Dynamics of dense soft colloids: shape and osmotic effects

Dimitris Vlassopoulos

FORTH, Institute of Electronic Structure & Laser, and
University of Crete, Department of Materials Science & Technology
Heraklion, Crete, Greece

Daniele Parisi

Leo Gury

M. Cloitre (Paris)

R. Bitton (Beer Sheva)
Y. Ruan, C.-Y. Liu (Beijing)
M. Gauthier (Waterloo)

COLLDENSE
COLLOIDS with
DESIGNED RESPONSE

Outline:

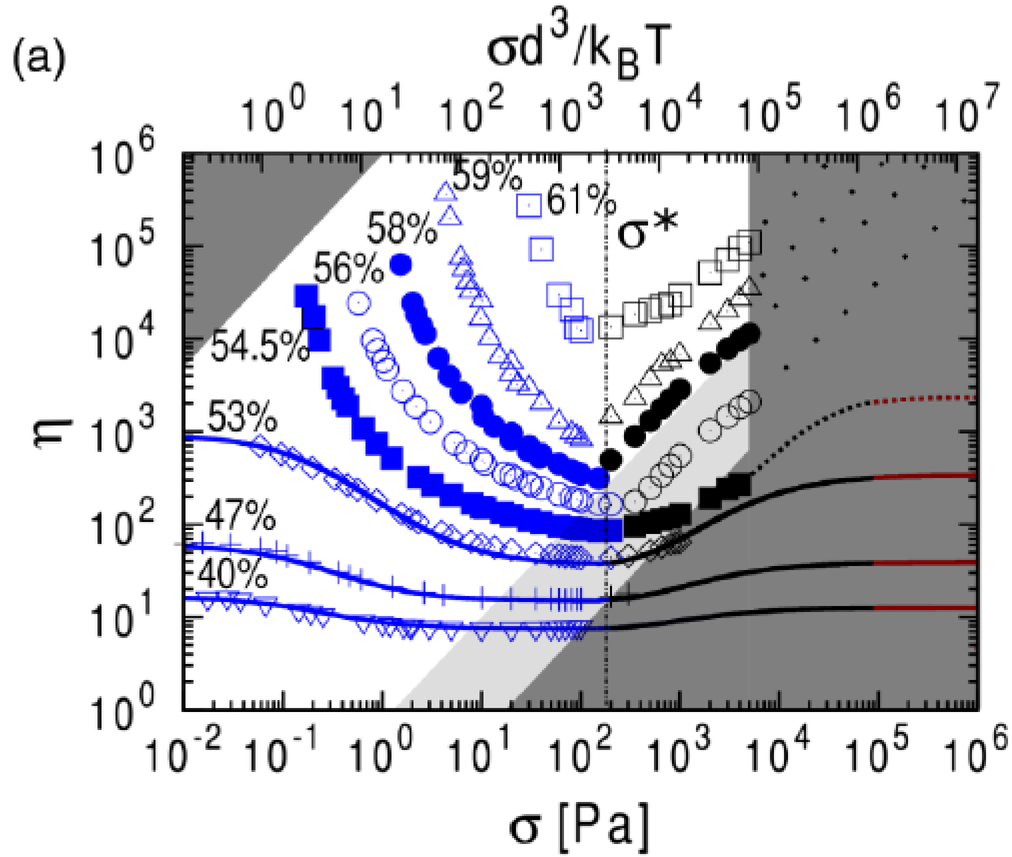
Ingredients for (invariant) constitutive equations (link to microstructure)
Softness, shape & entroping mixing: routes to tailor flow
Molecular design of soft composites with tailored flow properties

Compare stars and microgels (with hard spheres)

Grafted cylinders vs. grafted spheres in dense state
- Packing and order control dynamics & flow

Soft spheres + big linear polymers
- From colloidal to polymeric response
- Polymer-mediated arrest of particles

Discussion with Wilson Poon (March 7)



