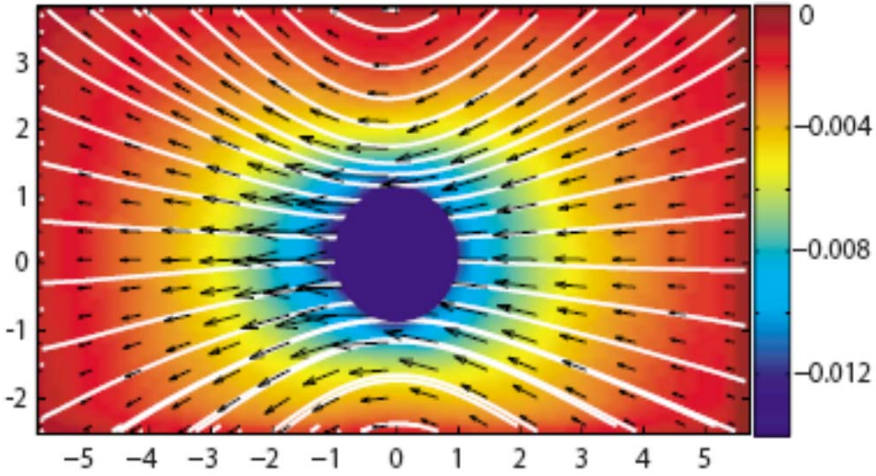
Emulsion: 46.2 wt% ultra-pure water and 53.8 wt% glycerol as the continuous phase, silicone oil with kinematic viscosity 500 cSt as the dispersed phase, stabilized by dissolving 1 wt% sodium dodecyl sulfate (SDS) in the water-glycerol solution.

$\tau_y = 90.7\ Pa,\ K = 35.8\ Pas^n$ and $n = 0.42$.





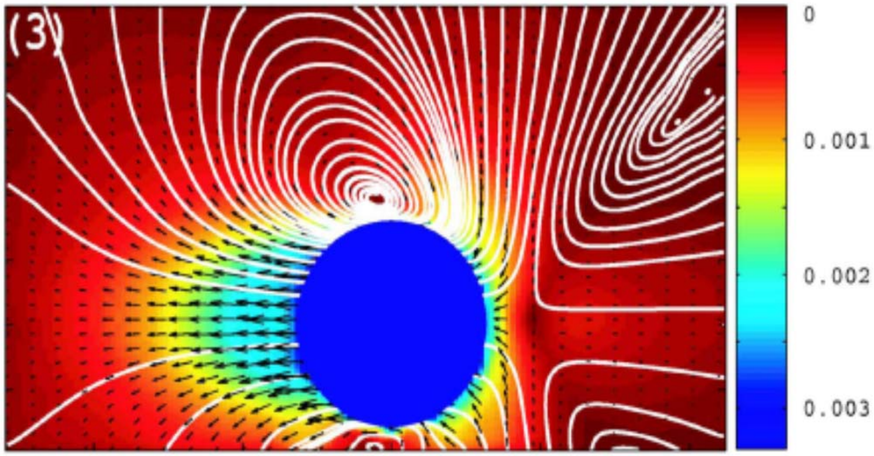
Peixinho et al., 2005



Newtonian

Re << 1

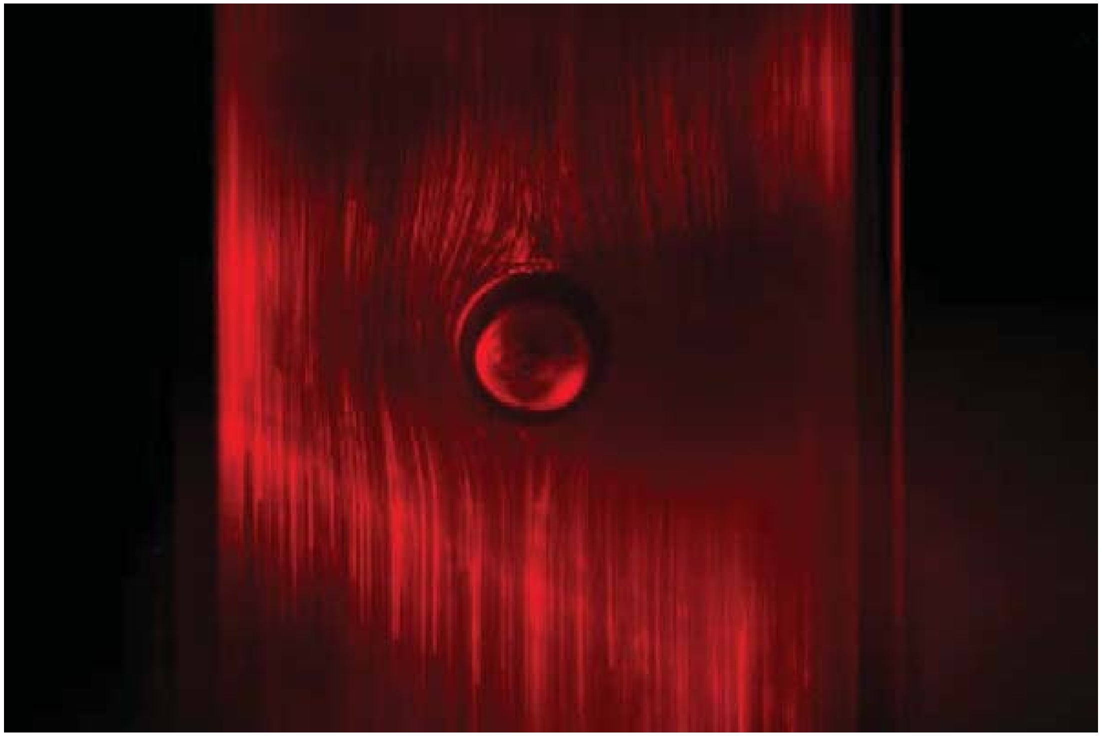
movement R to L
color = velocity magnitude
full lines = streamlines
Putz *et al*, *Physics of Fluids* (2008)



Yield Stress

Sphere in Carbopol (apparently a thixotropic Carbopol)

Loss of fore-aft symmetry



Visualizing the streamlines around a steel ball falling through non-thixotropic Carbopol

Yield-stress fluids may be viscoelastic solids prior to yielding. The yielding condition itself may be deformation dependent, and the fluidized state sometimes appears to exhibit viscoelasticity. The first viscoelastic-plastic constitutive equation, intended for filled elastomers, appears to have been published by the late Jim White in 1993, but it received little attention. Viscoelastic-plastic constitutive equations for complex flows have been developed by Saramito, de Souza Mendes, and M. Renardy, with some novel ideas adapted from other fields by McKinley and Ewoldt. The Saramito + McKinley formulation has been applied by Tsomopoulos and coworkers to describe the flow around a falling sphere, which includes loss of fore-aft symmetry for some (apparently hysteretic) Carbopol formulations and cannot be described by classical Bingham and Herschel-Bulkley equations.

There has been an extensive literature on developing an understanding of the mechanics of the yield stress and placing the phenomenon into the context of glassy materials.

Some recent reviews

N. J. Banforth, I. A. Frigaard, G. Overlez, Yielding to Stress: Recent developments in viscoplastic fluid mechanics, Annual Review of Fluid Mechanics, 46:121-146 (2014)

D. Bonn, M. M. Denn, L. Berthier, T. Divoux, S. Manneville, Yield stress materials in soft condensed matter, Reviews of Modern Physics, 89: 035005 (2017)

P. Coussot, Bingham's heritage, Rheologica Acta, 56: 163-176 (2017)

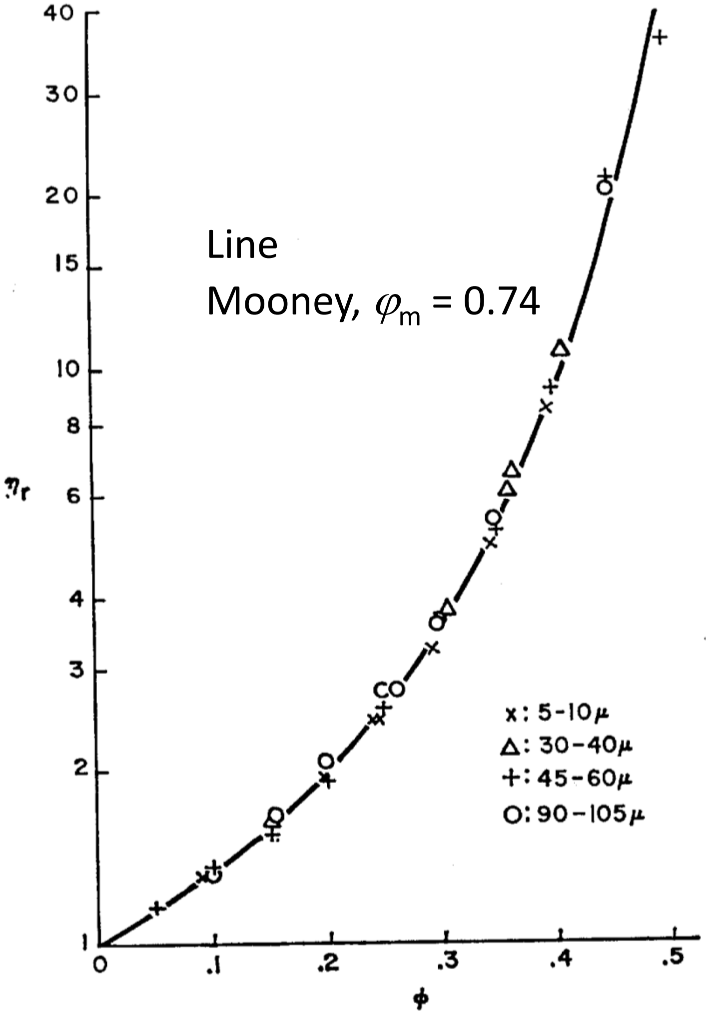
Plus some special issues of J. Non-Newtonian Fluid Mechanics and Rheologica Acta

Suspensions

Everyone has seen pictures and videos of someone running over a pool of corn starch and water (*Oobleck*) but sinking when standing still. Most of the phenomena observed for corn starch and water, which is a complex system with large faceted particles of about 20 μm, are also observed in concentrated suspensions of hard spheres in Newtonian suspending fluids, so this is where we focus.

The major differences between sub-micron (colloidal) and super-micron spheres are (1) the former exhibit Brownian motion, which is a randomizing force and (2) interfacial chemistry is more likely to be important for colloidal systems. Indeed, *concentrated suspensions of colloidal particles can exhibit a yield stress.*

Relative viscosity $\eta_r = \dfrac{\eta}{\eta_s}$



Line

Mooney, φ_m = 0.74

Lewis and Nielsen (1968)
Glass beads

Krieger & Dougherty $$\eta_r = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-2.5\varphi_m}$$

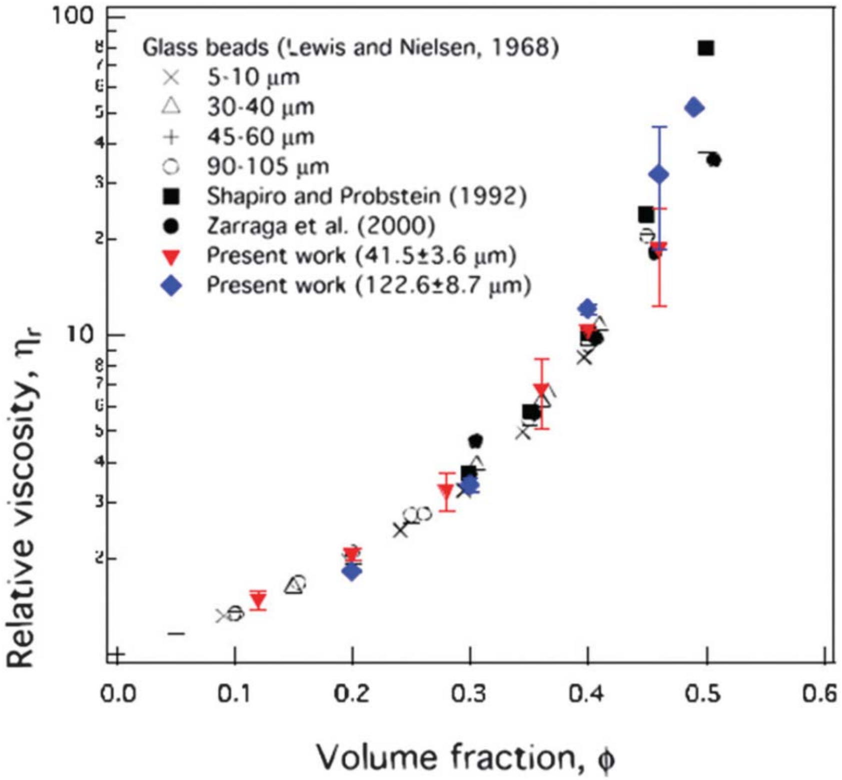
Mooney $$\eta_r = \exp[2.5\,\varphi/(1 - \varphi/\varphi_m)]$$

Zarraga $$\eta_r = e^{-2.34\varphi}\left(1 - \frac{\varphi}{\varphi_m}\right)^{-3}$$

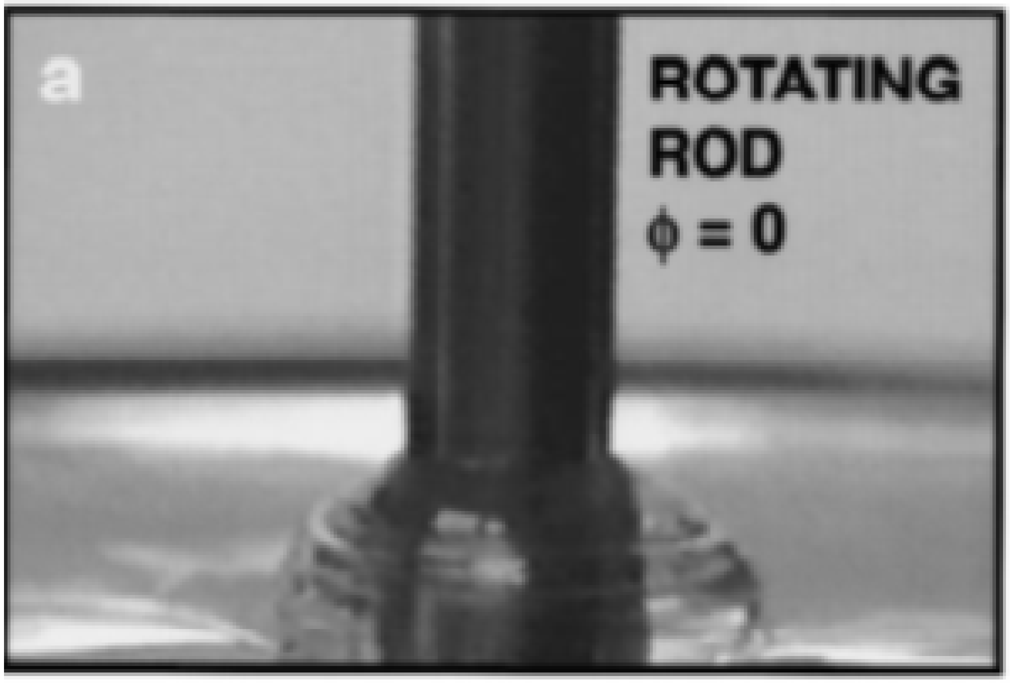
All → $1 + 2.5\varphi$ as $\varphi \to 0$

Viscosity ***diverges*** at a volume fraction that is typically near 0.6

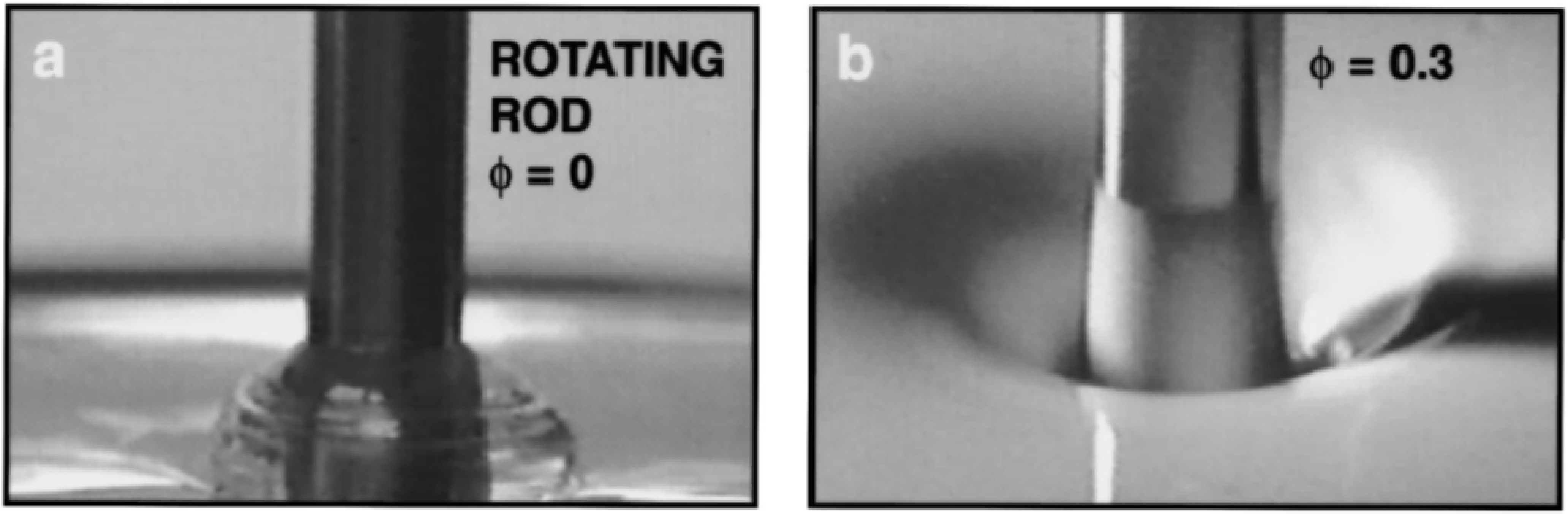
Appears to be ***scale-free*** (no size dependence)



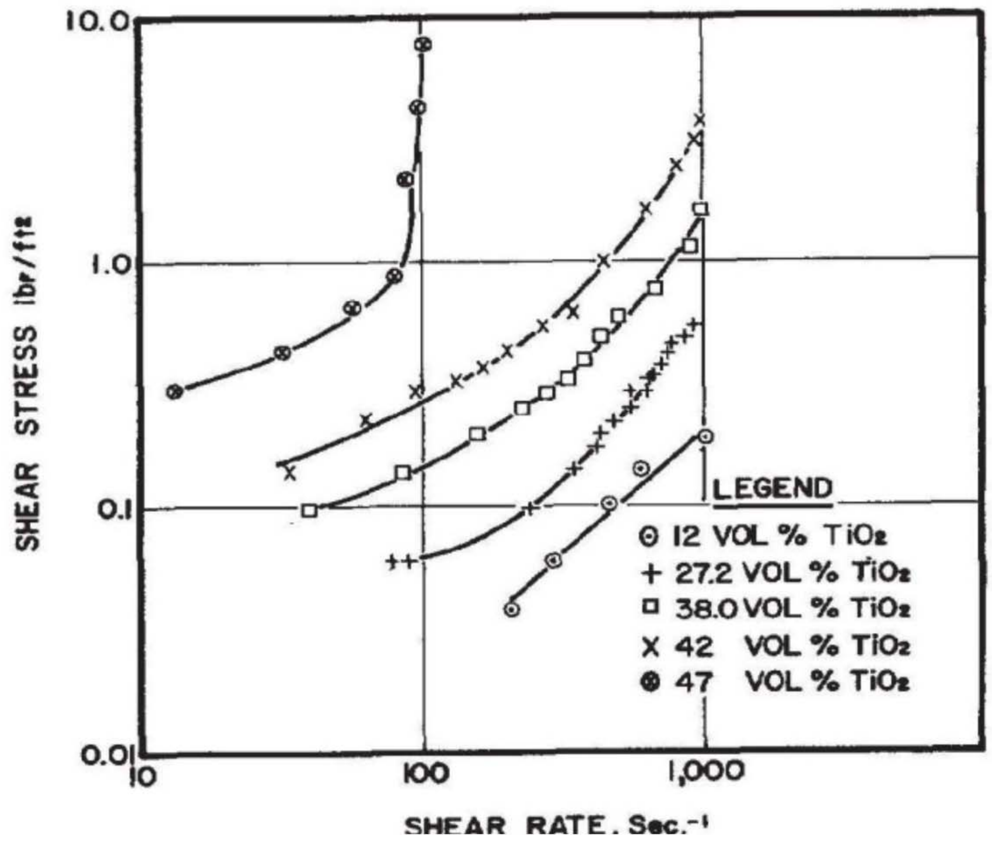
Classic work of Lewis and Nielsen (1968) reproduced a number of times: low-shear viscosity depends on volume fraction but is independent of particle size.