<u>What is the role of softness?</u>

** Prabhu Nott (80 μm PDMS)

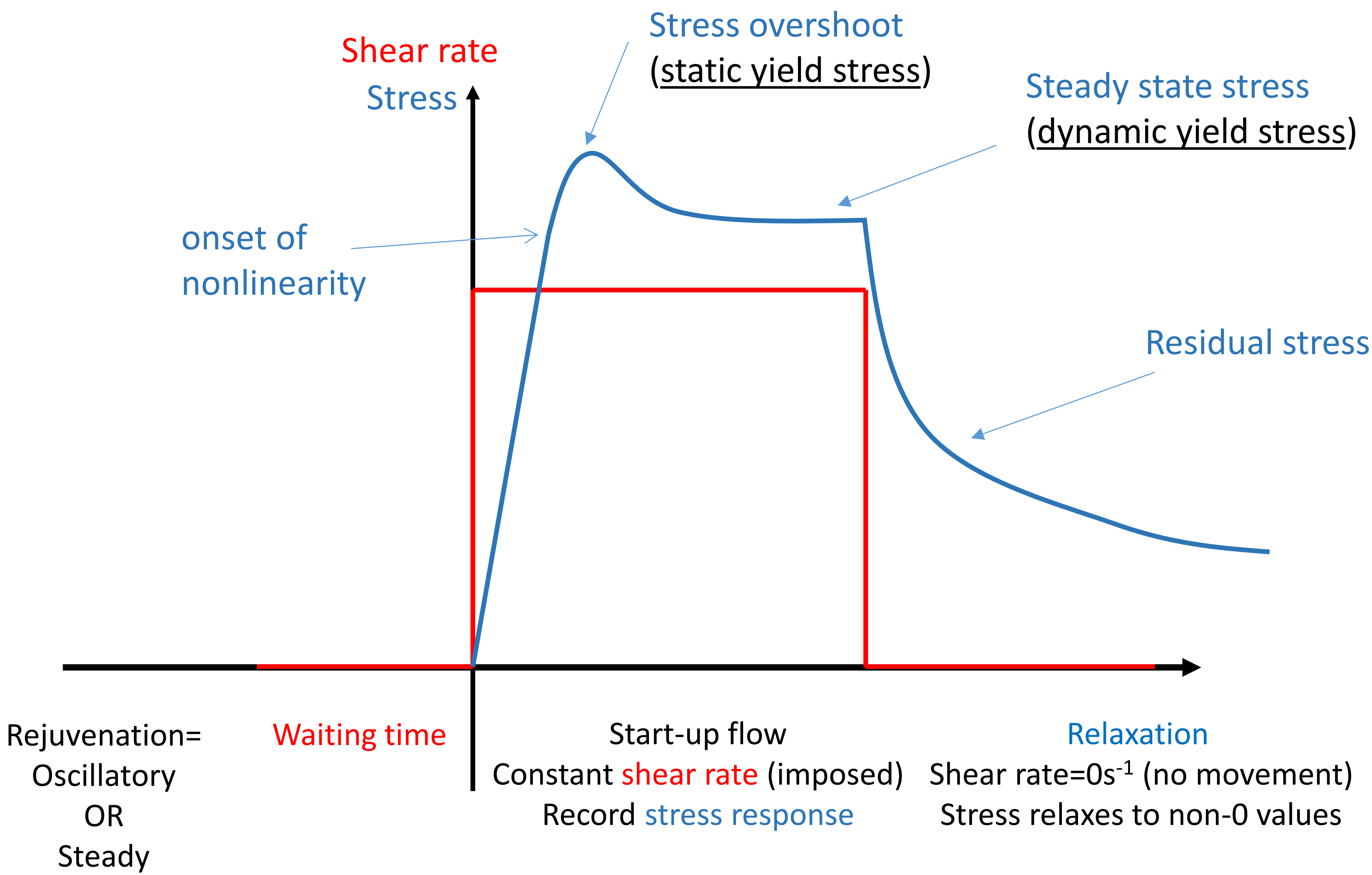
DST, reduced effect

Guy et al. PRL 2015

Lin et al. PRL 2015

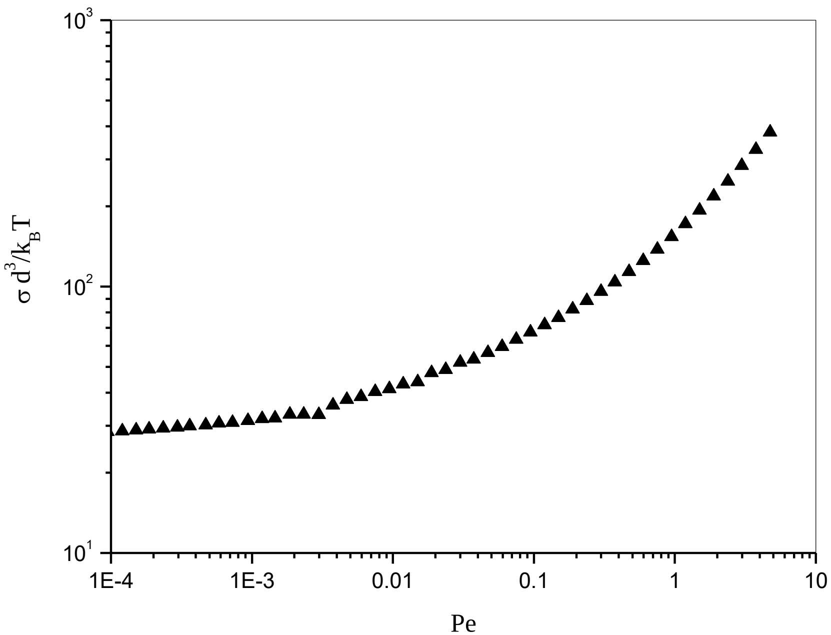
Krishnamurthy et al. JOR 2005

Main experimental test

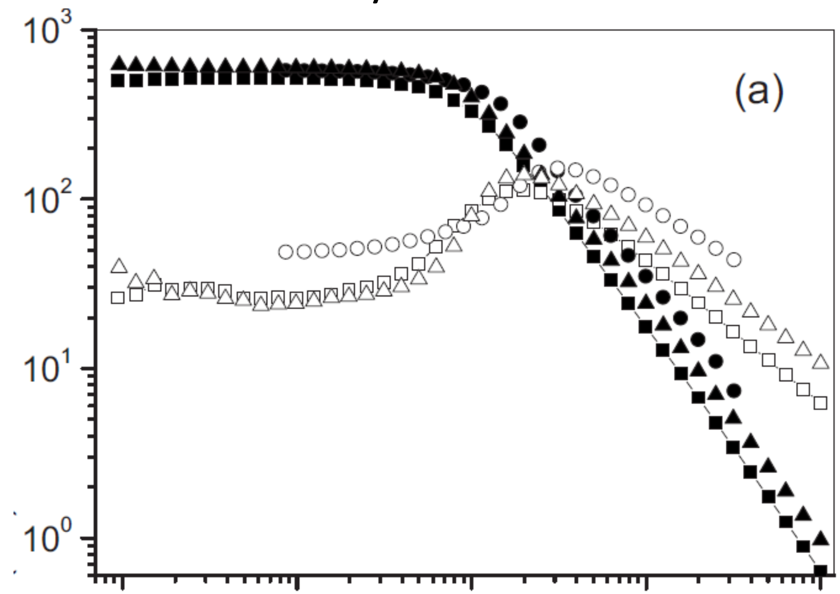


Yield stress

steady shear



oscillatory shear

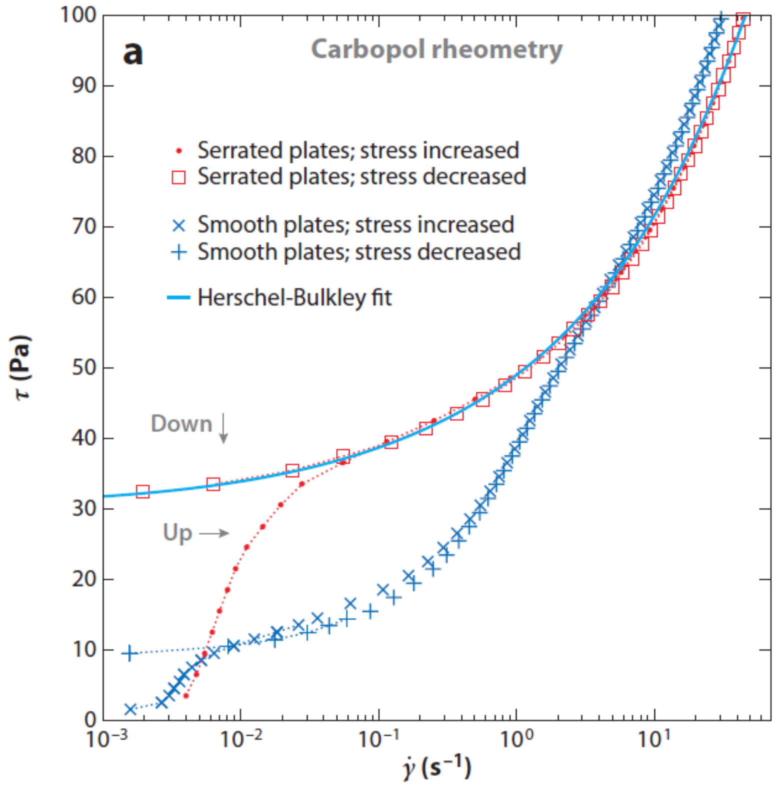


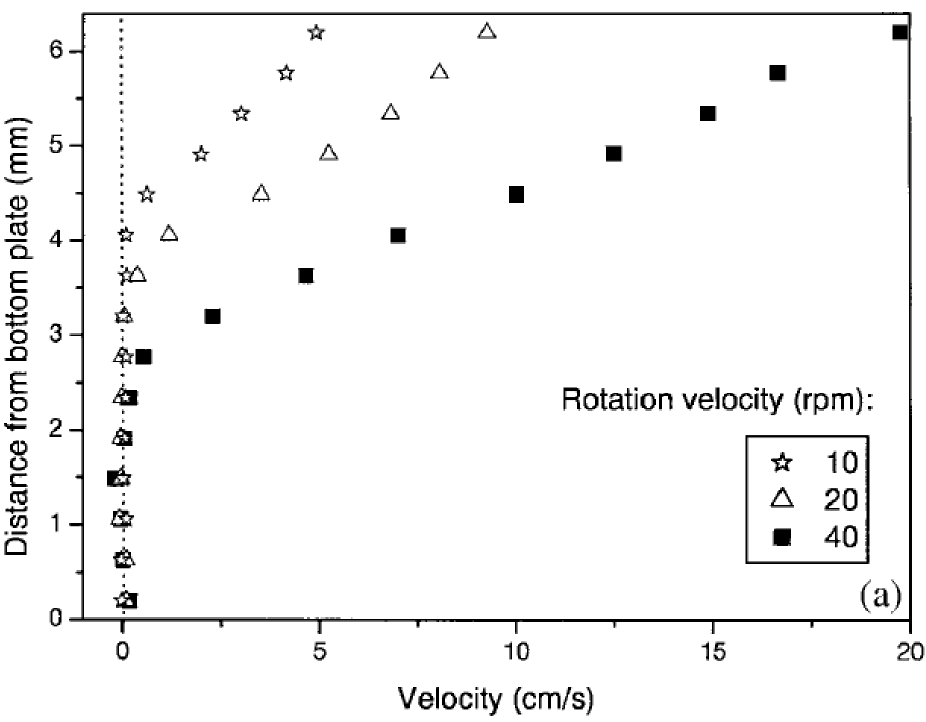
Bonn et al. Rev. Mod. Phys. 2017

Christopoulou et al. Phil. Trans. R. Soc. A 2009

The “standard” picture: YSF

Memory not necessary
Viscoplasticity



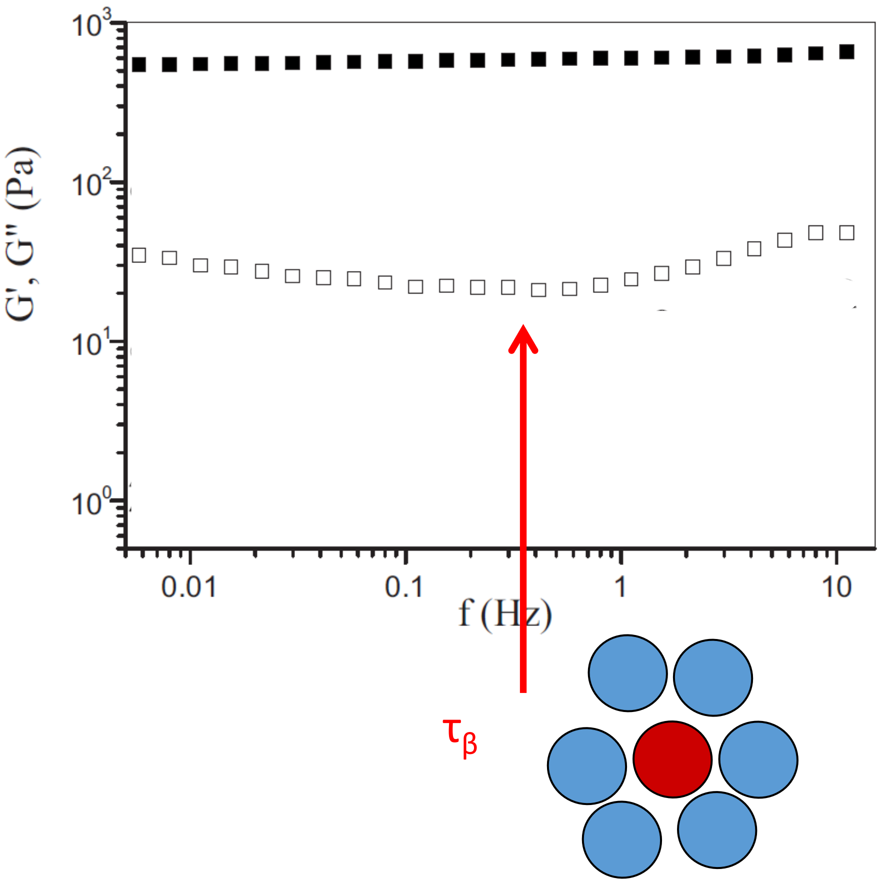


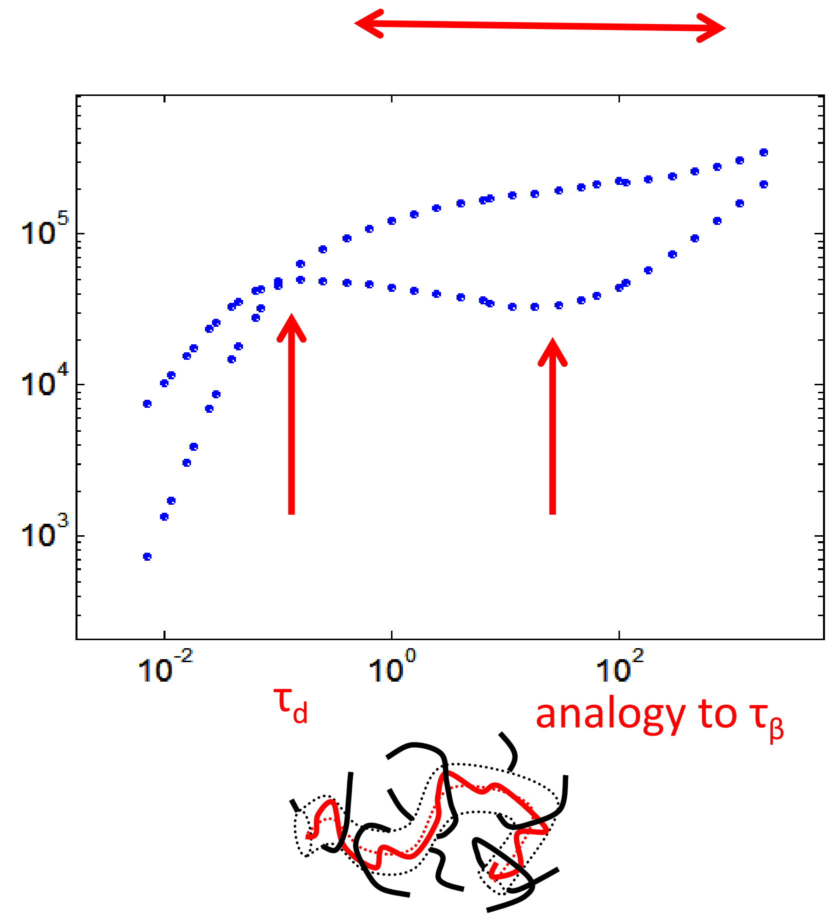
hysteresis (thixotropy), yield stress, wall slip, shear banding