Rod climbing (*Weissenberg Effect*), neat PDMS
(Aral and Kalyon, 1997)

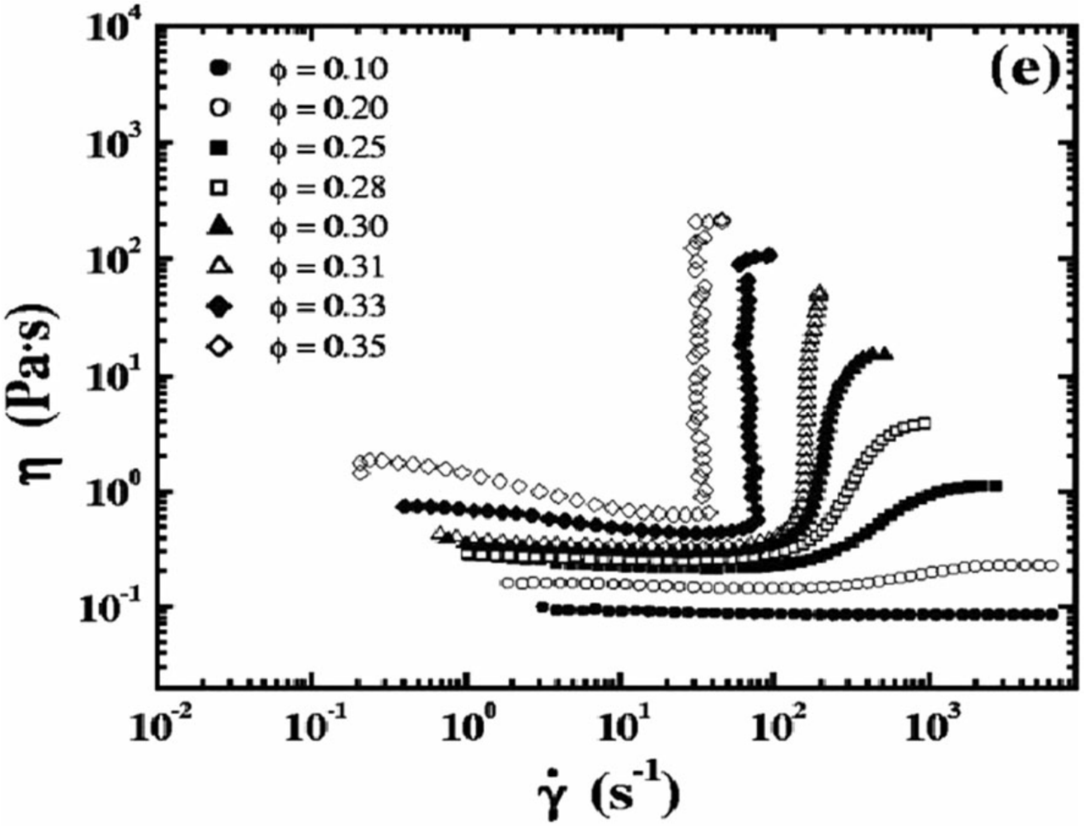


(a) neat PDMS and (b) a 30% suspension of 12 μm glass spheres in PDMS (*Negative* Weissenberg Effect)
(Aral and Kalyon, 1997)

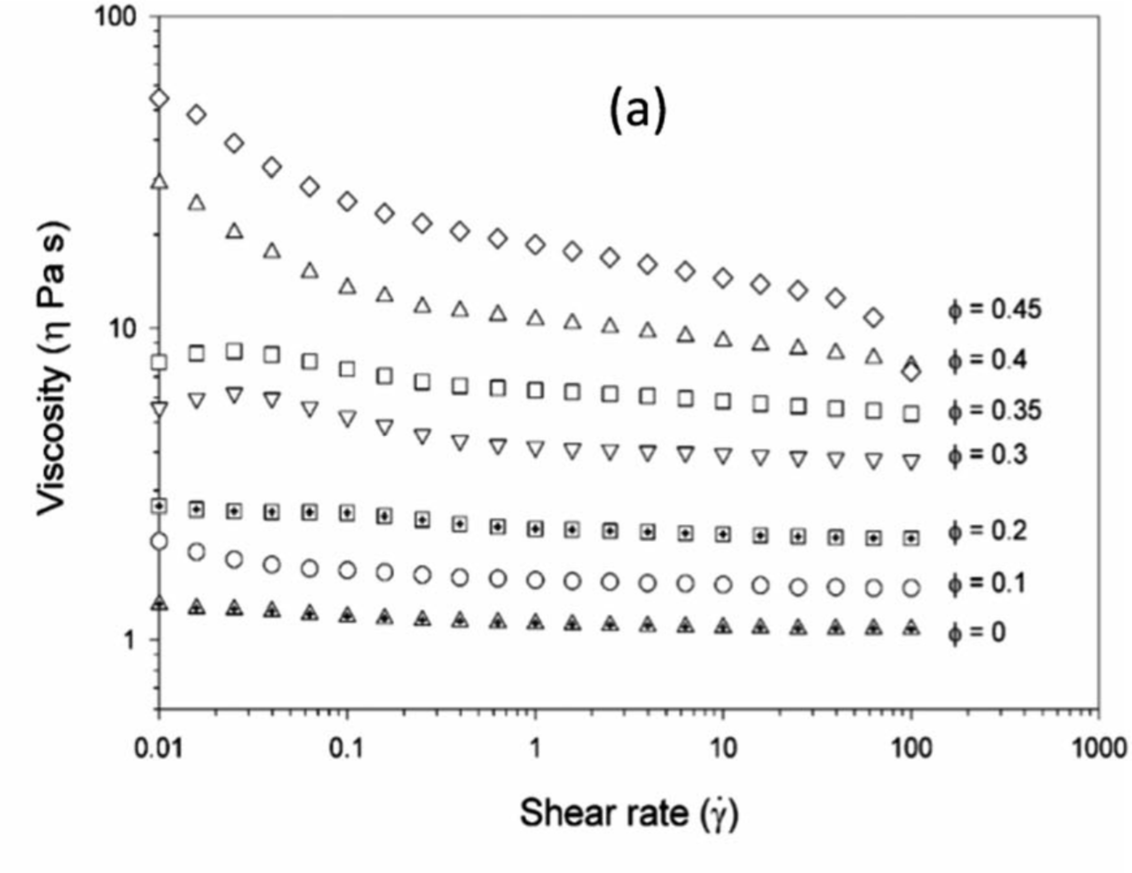


Metzner and Whitlock, 1958

Diverging viscosity at 47%. Jamming? Metzner and Whitlock noted that ‘‘fracturing of the fluid was not only visible but audible’’. Probably also a yield stress at low rates. The “jamming” at high rates is stress or rate driven and is totally different from the yield-stress behavior at low stresses and vanishing rates.

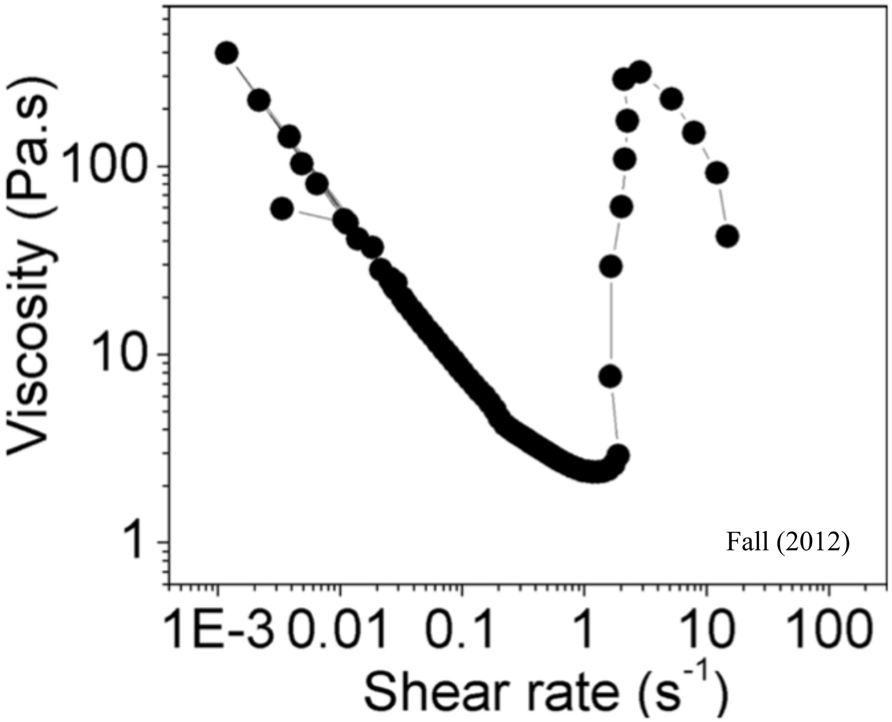


Measured viscosity in a suspension of calcium carbonate particles of acicular form in a low-molecular-weight poly ethylene glycol. Egres and Wagner, 2005.
Note transition from continuous to discontinuous shear thickening.



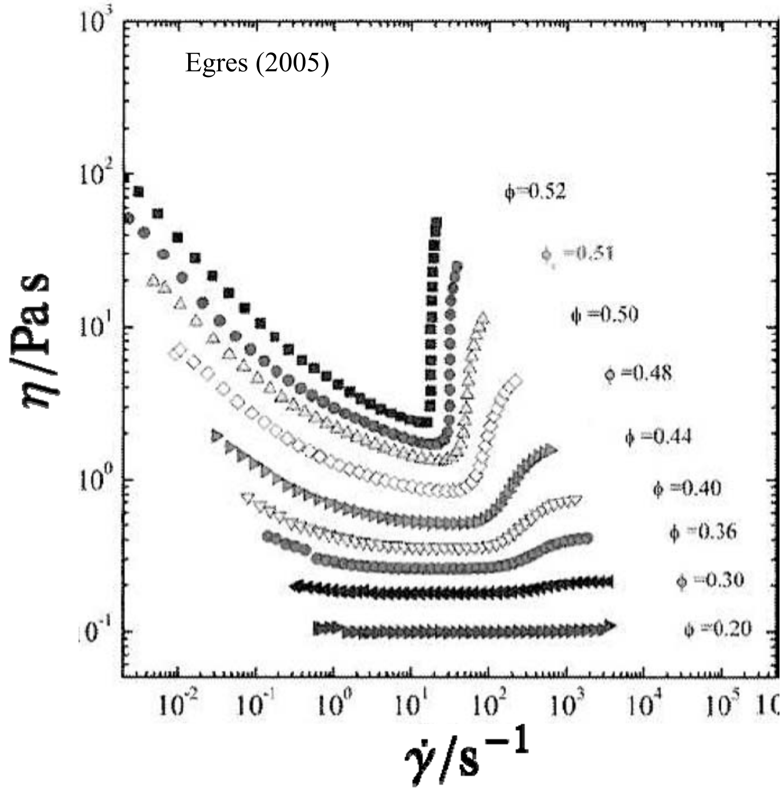
Relative viscosity as a function of shear rate for 40.3 mm polystyrene spheres in a Newtonian 1000 cS silicone suspending fluid. Data of Dai et al. (2013). Measurements stopped prior to edge fracture.

Shear Thinning/Shear Thickening



Fall (2012)

Cornstarch (≈14µm) in water
(Bonn group, Amsterdam)

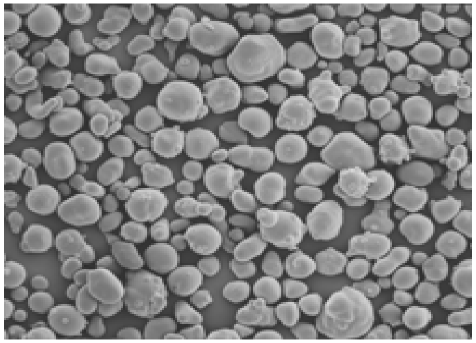


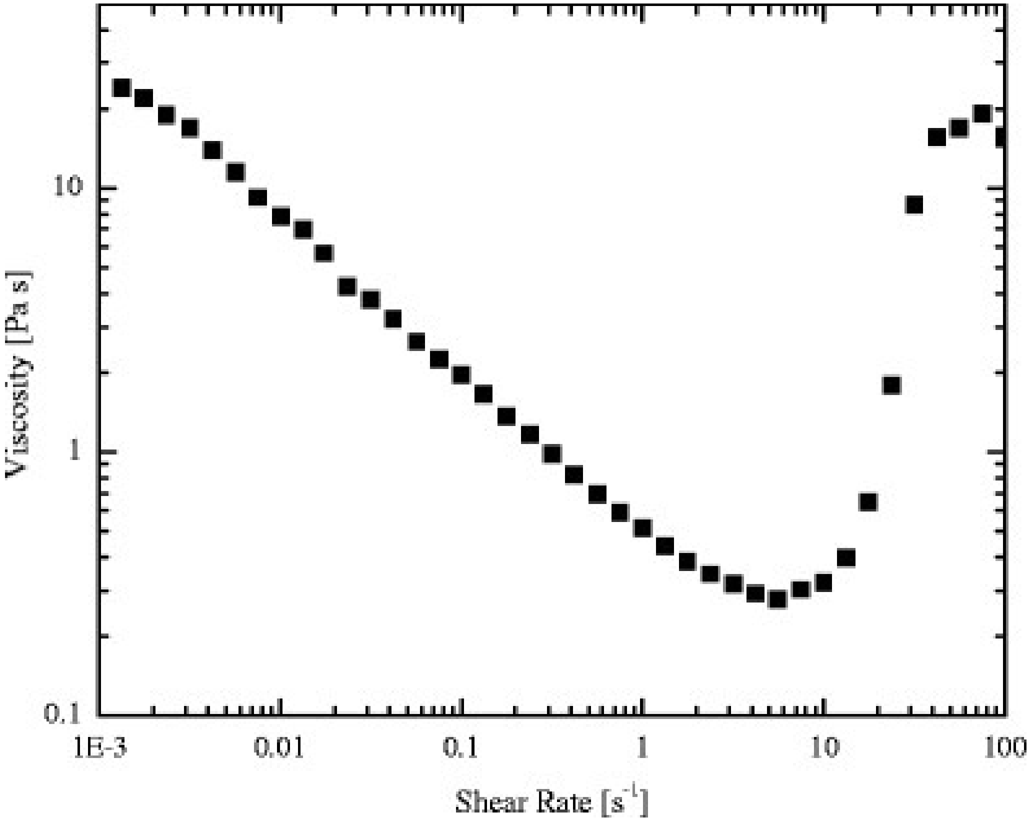
Egres (2005)

Silica spherical particles (≈0.5µm) in
PEG solution (Wagner group, Delaware)