Balmforth et al., Annu. Rev. Fluid Mech. 2014
Oppong, de Bruyn, Rheol. Acta 2011

Coussot et al., PRL 2002

Colloidal glass/paste vs entangled polymer

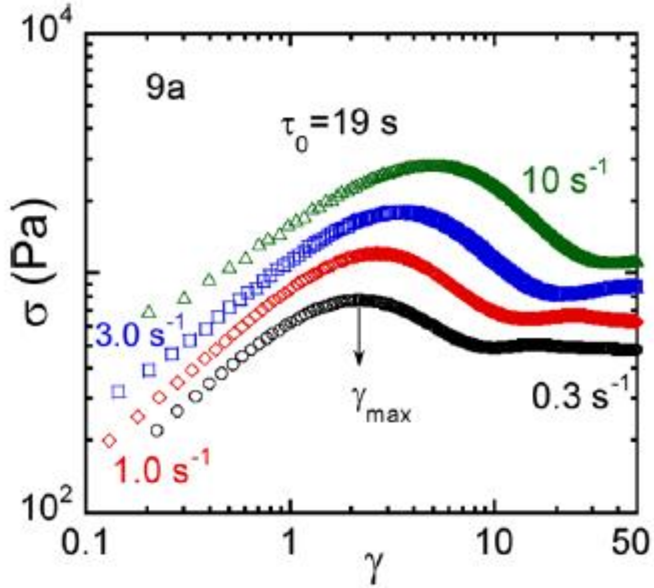


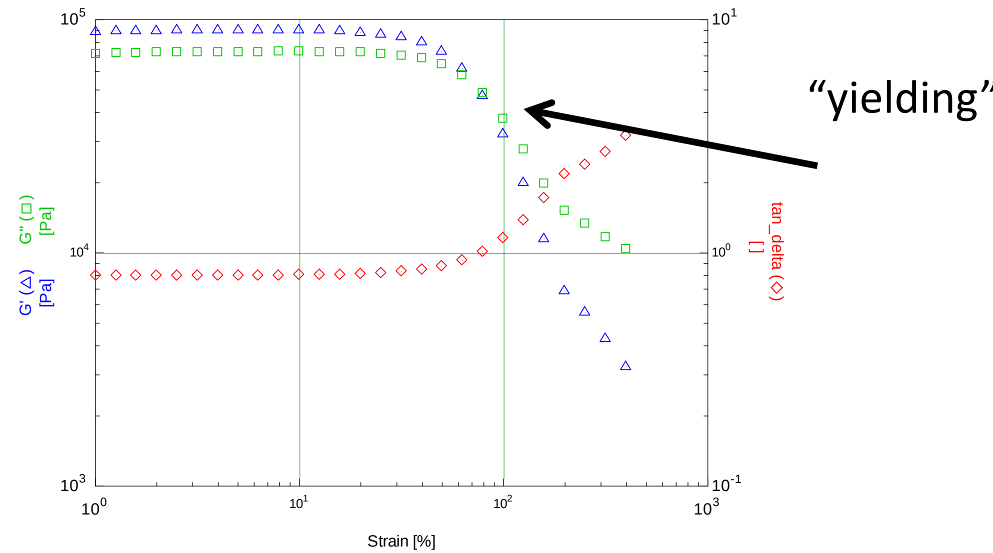


Yielding in polymers?

Memory

Viscoelasticity

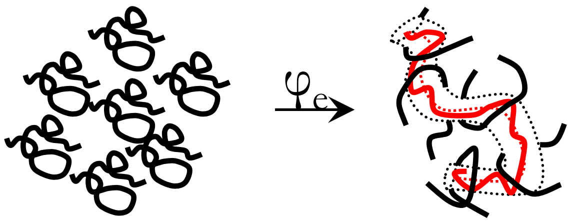




S. Q. Wang, Macromolecules 2013

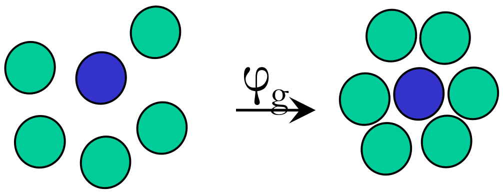
F. Snijkers, 2011

Topological constraints in small (nm scale) systems: caging



$\phi_{eff} > 1$

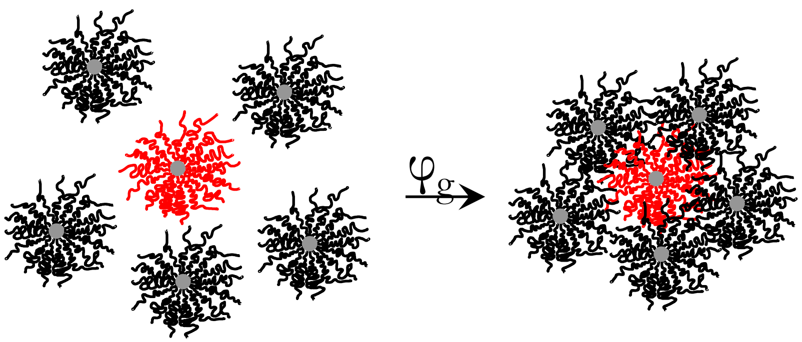
Edwards, deGennes, Doi, 1970s



repulsive

$\phi_g \sim 0.56$

MCT, SGR
Götze, Cates, Fuchs, Fielding, Sollich



$\phi_{eff} > 1$

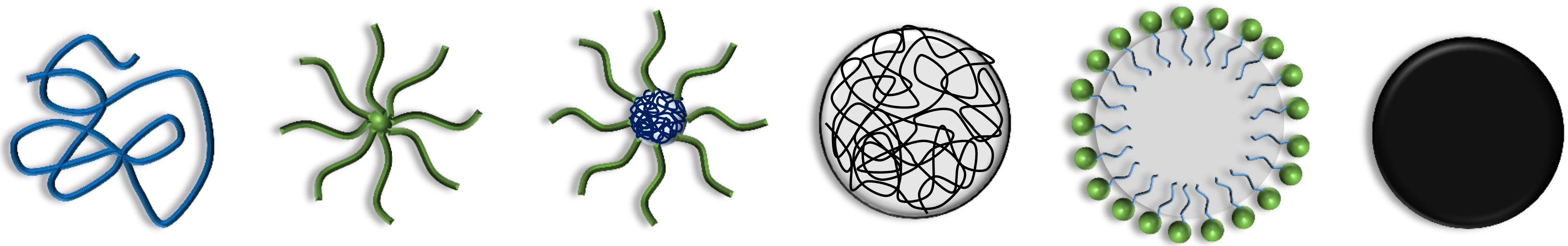
Frenkel, 1941 ; Pusey, 1991 ; Cates, 2003

Softness: from polymers to colloids

$$\varepsilon = \frac{\Delta F}{k_B T}$$

$\varepsilon \cong 1$

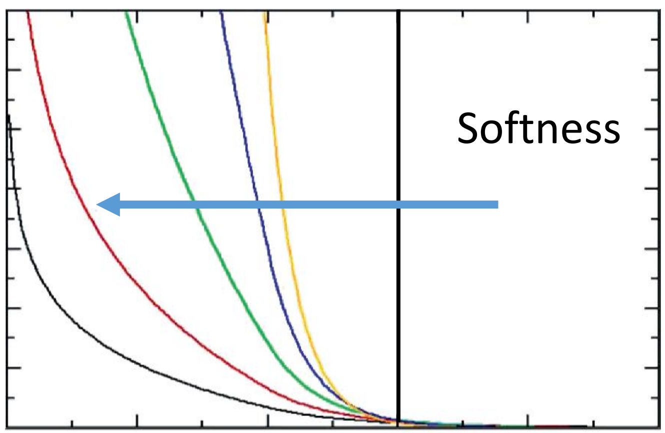
$$\varepsilon = \frac{ER^3}{k_B T} \to \infty$$



Polymer coil

volume fraction>1

Hard sphere

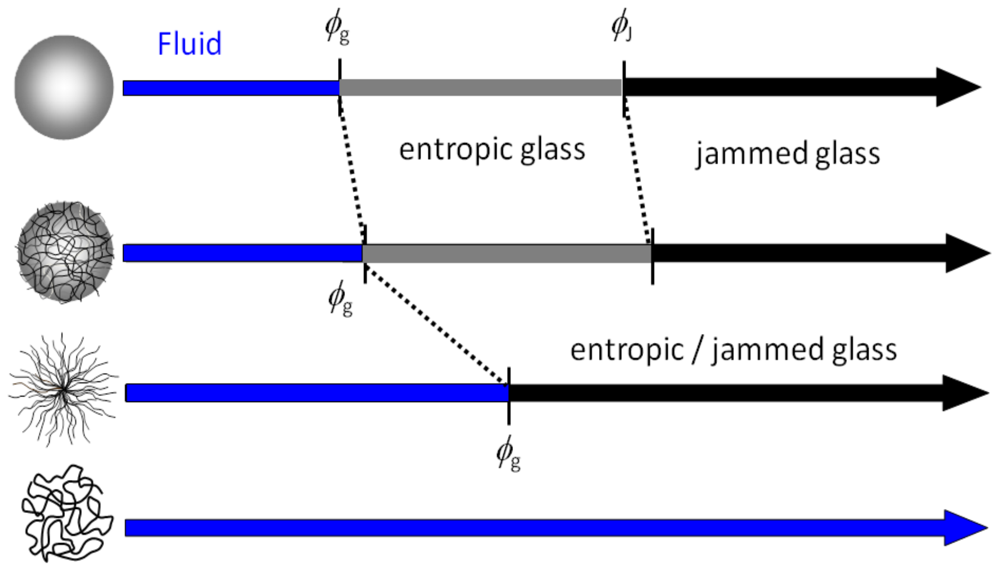


$$V_{Hertz}(r) = \begin{cases} \epsilon\left(1 - \frac{r}{R_i + R_j}\right)^{\frac{5}{2}} & \text{for } r < R_i + R_j \\ 0 & \text{for } r > R_i + R_j \end{cases}$$

$$\frac{V_{star}(r)}{k_B T} = \begin{cases} (5/18) f^{3/2}\left[-\ln(r/\sigma) + \left(1 + \sqrt{f}/2\right)^{-1}\right] & \text{for } r \leq \sigma \\ (5/18) f^{3/2}\left(1 + \sqrt{f}/2\right)^{-1}(\sigma/r)\exp\left[-\sqrt{f}(r-\sigma)/2\sigma\right] & \text{for } r > \sigma \end{cases}$$

DV & M. Cloitre, COCIS 2014
Likos et al. PRL 1998

Softness: state transitions



Challenge: determine volume fraction $\phi_{eff}=c/c^*_h=nV_0$

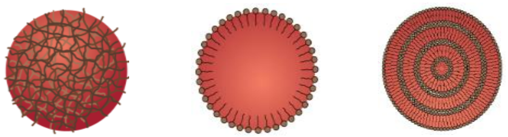
Poon et al. SM 2012
Conley et al. Sci. Adv. 2017
Bouhid de Auiar et al. Sci. Rep. 2017
van der Scheer et al. ACS Nano 2017

Paddy Royall (March 9)
Gardner transition (thermal glass to Gardner phase to jammed glass)

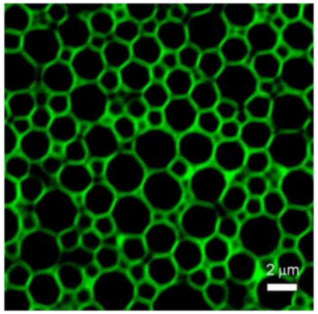
Charbonneau et al., Annu. Rev. Condens. Matter Phys. 2017

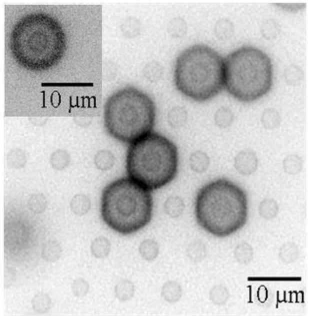
Dense Soft Colloids: shape adjustment and interpenetration (with Michel Cloitre, ESPCI)

Microgels and similar

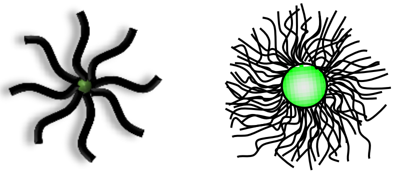


Microgels Emulsions Vesicles





Stars and similar



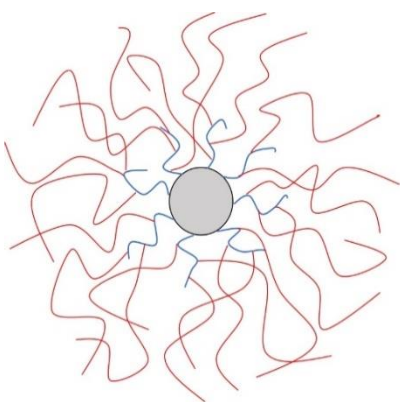
Cloitre & Bonnecaze, Adv. Polym. Sci. 2010
Seth et al., Nat. Mat. 2011
Helgeson et al., Nat. Mater. 2012 ; JOR 2014
Peng et al., Nat. Mat. 2015
Mohanty et al., PRX 2015; Sci. Rep. 2017
Conley et al., Sci. Adv. 2017
Semenov et al., Langmuir 1999
DV & G. Fytas, Adv. Polym. Sci. 2010
Zhang et al., PRL 2014
Senff, Richtering, Langmuir 1999

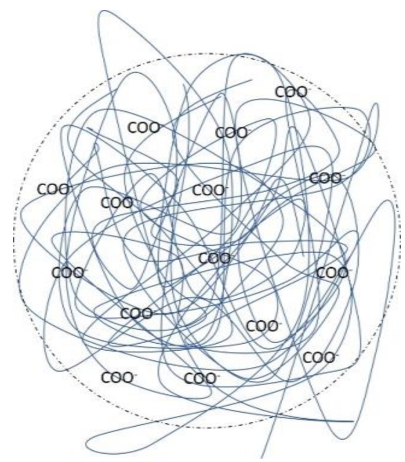
Compare stars and microgels

Star polymers in squalene

Number and size of arms

- 800 arms
- Each arm 5kg/mol (M_w/M_n<1.1)
- Carbosilane dendrimer core
- Polybutadiene arms
- Radius 25-30nm





Roovers et al., *Macromolecules* 1993
Gauthier and Munam, *Macromolecules* 2010

Microgels in water

Number and distance between crosslinks

- Spherical cross-linked polymer network with 128 units/crosslink
- 35% methacrylic acid
- 64% ethylacrylate
- 1% difunctional crosslinker
- No dangling chains
- Radius 305nm (swollen)