Cornstarch dispersion

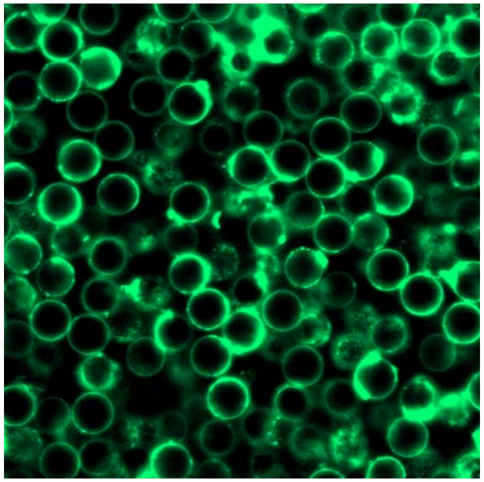
diameter ~ 15μm

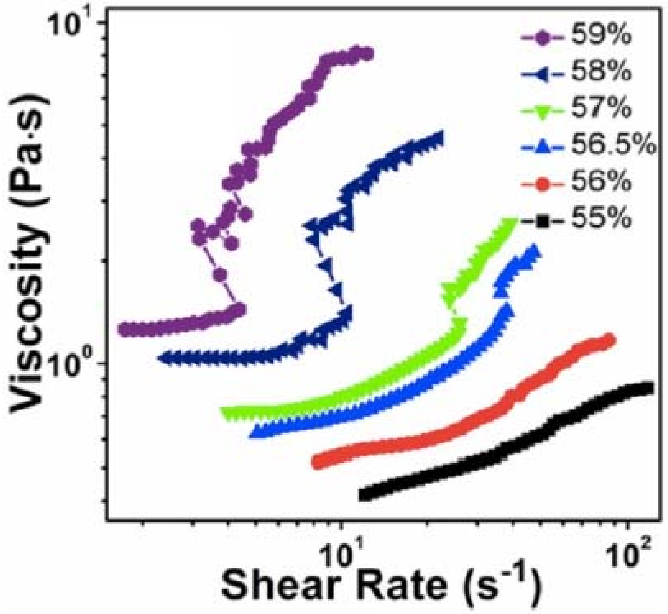


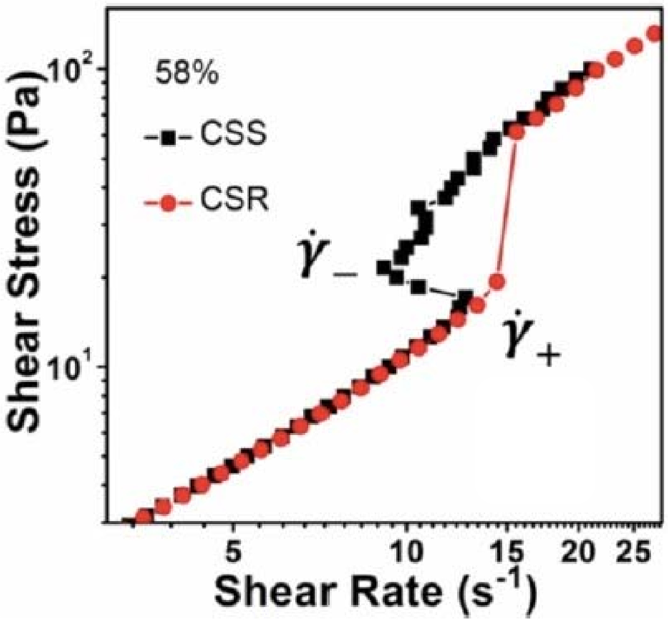


Khandavalli & Rothstein *Rheol. Acta* 2015

Non-Brownian spheres: 10 μm PMMA in density-matched H2O/NaI

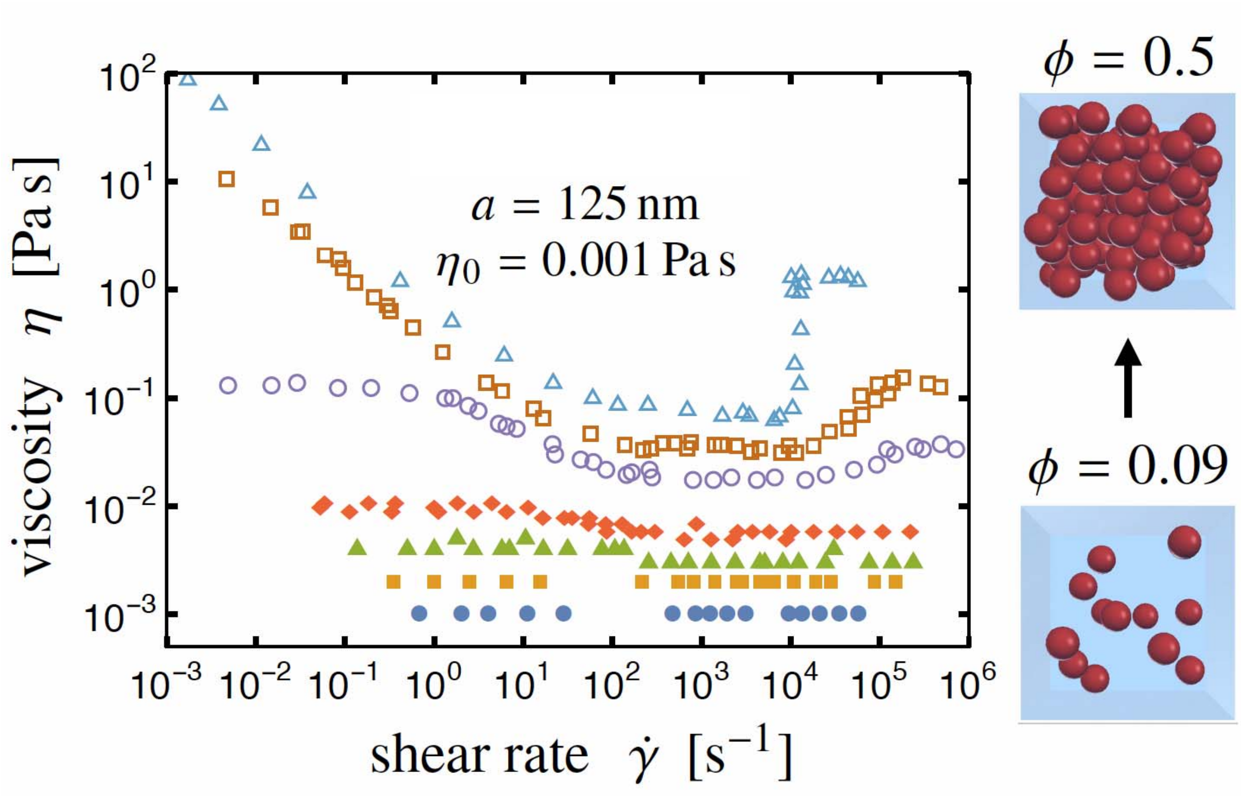






Pan, de Cagny, Weber & Bonn *Phys. Rev. E* 2015

Brownian spheres: Acrylic polymer in water + salt

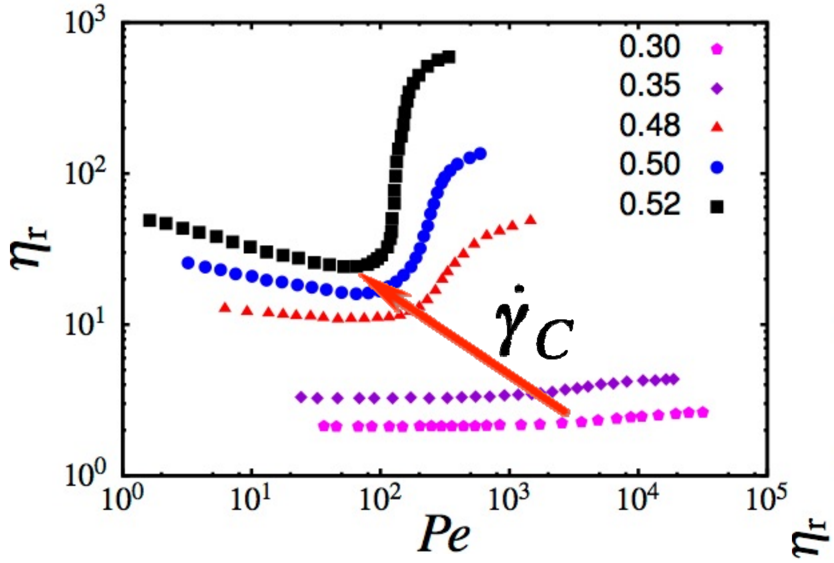


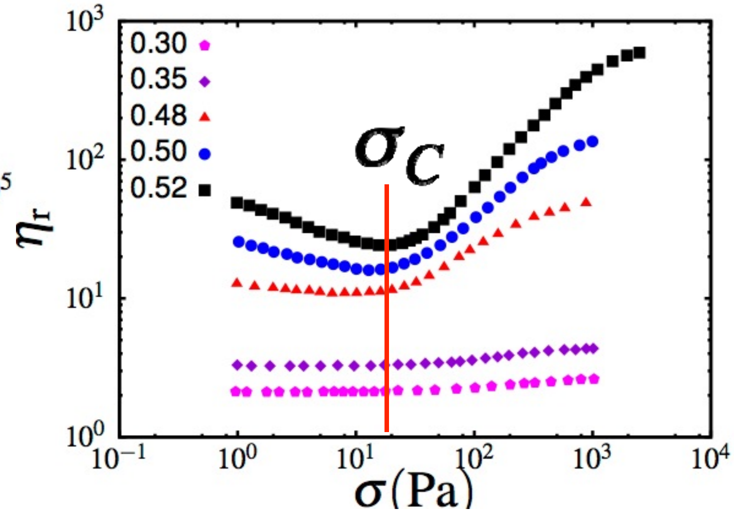
Highest concentration exhibits a yield stress (slope of – 1) and discontinuous shear thickening

Laun *Angewandte Makromol.* 1984

Brownian spheres: silica in low-MW PEG

radius $a = 0.26\mu m$ = 260 nm

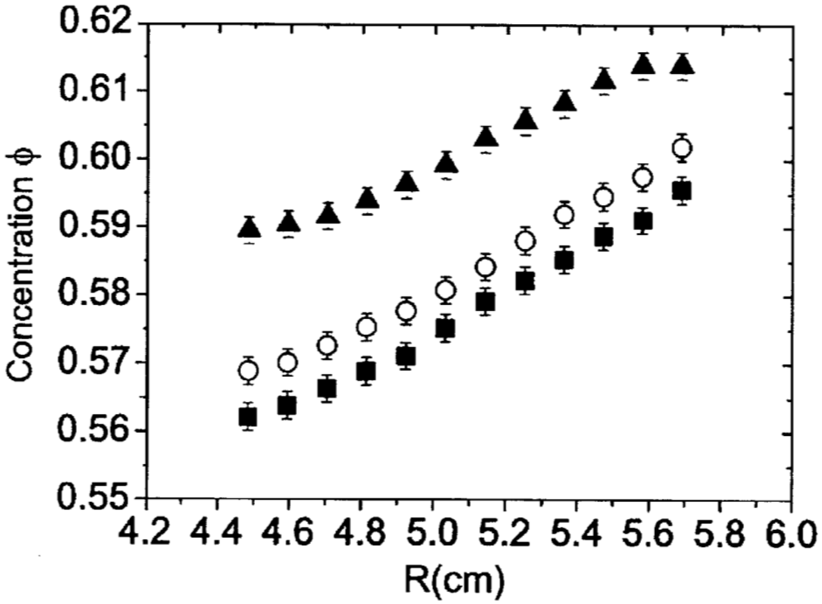




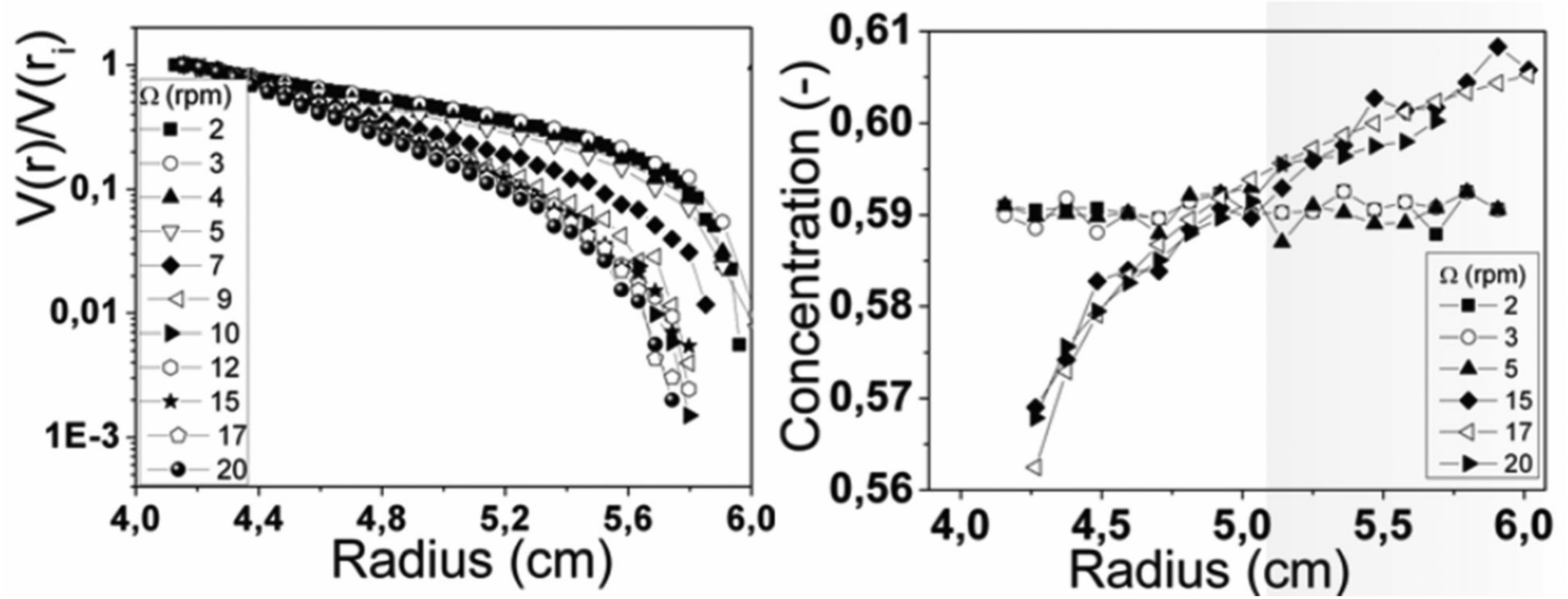
$$Pe \propto \frac{\eta_0 \dot{\gamma} a^3}{kT}$$

Cwalina & Wagner *J. Rheol.* 2014

Shear-induced particle migration (Leighton & Acrivos, 1987)



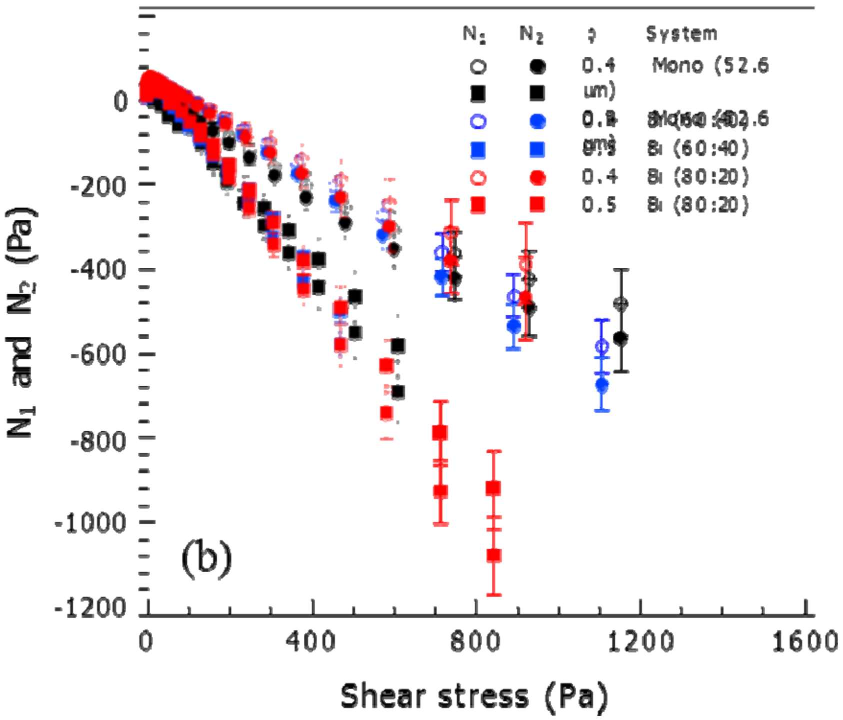
Concentration profiles measured across the gap between rotating concentric cylinders using magnetic resonance imaging for suspensions having mean values of φ = 0.58 (■), 0.59 (○), and 0.60 (▲). (Ovarlez et al., 2006)



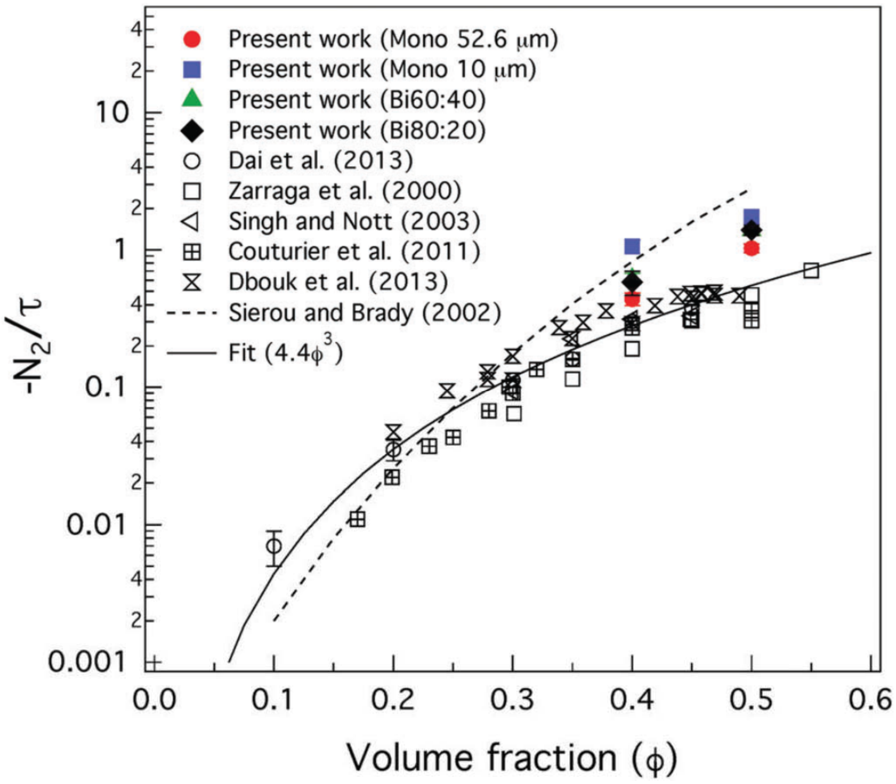
Magnetic resonance imaging measurements of (a) velocity and (b) volume fraction profiles in a wide-gap cylindrical Couette for a suspension of density-matched 40 mm polystyrene spheres in water and NaI, with ϕ= 0.59. Fall et al., 2010.