Pellet and Cloitre, *Soft Matter* 2016

Partial overview of entropic mixtures

Hard colloid-linear polymer mixture

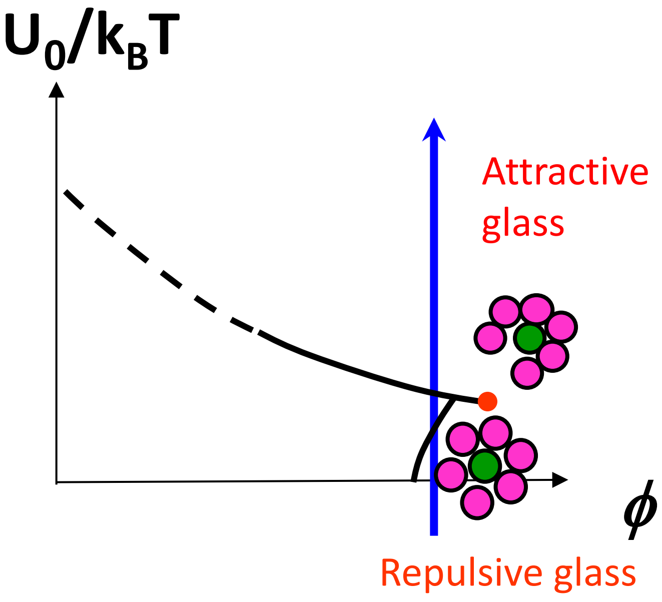
Repulsive glass → Attractive glass

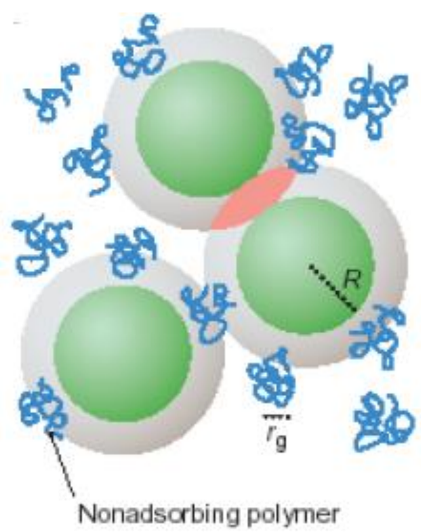
Pham et al Science (2002)

Sciortino Nat. Mat. (2002); PRE (2004) ; EPL (2006)

Eckert & Bartsch PRL (2002) ; Coll. Surf. A (2011) ; Eberle et al PRL (2011)

Pham et al. JOR (2008) ; Petekidis et al. (2008+)

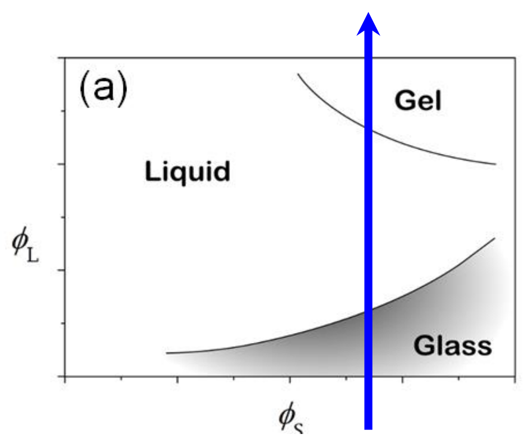


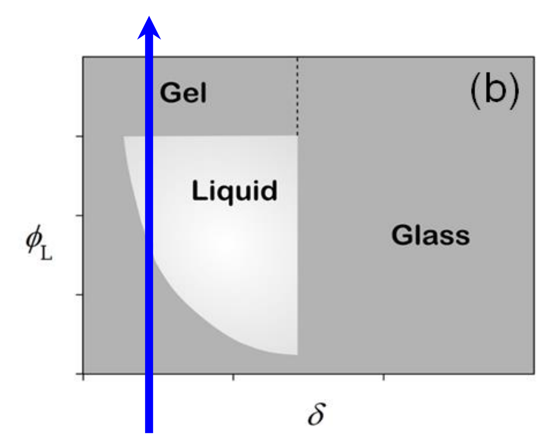


$$u(r) = -kT \bullet F[\sigma_S, \sigma_A, \phi_p]$$

Asakura-Oosawa, 1954, 1958

$\delta = R_{polymer}/R_{colloid}$





Soft colloid (star)-linear polymer mixture

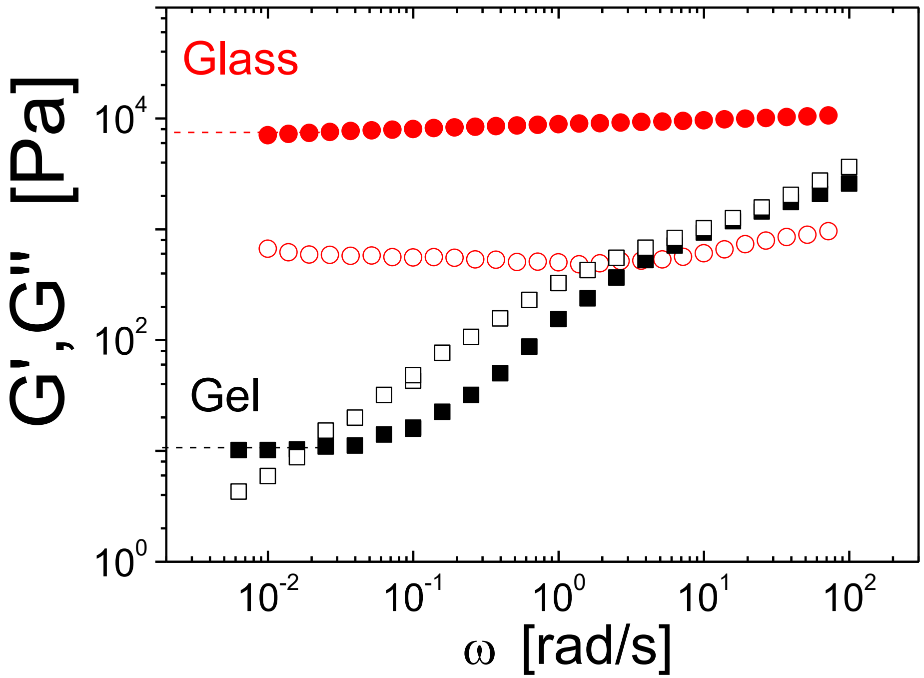
Repulsive glass → Gel

Stiakakis et al. PRL 2002 ; EPL 2005

Lonetti et al. PRL 2011

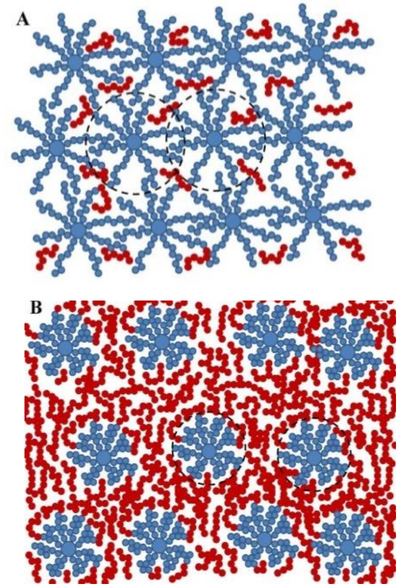
Truzzolillo et al. JoR 2014, Soft Matter 2013