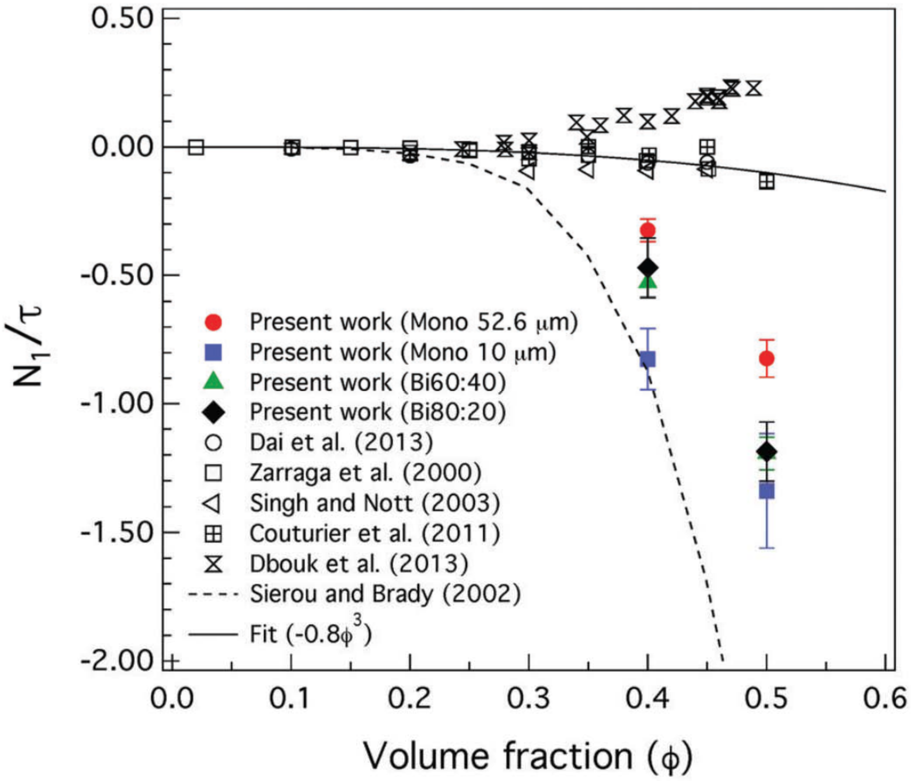
An aside on normal stress measurement

Parallel plate rheometry is commonly used for normal stress measurement in suspensions, because the finite gap can be made much larger than the particle size. This method gives $N_1 - N_2$. Cone-and-plate rheometry, which gives N_1, is usually not viable for non-colloidal particles, and non-traditional methods (Weissenberg effect, surface distortion in an open channel, separated cone and plate) have been used in order to obtain N_1 and N_2 individually. N_2 is generally reported to be *negative* and *much larger in magnitude* than N_1, for which the algebraic sign is uncertain.

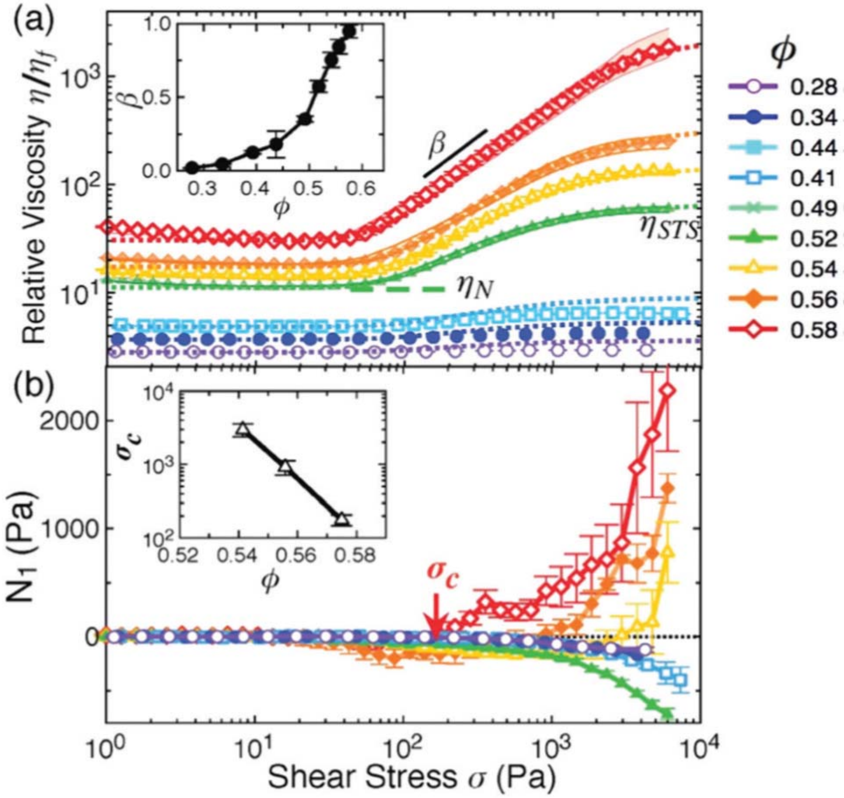


10 and 50 µm PMMA spheres in density-matched 77.93% Triton X100, 9.01% anhydrous zinc chloride, and 13.06% water. Gamonpilas et al. 2018 (corrigendum), separated cone and plate. Here both N1 and N2 < 0, and N1 ~ N2. Shear thickening is not observed for this system in this range.





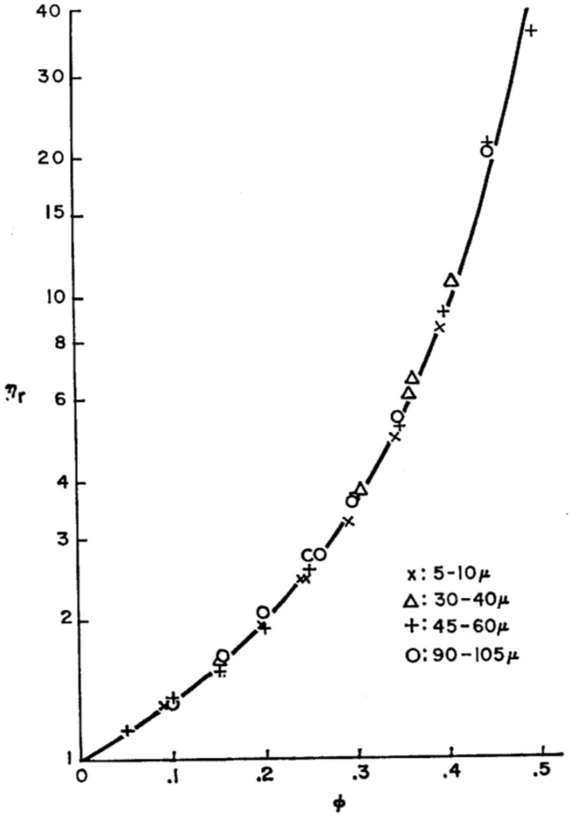
General agreement that $N_2 < 0$. Sign and magnitude of N_1 less clear.



Viscosity (top) and first normal stress difference (bottom) of a colloidal suspension of 1.54 mm diameter silica spheres in a mixture of 92 wt% glycerol with water, with a small amount of NaCl added to screen electrostatic interactions. Royer et al., 2016

In a dilute suspension the particles **do not interact**. Einstein (1906, 1911) obtained an exact solution for the viscosity of the suspension, treated as a continuum:

$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5\varphi$$



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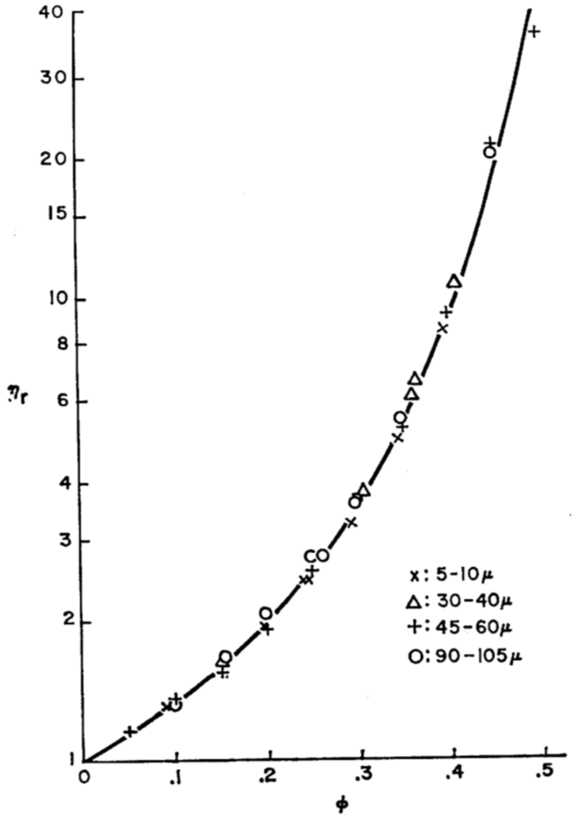
$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5\varphi$$

Batchelor and Green (1972!) obtained the quadratic correction:

$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5\varphi + 5.2\varphi^2$$



The multi-body problem for a concentrated suspension cannot be solved analytically. There have been attempts at generating continuum theories for concentrated suspensions, but none has been particularly successful (see Denn and Morris, 2014).

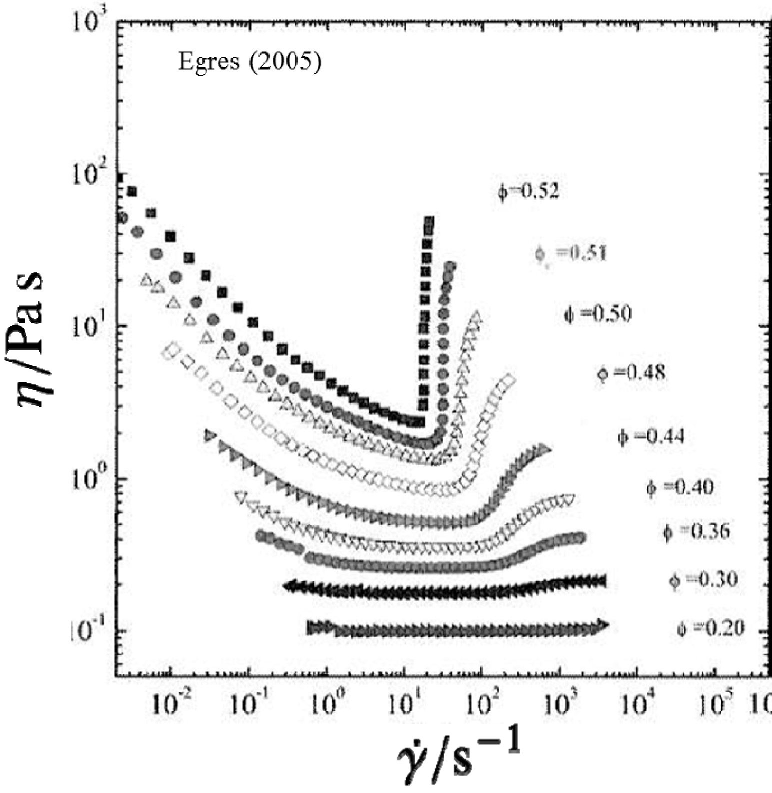
The multi-body problem for a concentrated suspension cannot be solved analytically. There have been attempts at generating continuum theories for concentrated suspensions, but none has been particularly successful (see Denn and Morris, 2014).

Stokesian Dynamics (Brady and Bossis, 1988) is a computational tool akin to molecular dynamics for solving the equations of motion for a collection of spheres in a Newtonian fluid, and it has been an effective tool, *but* ...

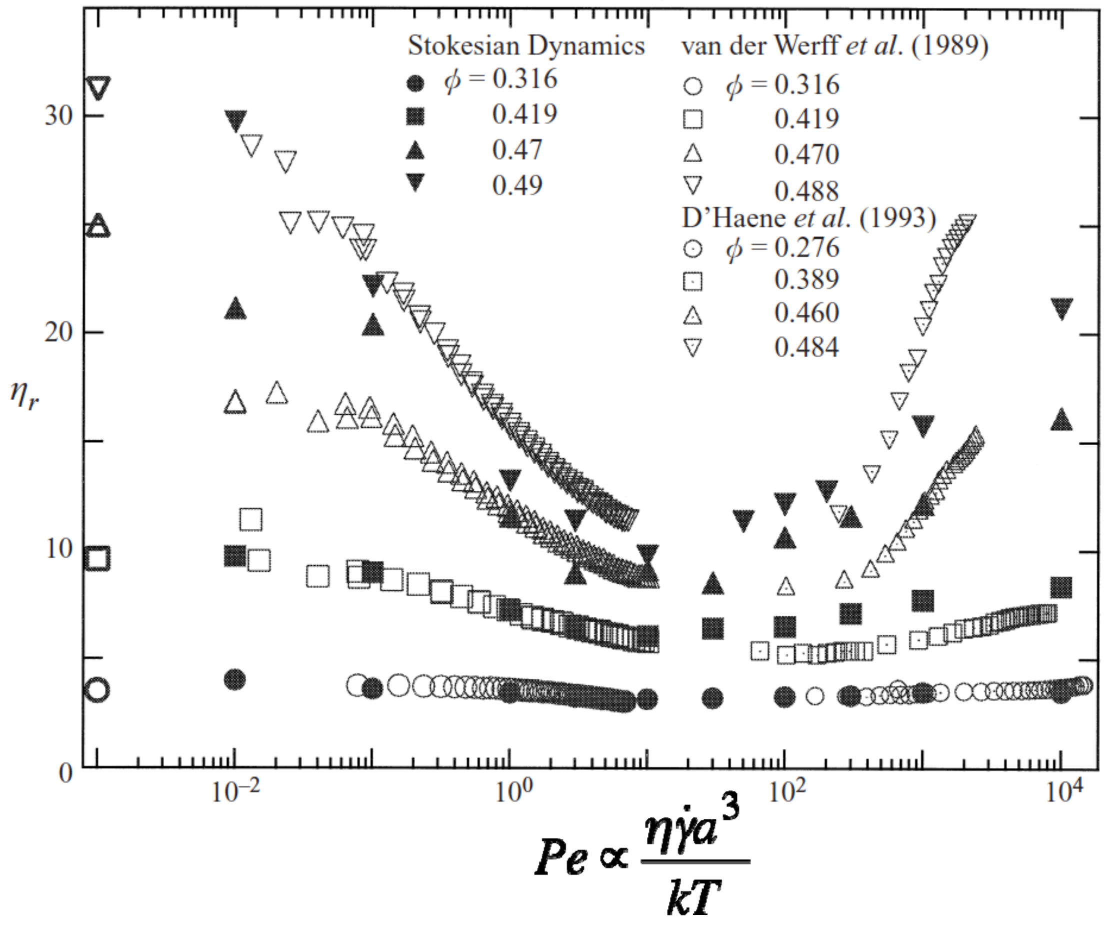
but

Shear thickening predicted by Stokesian Dynamics is too weak (logarithmic)

Discontinuous Shear Thickening *has never been predicted in hydrodynamic simulations*

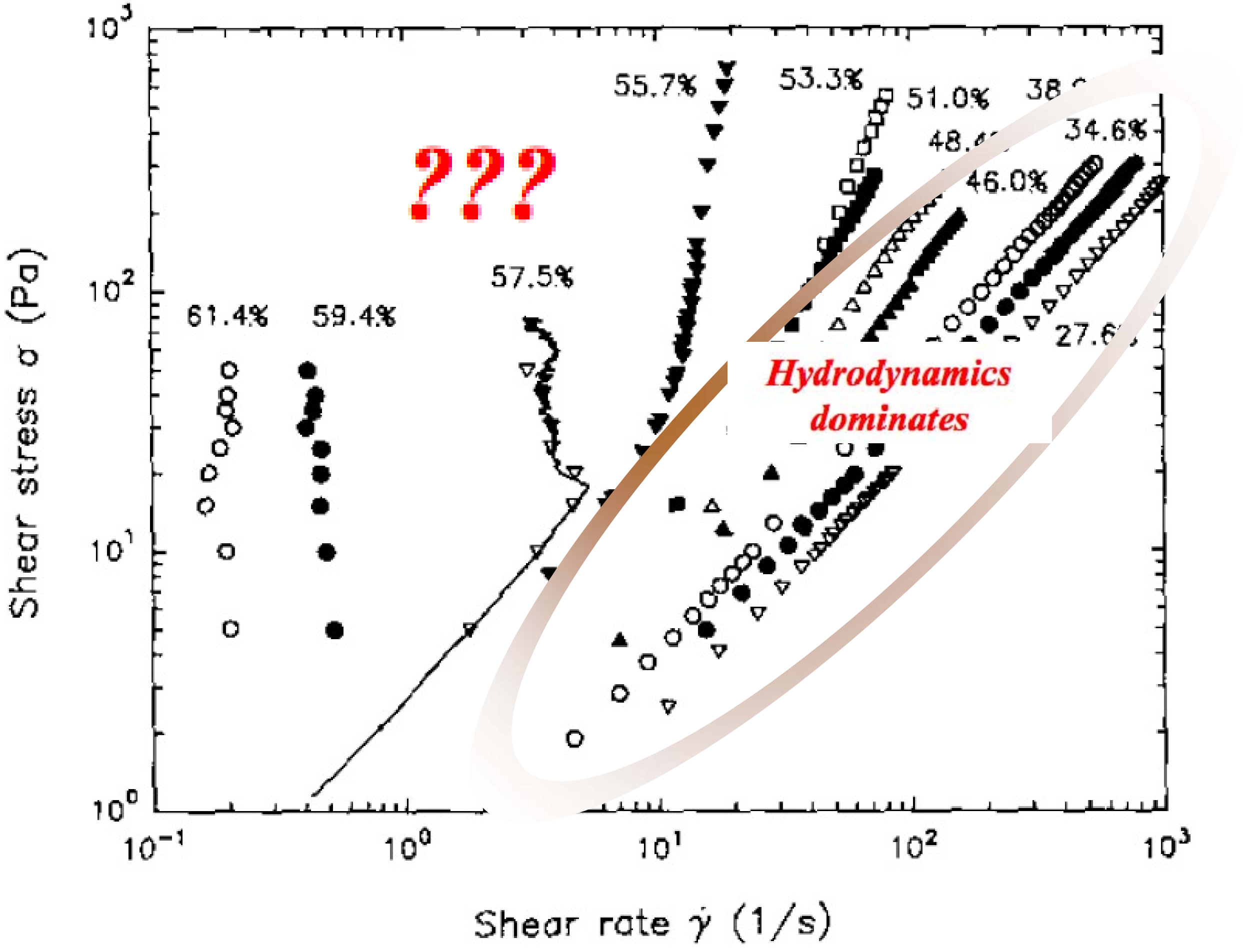


Stokesian Dynamics and experiments — Brownian hard spheres



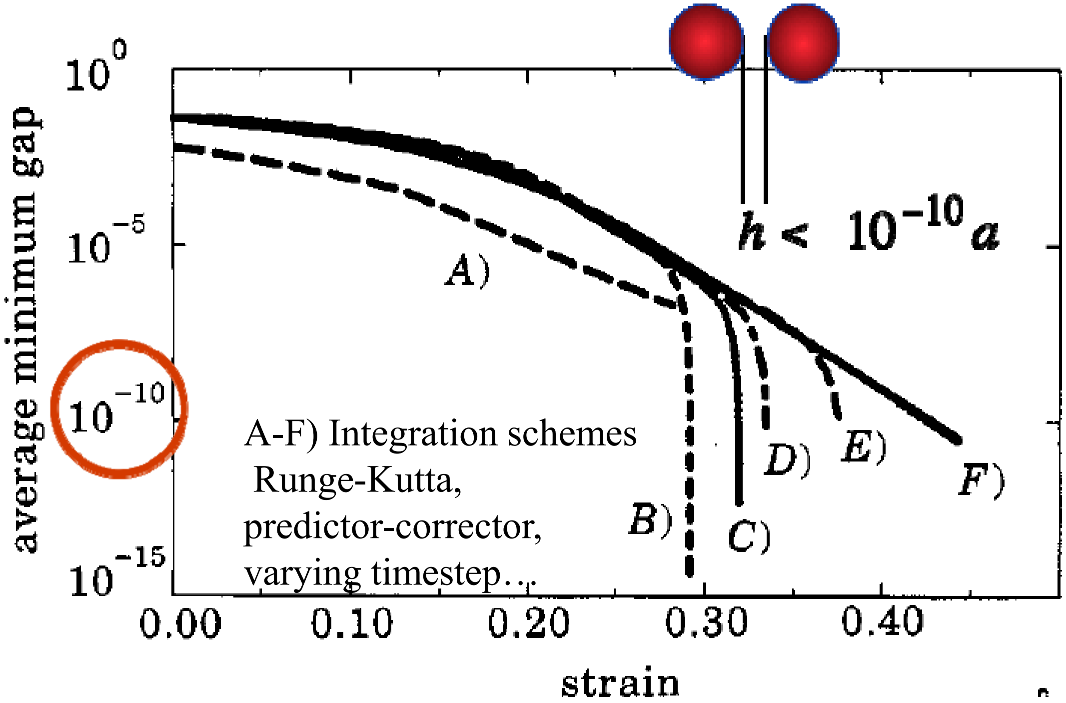
Foss & Brady *JFM* 2000

But at higher loadings…



D'Haene, Mewis & Fuller *Rheol. Acta* 1993

Lubrication breakdown: Stokes (*Re* = 0) shear flow of hard spheres



A-F) Integration schemes
Runge-Kutta,
predictor-corrector,
varying timestep…

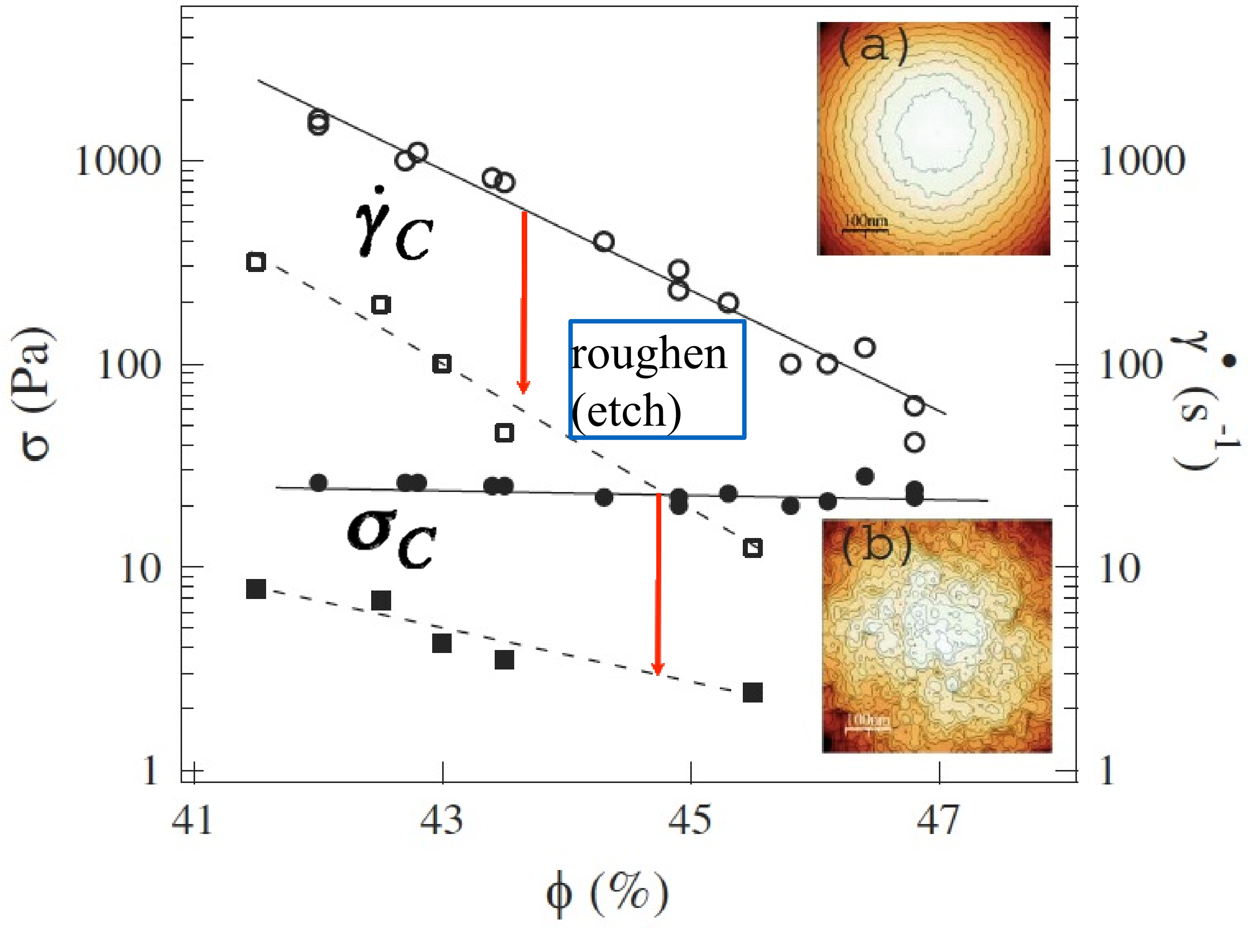
$\phi = 0.51$

$\phi \ll \phi_{RCP} = \phi_J^o \approx 0.64$

$\phi < \phi_{RLP} \approx 0.58$

Melrose & Ball *Europhys. Lett.* 1995
Roughness effects at 1%RMS: Lootens *et al. Phys. Rev. Letters* 2003, 2005

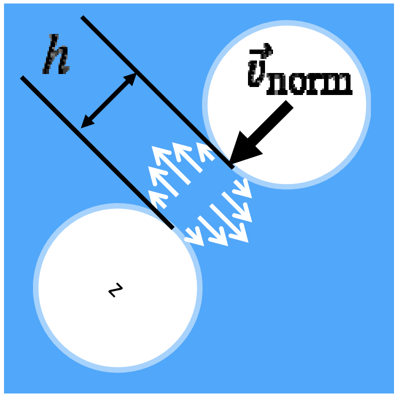
Effects of roughness (~ 1% RMS)



Lootens *et al. Phys. Rev. Letters* 2003, 2005

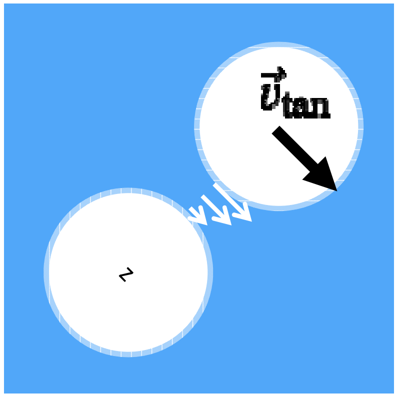
The problem lies with the *lubrication singularity*. The hydrodynamic forces between spheres diverge at contact, so particle-particle friction is never possible in a hydrodynamic simulation.

squeeze mode



$$\vec{F}_{\mathrm{lub}} \propto -\frac{1}{h}\vec{v}_{\mathrm{norm}}$$

tangential mode



$$\vec{F}_{\mathrm{lub}} \propto -\log\left(\frac{1}{h}\right)\vec{v}_{\mathrm{tan}}$$

Purely hydrodynamic simulations cannot explain discontinuous shear thickening.

To get around the lubrication singularity:

Regularize lubrication singularity to permit contact.

Employ a simple friction model, like those used in dry granular flow.

Include a repulsive force.

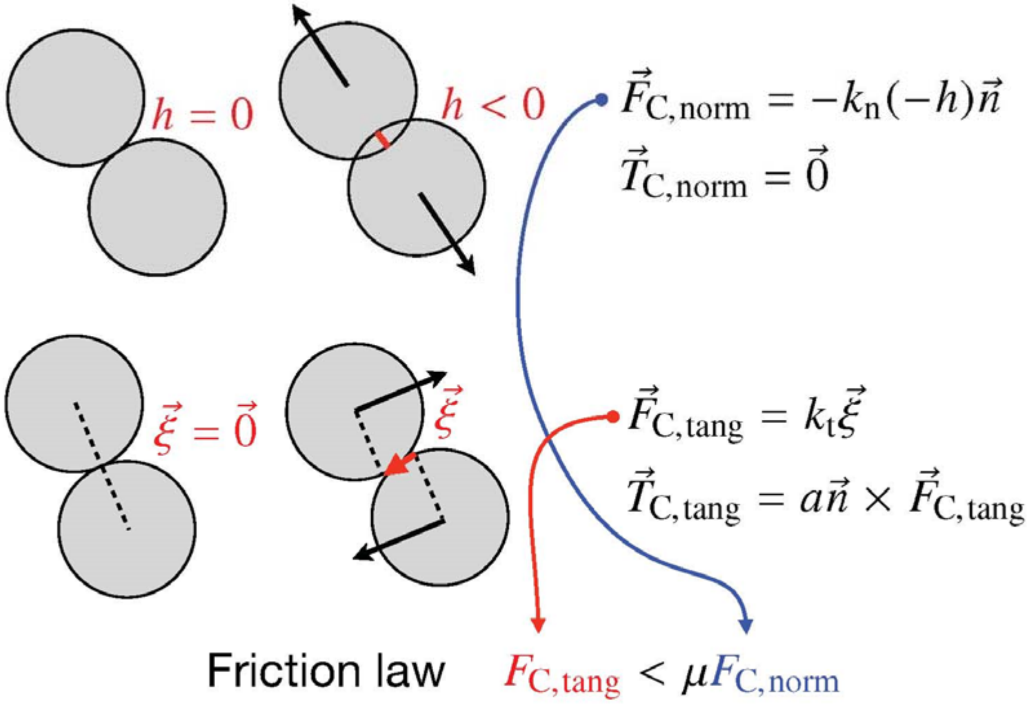
Seto, Mari, Denn, Morris, *Phys. Rev. Letters* (2013)
Mari, Seto, Denn, Morris, *J. Rheology* (2014)

Regularized lubrication

$$\vec{F}_{\mathrm{lub}} \propto -\frac{1}{h+\delta}\vec{v}_{\mathrm{norm}} \qquad \vec{F}_{\mathrm{lub}} \propto -\log\left(\frac{1}{h+\delta}\right)\vec{v}_{\mathrm{tan}}$$

Frictional contact

(Contact model in granular physics)



$$\vec{F}_{\mathrm{C,norm}} = -k_{\mathrm{n}}(-h)\vec{n}$$

$$\vec{T}_{\mathrm{C,norm}} = \vec{0}$$

$$\vec{F}_{\mathrm{C,tang}} = k_{\mathrm{t}}\vec{\xi}$$

$$\vec{T}_{\mathrm{C,tang}} = a\vec{n} \times \vec{F}_{\mathrm{C,tang}}$$

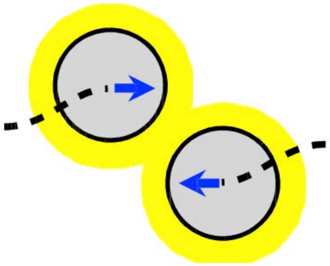
Friction law $F_{\mathrm{C,tang}} < \mu F_{\mathrm{C,norm}}$

Shear rate dependence requires a force that is independent of the shear rate

Electrostatic repulsion model (*ERM*)

Center-to-center force $\boldsymbol{F}_R = \boldsymbol{F}^* e^{-h/\lambda}$

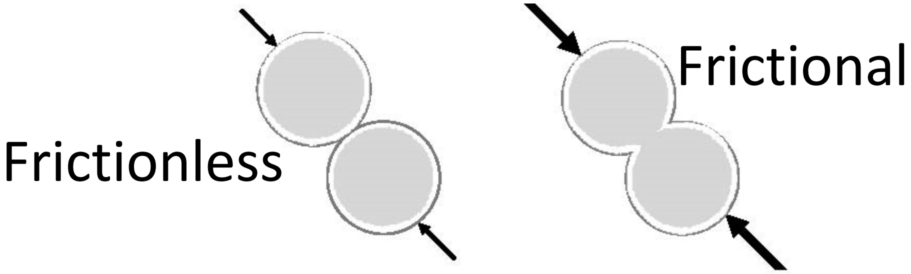
Debye length λ typically ~ 0.05*a*

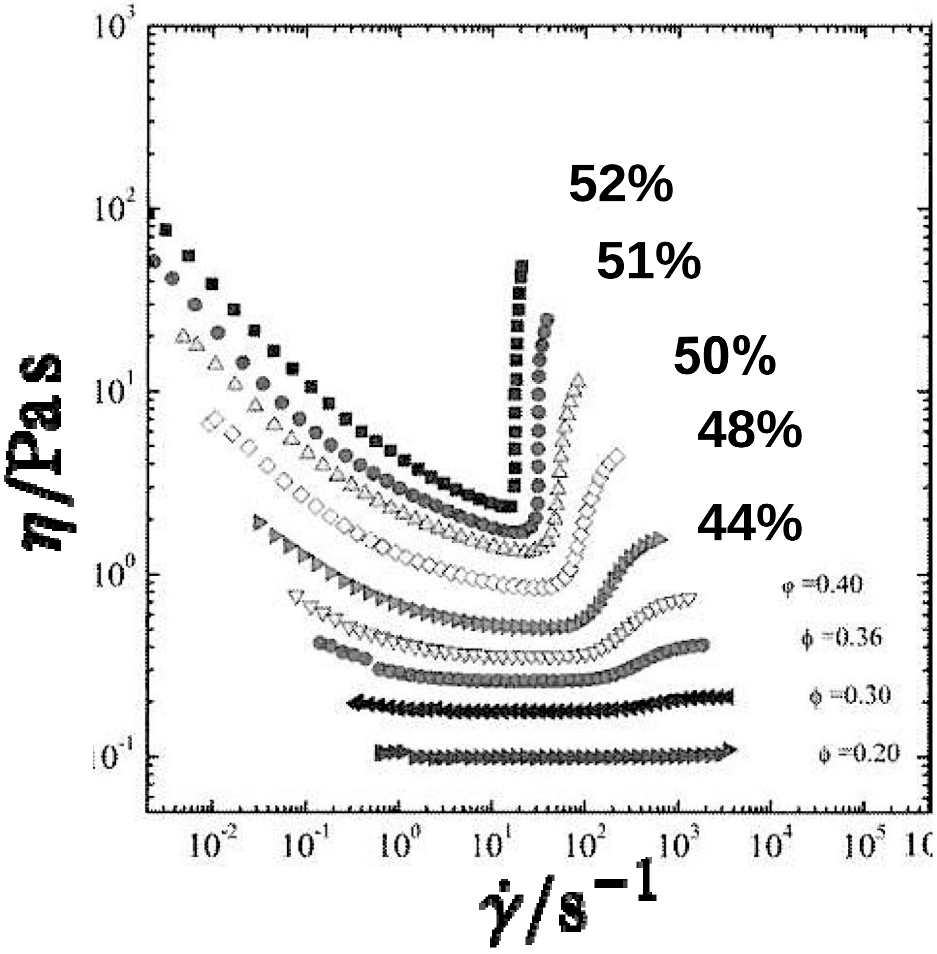


Critical load model (*CLM*)

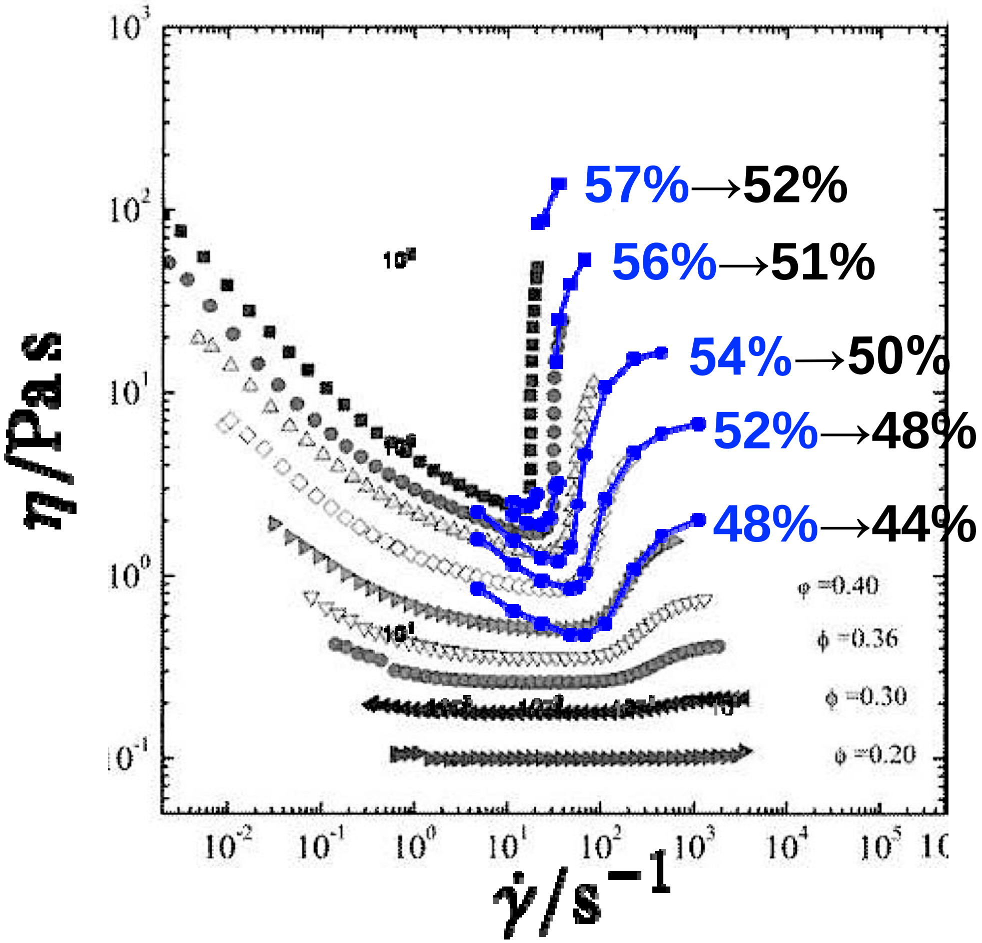
Replace tangential friction law with

$$\left|\boldsymbol{F}_{C,\text{tang}}\right| \le \begin{cases} \mu(|\boldsymbol{F}_{\text{norm}}| - \boldsymbol{F}^*) & \text{for } |\boldsymbol{F}_{\text{norm}}| \ge \boldsymbol{F}^* \\ 0 & \text{otherwise} \end{cases}$$