Softness: from repulsive glass to gel



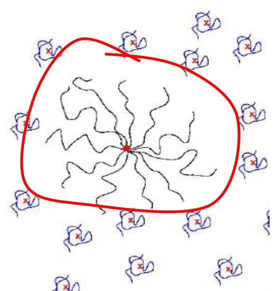
$\phi \sim 3.75$

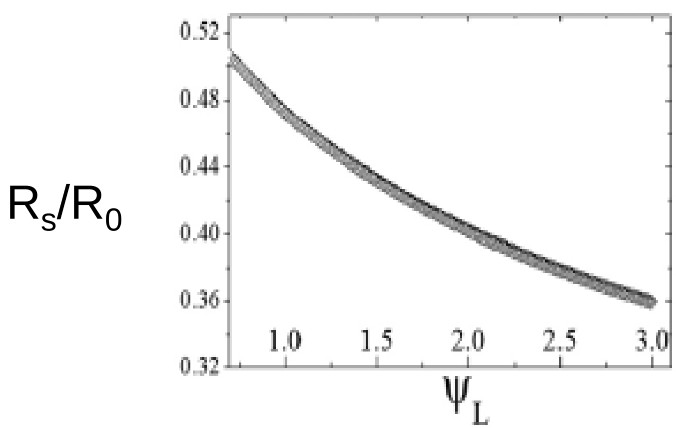
$\phi \sim 0.2$



Osmotic compression

$$F_{tot}(R) = F_{os} + F_{el} + F_{\text{int}}$$

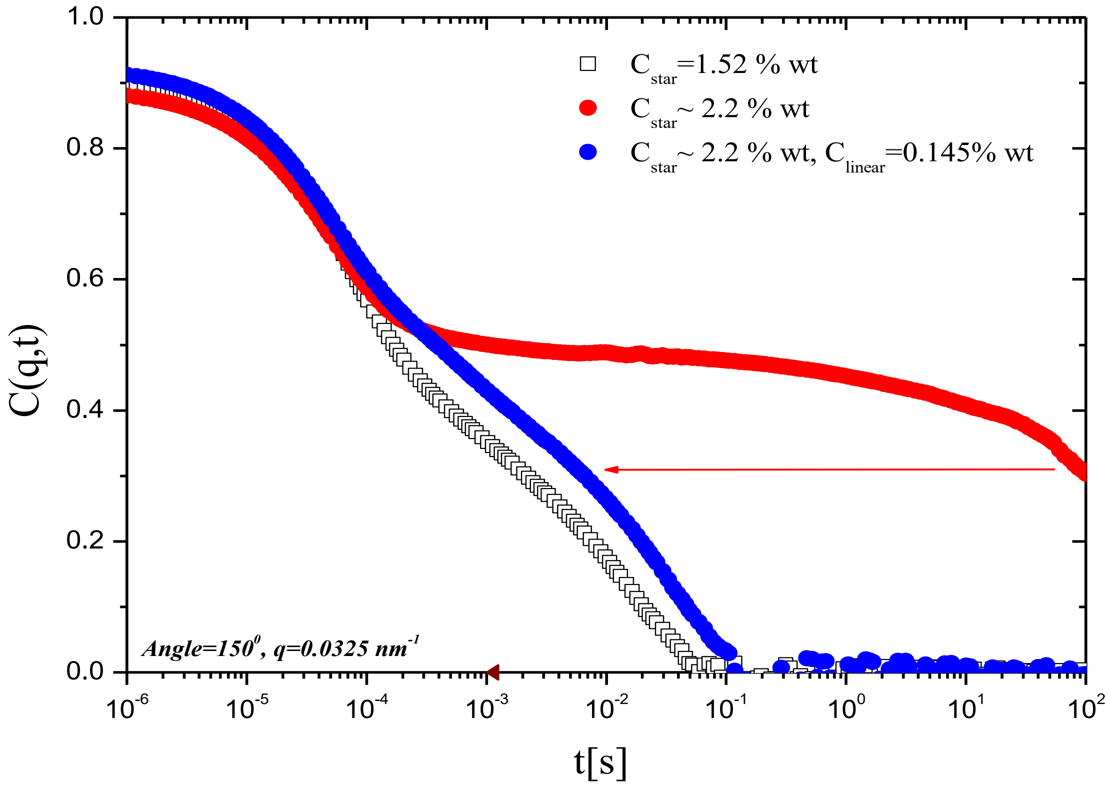




Wilk et al. EPJ E 2010

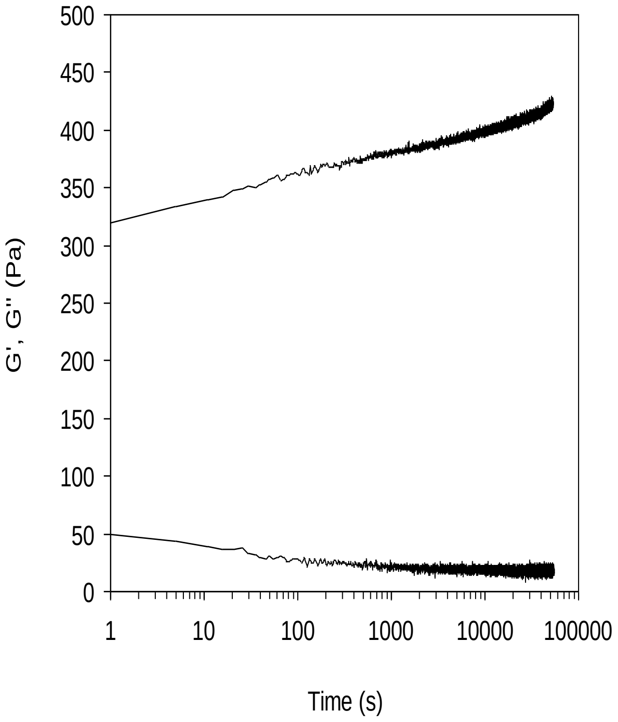