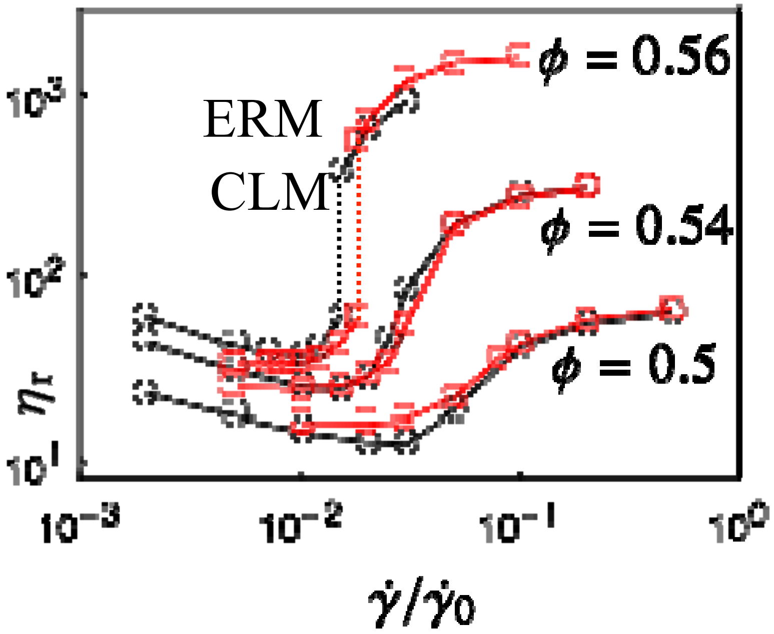


Simulations with electrostatic repulsion model



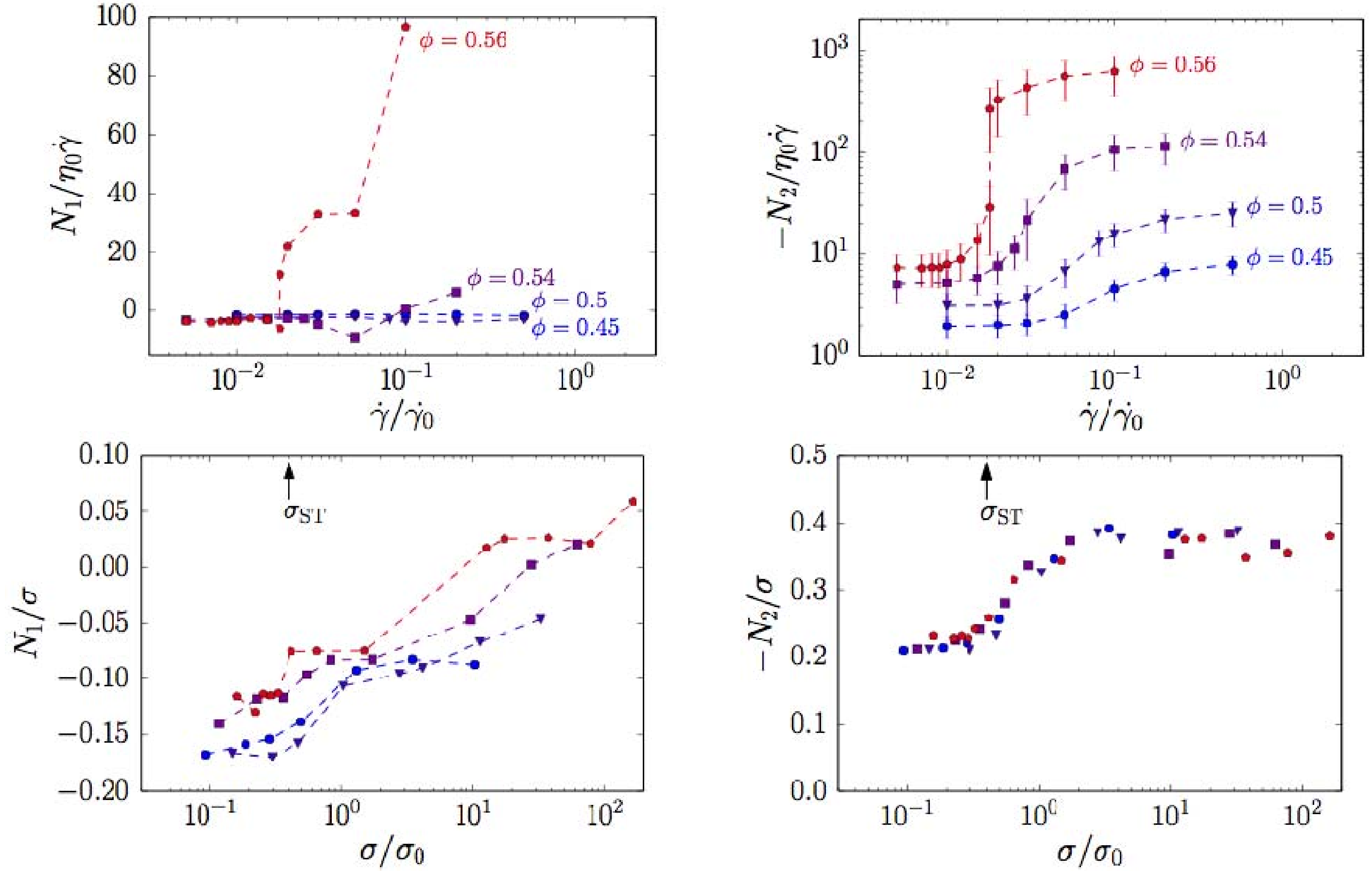
Simulations together with Egres's data

Electrostatic repulsion model vs. Critical load model



Shear thinning is seen with ERM, but not CLM. They are essentially the same after shear thickening begins.

Normal stress differences (CLM)

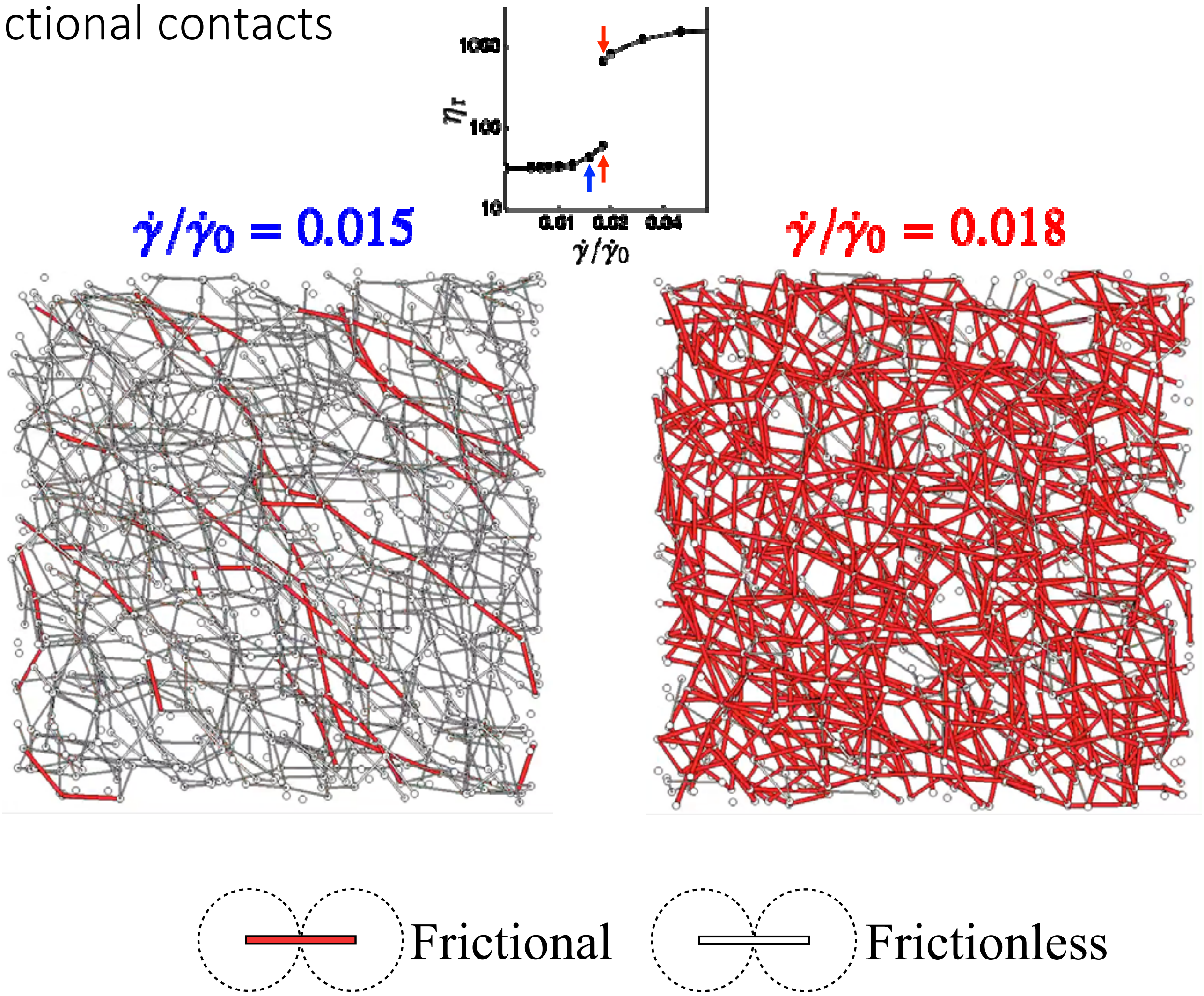


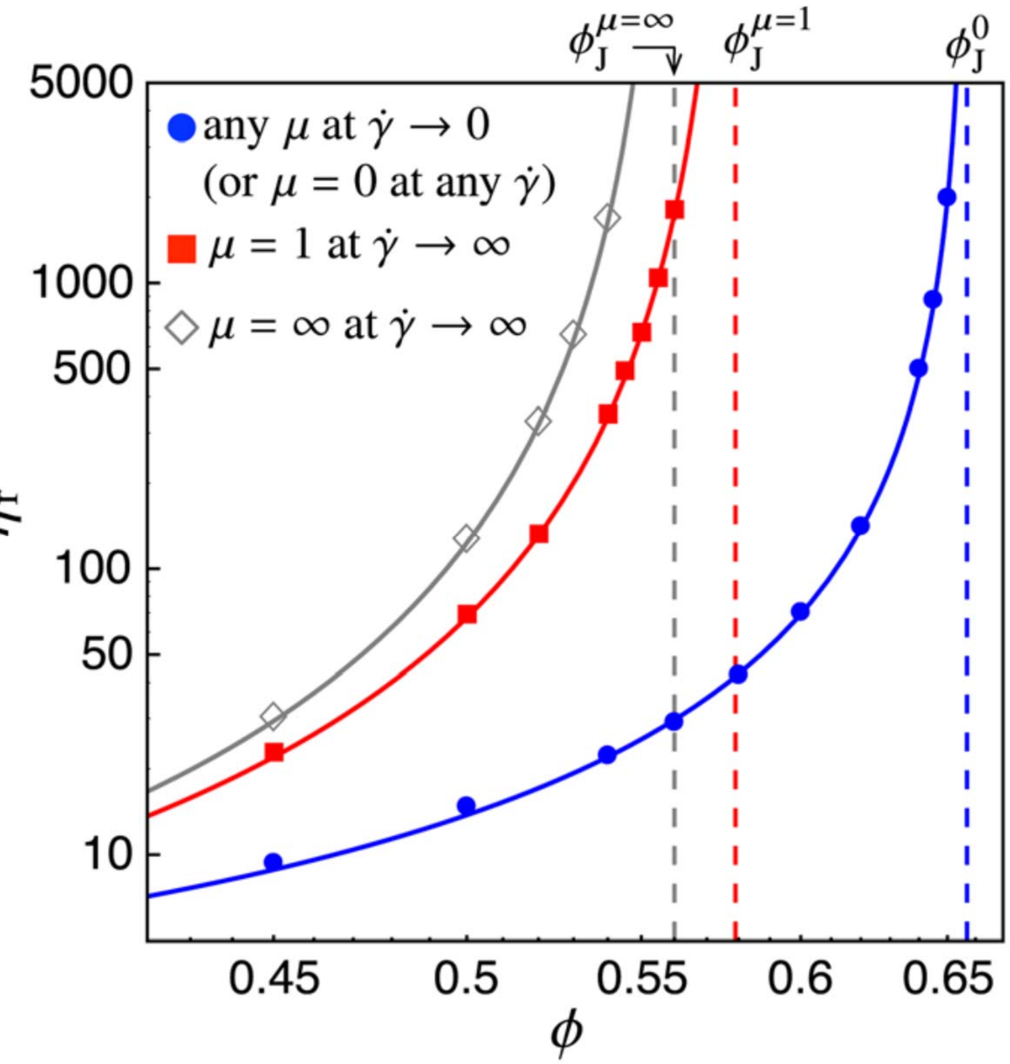
$N_2 < 0$

$|N_2| >> |N_1|$

N_2/σ (and maybe N_1/σ) *plotted* as a function of σ is *independent* of φ

Frictional contacts





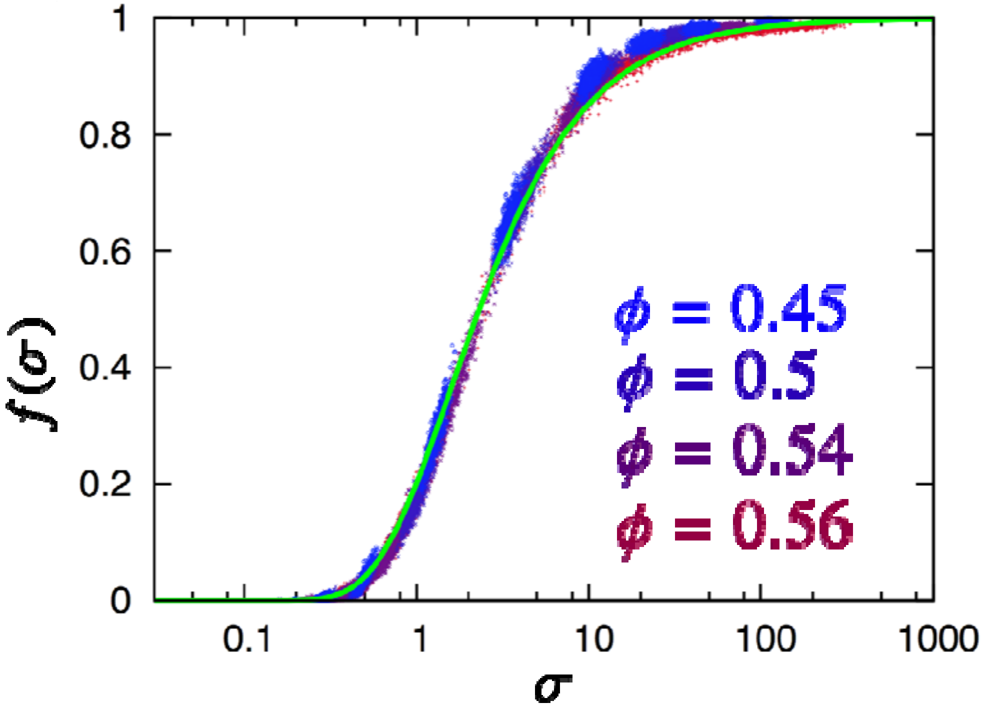
Two possible states, depending on density of force chains, which depends in turn on volume fraction and shear rate:

Frictionless, jams at $\varphi_j^{\mu=0} \sim 0.65$

Frictional, jams at $\varphi_j^{\mu=1} \sim 0.58$

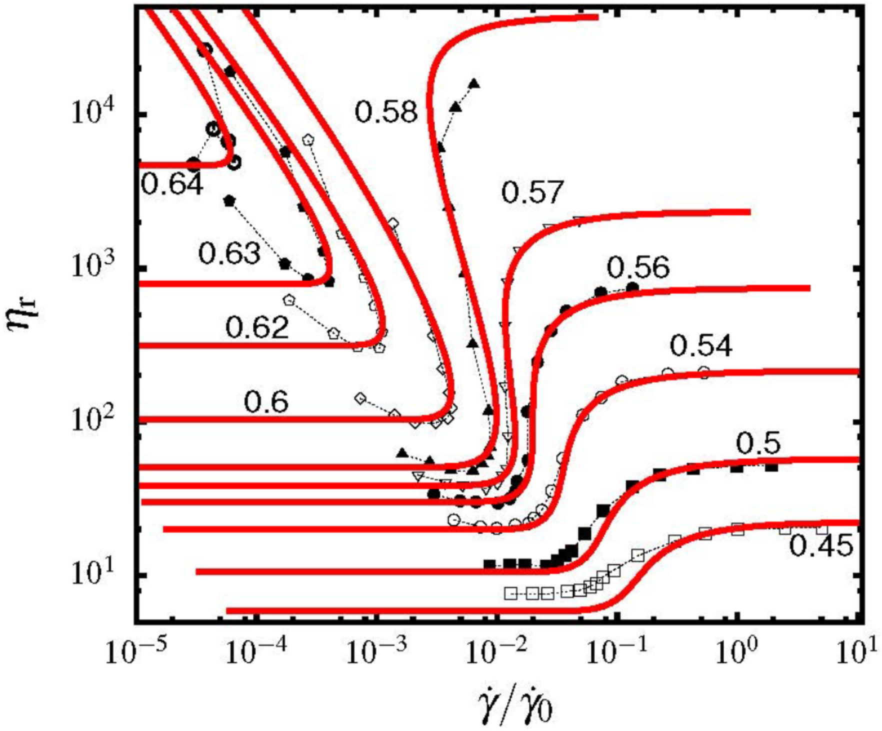
Discontinuous Shear Thickening is a jump from the frictionless to frictional state.

$$f \equiv \frac{\#\ \text{frictional contacts}}{\#\ \text{total contacts}}$$



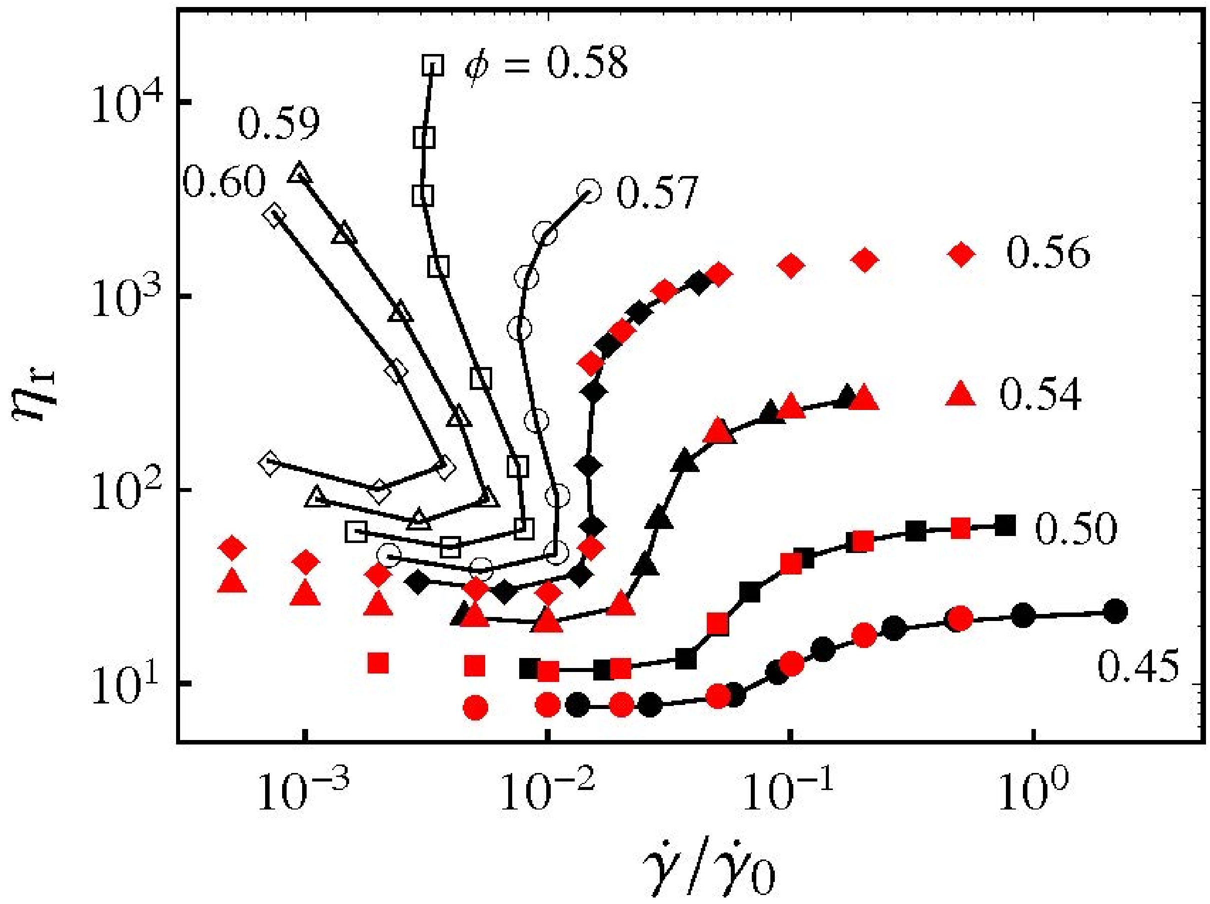
A universal relation!

Interpolation between two rheologies



Solid curves are an interpolation between the frictional and frictionless modes, using the function $f(\sigma)$. Only two parameters are required to compute the viscosity and both normal stress differences for a given concentration: the friction coefficient and the magnitude of the repulsive force. All other parameters are universal. Singh et al., 2018. Based on an idea of Wyart & Cates, *Phys. Rev. Lett.,* 2014.

For non-Brownian systems it is possible to *invert* the equations and do simulations under stress control



RED = shear-rate control

Simulations with stress control

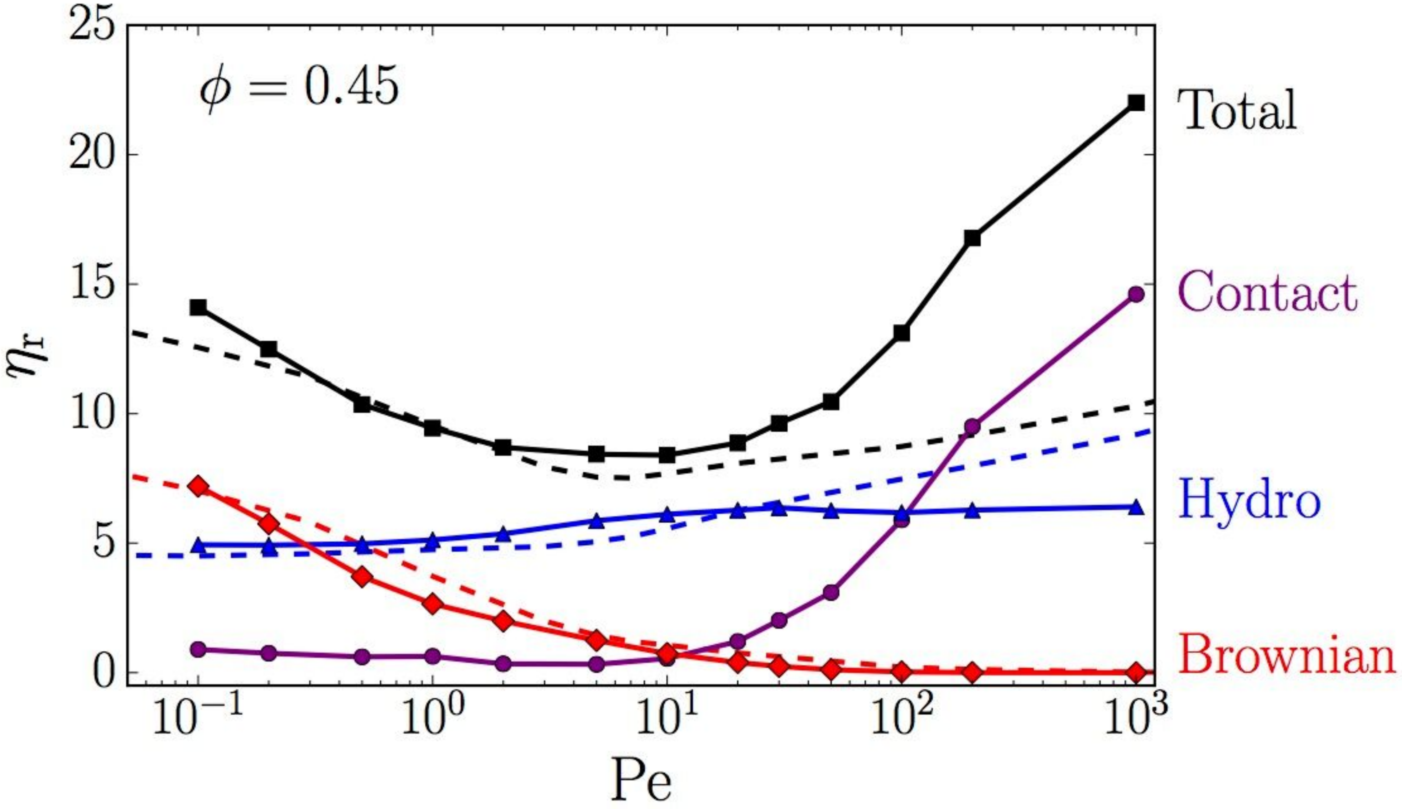
Mari, Seto, Denn, Morris, *Phys. Rev. E* (2015)

Brownian systems (typically < 1μm)

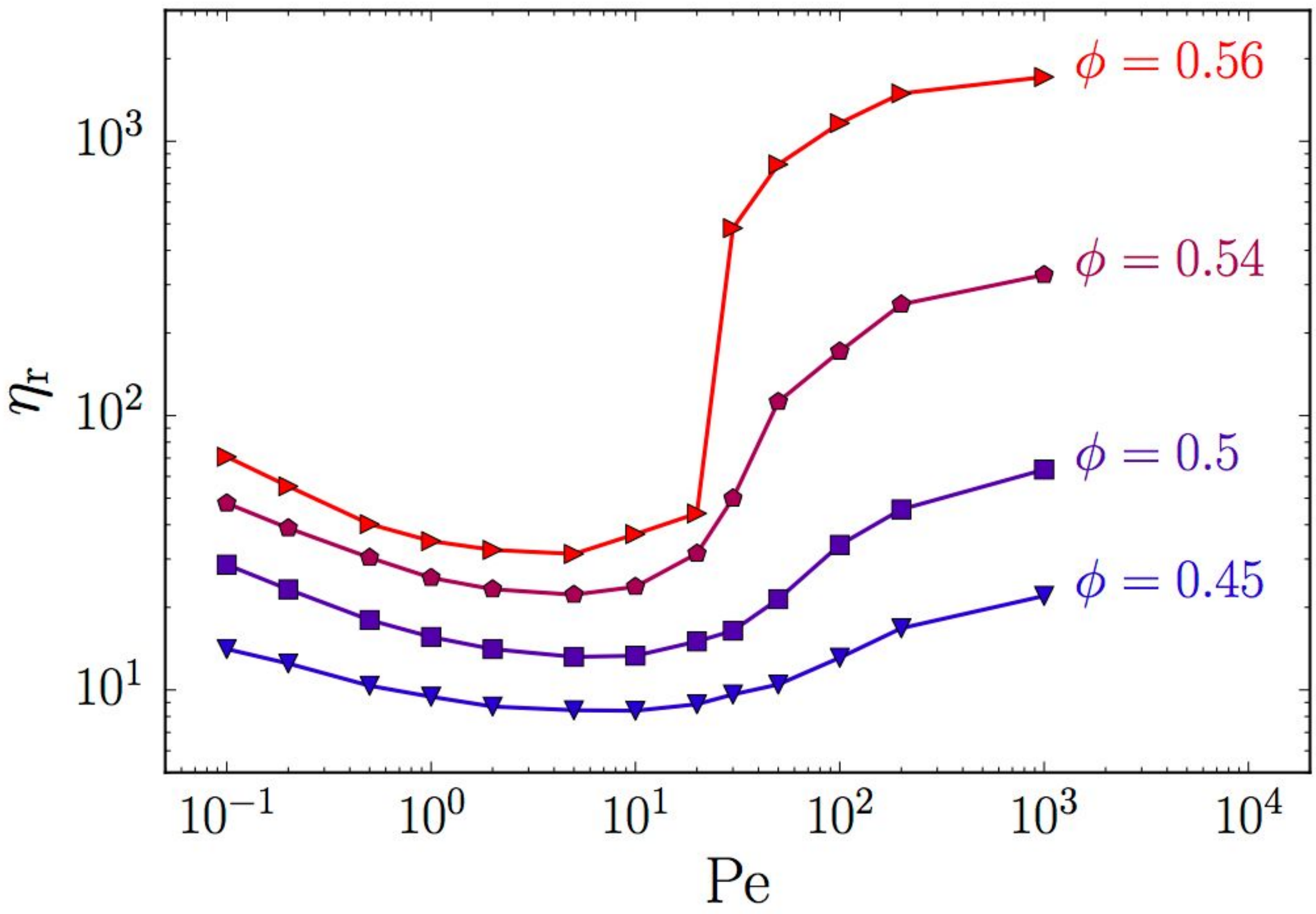
Independent variable usually taken to be the Péclet number,

$$Pe \equiv 6\pi\eta_o a^3\dot{\gamma}/kT$$

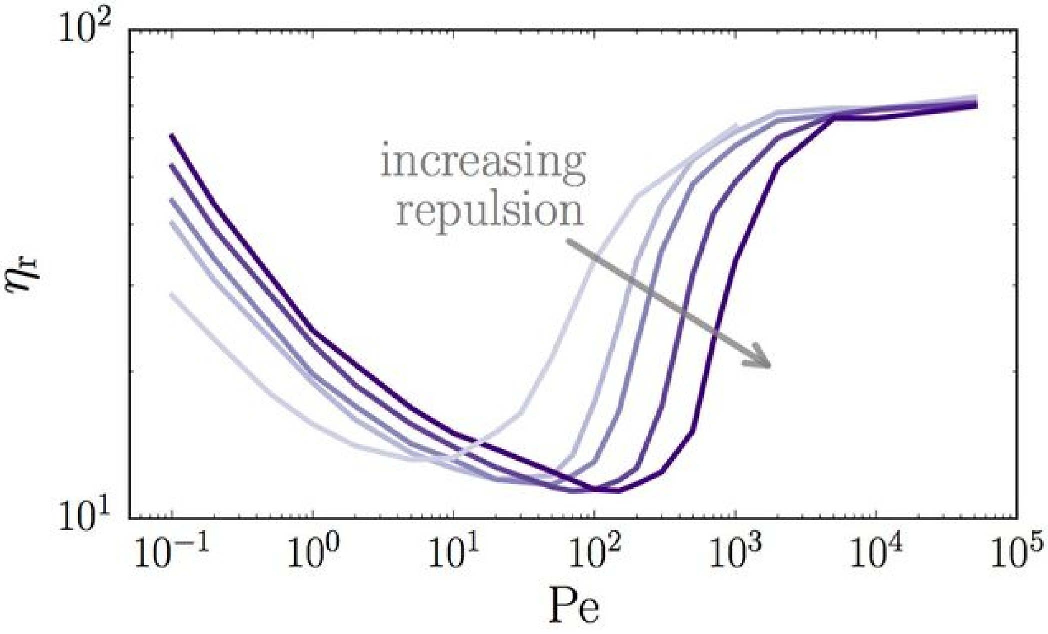
Particles experience a Brownian force as well as a stabilizing repulsive force $F_R = F^* e^{-h/\lambda}$.

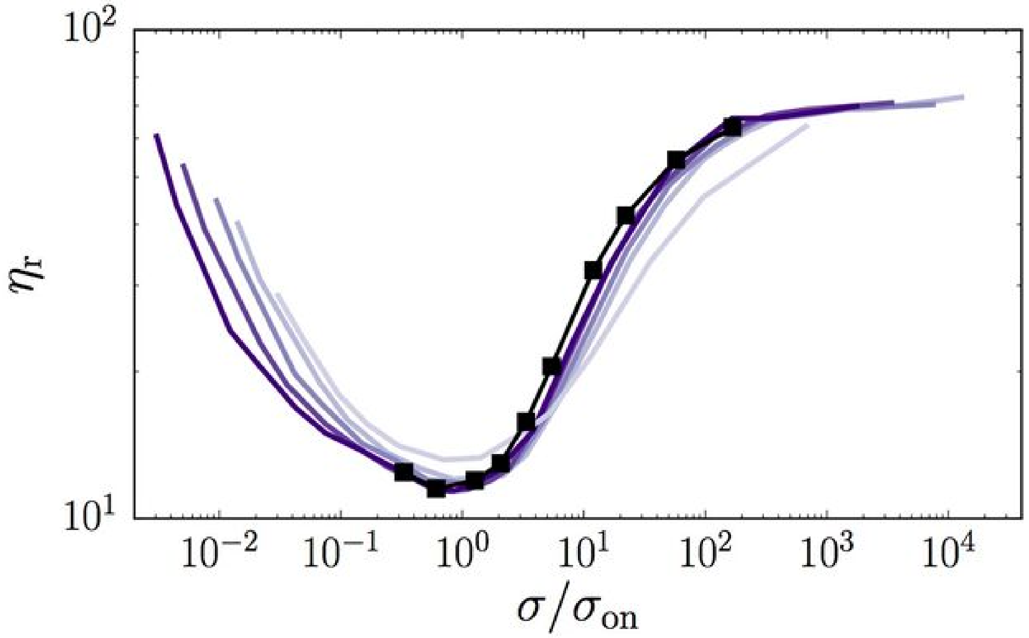


Comparison of Brownian simulation *without* a repulsive force with Stokesian Dynamics simulations (broken lines) of Foss and Brady (2000)



Brownian simulation, no repulsive force

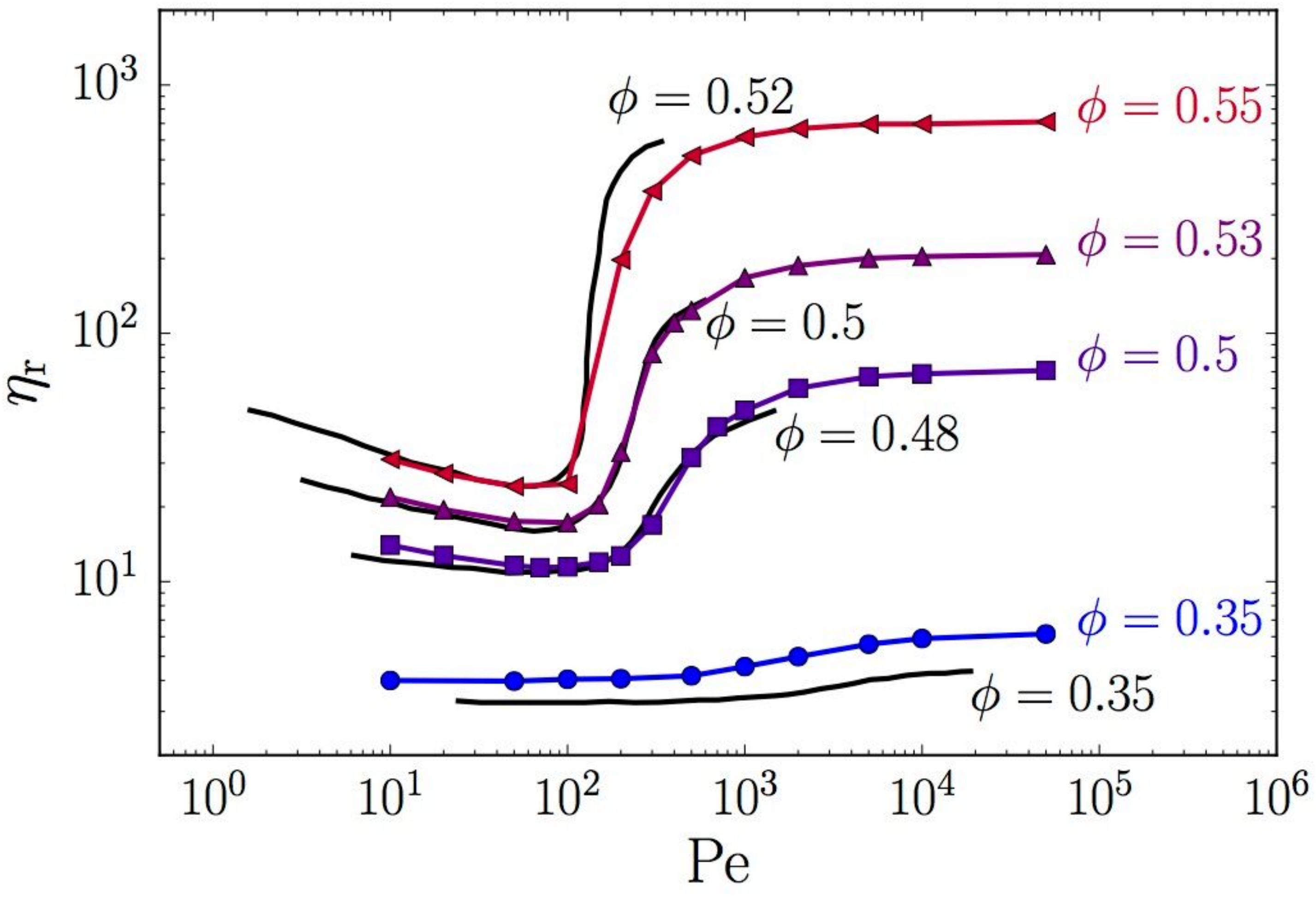




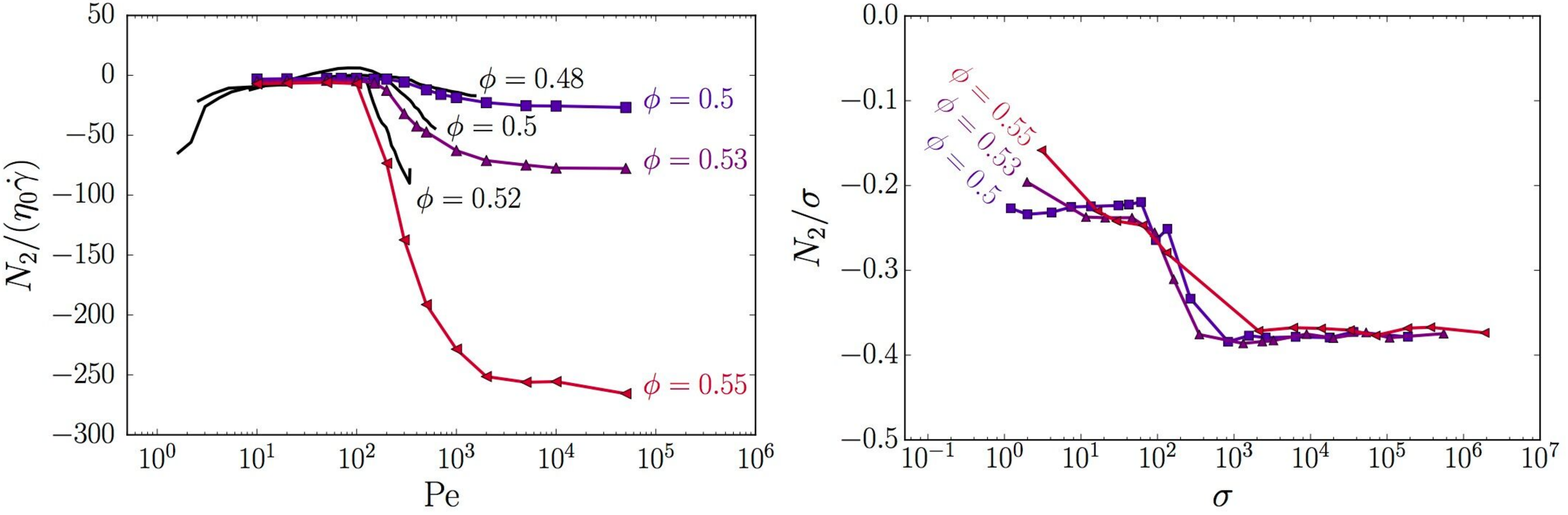
$$0 \le F^* \le 10^4 kT/a$$

$$\sigma_{on} = \frac{5kT}{a^3} + \frac{0.01F^*}{a^2}$$

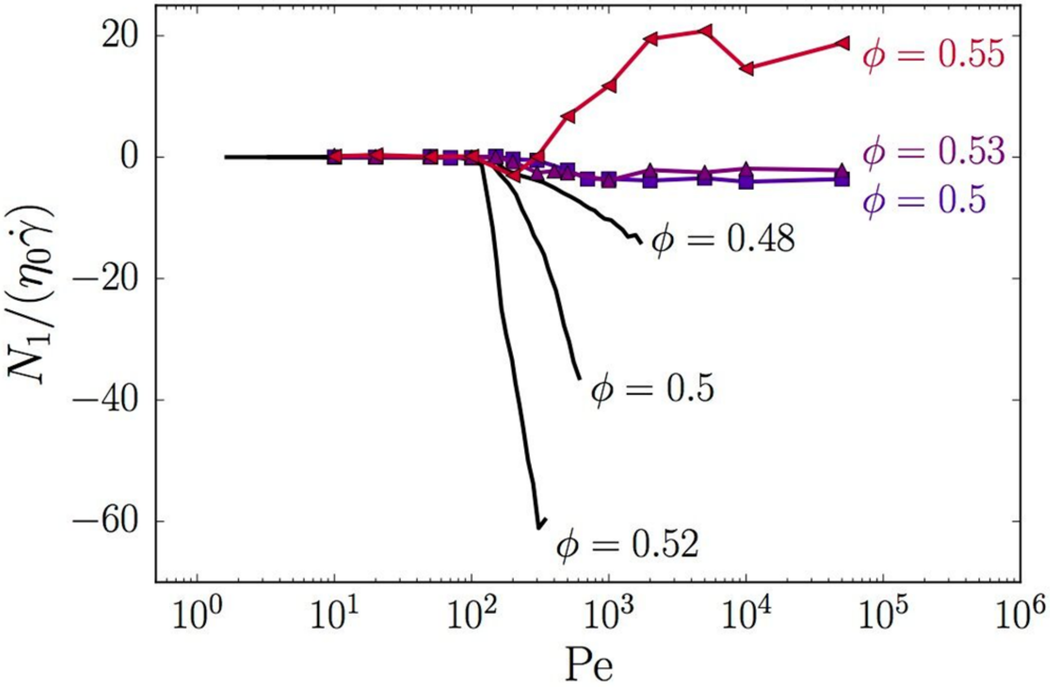
Black squares are the non-Brownian simulation



Comparison with viscosity data of Cwalina and Wagner (2014)
$F^* = 5\text{x}10^3 kT/a$, λ = 0.02a



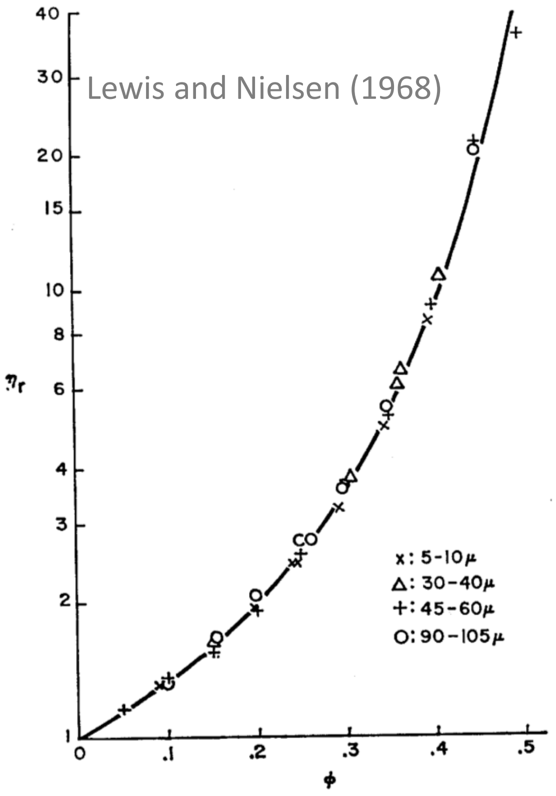
Comparison with N_2 data of Cwalina and Wagner (2014)

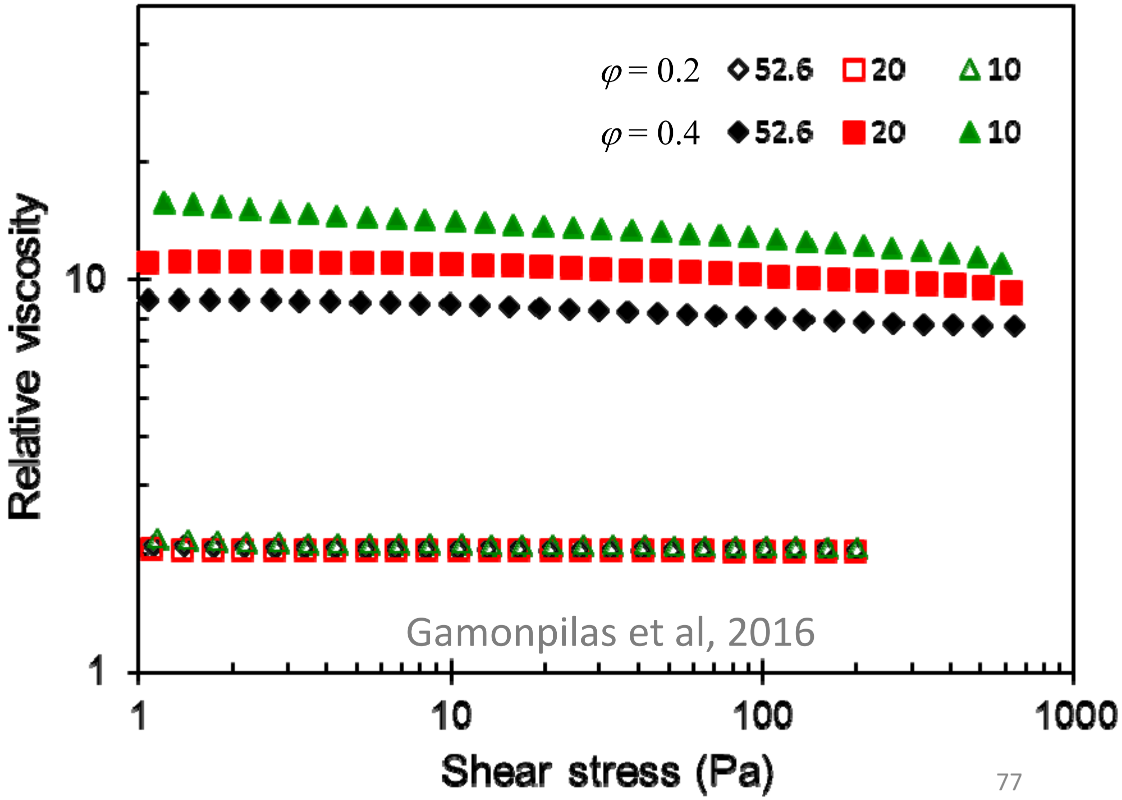


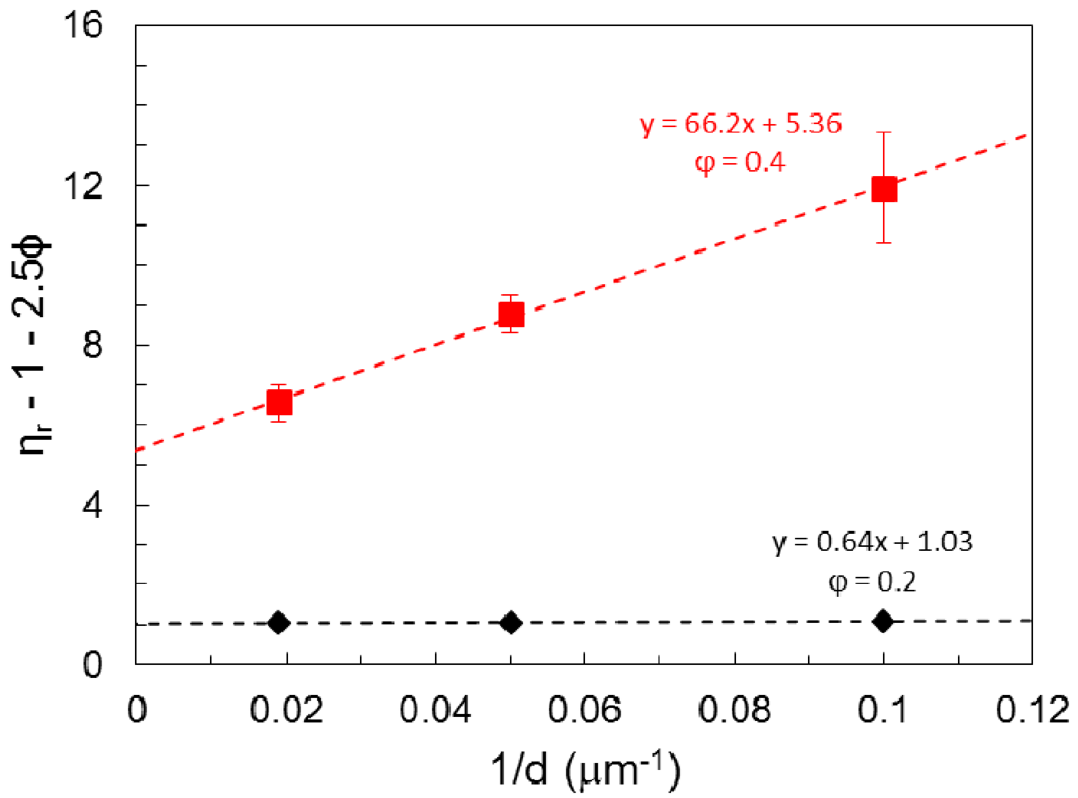
Comparison with N_1 data of Cwalina and Wagner (2014)

Are these systems really scale free?

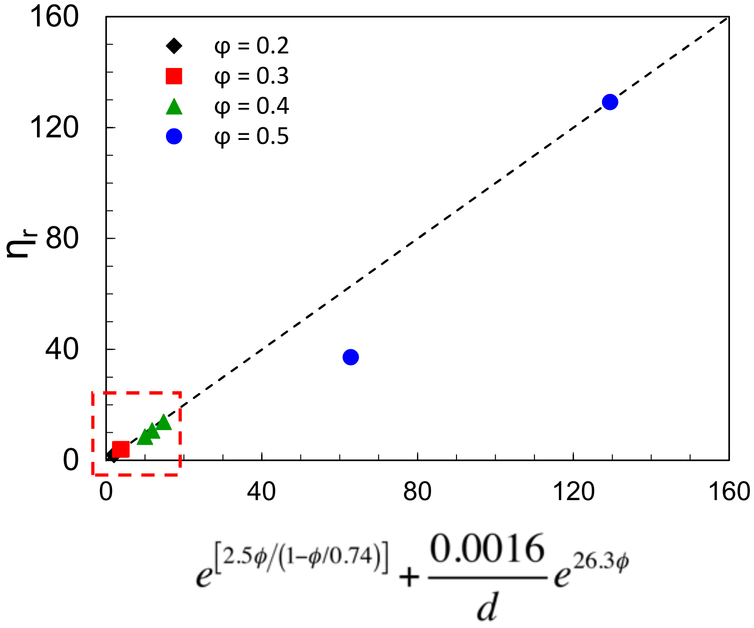
10 to 52.6 µm PMMA spheres in 77.93% (wt) Triton x-100 (t-Octylphenoxypolyethoxy-ethanol), 9.01% ZnCl, and 13.06% H_2O.

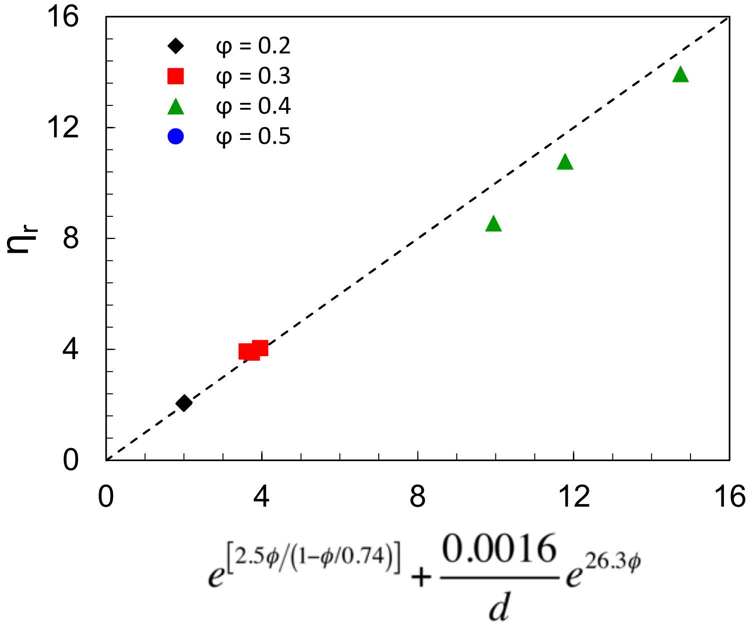

Lewis and Nielsen (1968)


Gamonpilas et al, 2016



There is a correction term independent of d, together with a term proportional to 1/d that is φ-dependent.


φ = 0.2
φ = 0.3
φ = 0.4
φ = 0.5
η_r
0
40
80
120
160
0
40
80
120
160
$e^{[2.5\phi/(1-\phi/0.74)]} + \frac{0.0016}{d} e^{26.3\phi}$


φ = 0.2
φ = 0.3
φ = 0.4
φ = 0.5
η_r
0
4
8
12
16
0
4
8
12
16
$e^{[2.5\phi/(1-\phi/0.74)]} + \frac{0.0016}{d} e^{26.3\phi}$

Some Issues for suspensions:

1. The friction coefficients required to match simulations to experimental data are about twice those measured experimentally. Clearly a lot more is going on than can be captured in a single scaler parameter.

2. Two distinct phenomena, namely the size dependence of the rheological properties in one particle/fluid system but not others, and the inability to match the algebraic sign of N_1 for at least one system, suggest that local interactions are far more complex than captured by simple simulation models.

Both suggest that studies need to be focused on the details of interactions in the narrow particle-particle gap.

Continuum Mechanics

The quest for useful continuum models requires good data for extensional flows. This topic is just now starting to receive attention.

Early attempts at constructing "fabric tensor" models for suspension of spheres were built around using the center-to-center vectors as the order parameter and were not particularly successful. Interest in this topic seems to have faded with the development of particle-based simulations. Force-chain eigenvectors, as computed in the particle-scale simulations, appear to be a more promising basis for developing continuum models for suspensions of spheres, and the topic is worth revisiting. Continuum models should be the ultimate target for applications.

Some recent reviews

M. M. Denn and J. F. Morris, Rheology of non-brownian suspensions, Annual Review of Chemical and Biomolecular Engineering, vol. 5, 2014, pp. 203-228.

M. M. Denn, J. F. Morris, and D. Bonn, Shear thickening in concentrated suspensions of smooth spheres in Newtonian suspending fluids, Soft Matter, 14, 170 – 184 (2018).

Some general measurement issues:

Both yield stress fluids and suspensions exhibit wall slip, which must be accounted for in any measurement. The standard analysis for slip in a rotating parallel-plate rheometer is not rigorously valid (i.e., it is wrong), but it does seem to be robust.

Rheometer /structure scale ratios are very important (and sometimes neglected). In particular, cone-and-plate rheometry is unlikely to give valid results for many systems because of an exclusion zone near the apex.

Heterogeneities in the flow (migration, shear banding, …) may not be obvious in rheological measurements, but they frequently occur and will invalidate the results.

Free-surface effects in rheometers are frequently ignored and can generate order-one errors.