Truzzolillo et al. Macromolecules 2011

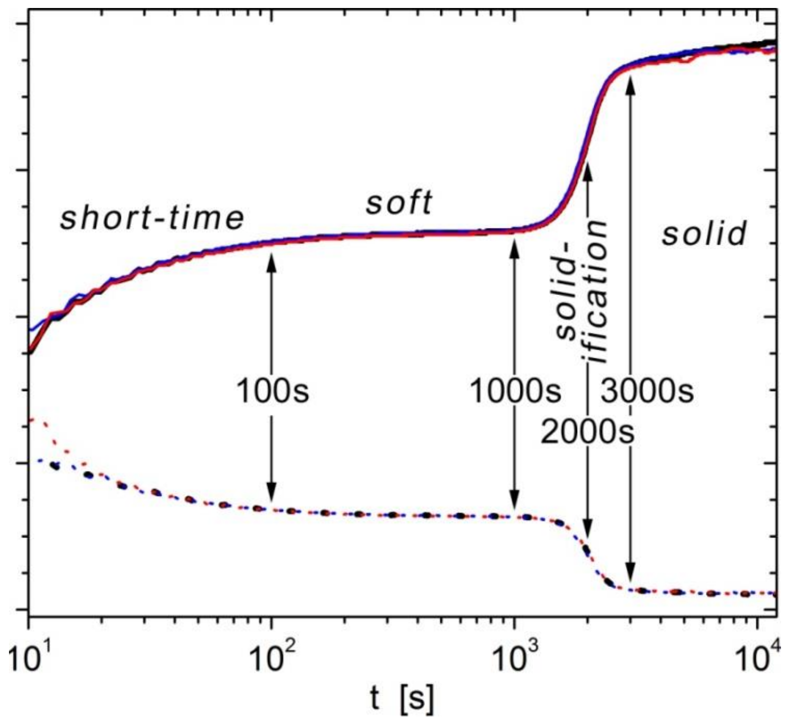
Polymer mediated melting of soft glass



Stiakakis et al. EPL 2005 ; JPCM 2011

Aging

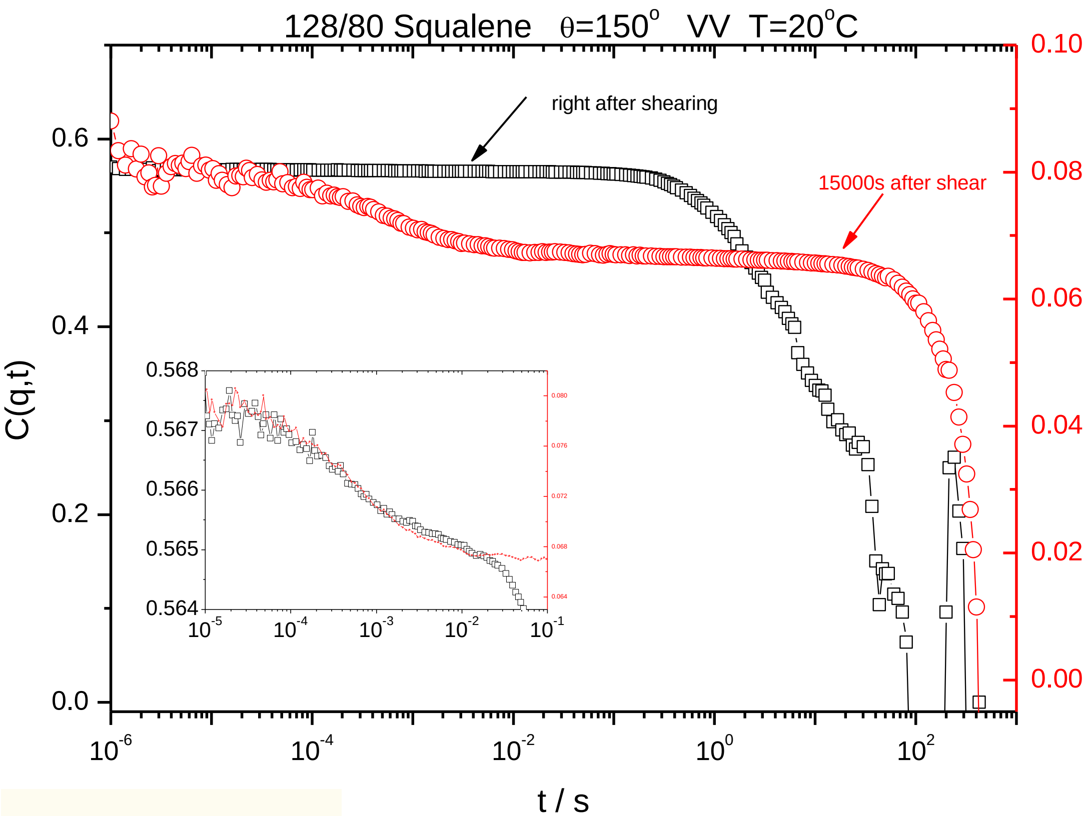


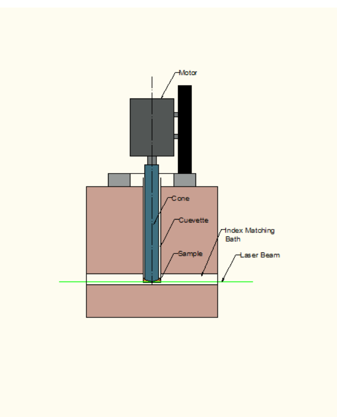


microgels, hard spheres

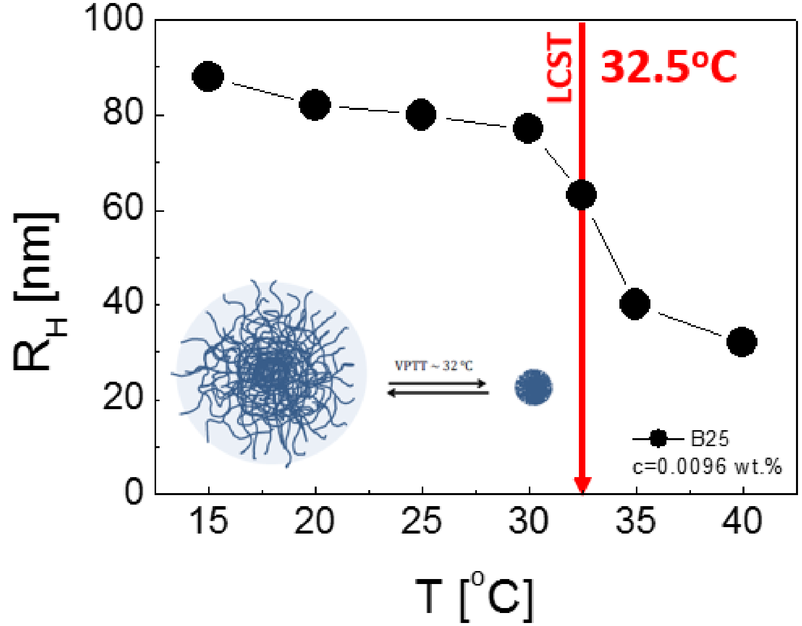
some stars

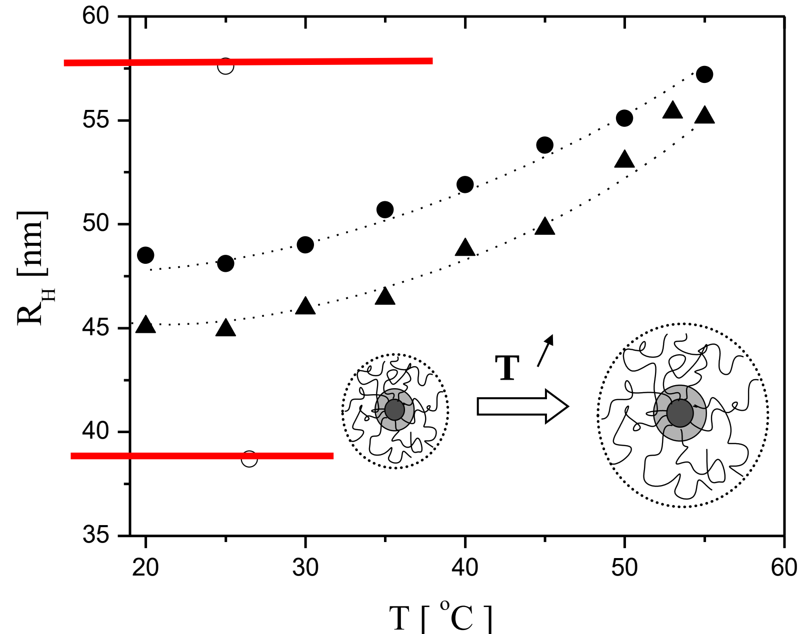
Aging

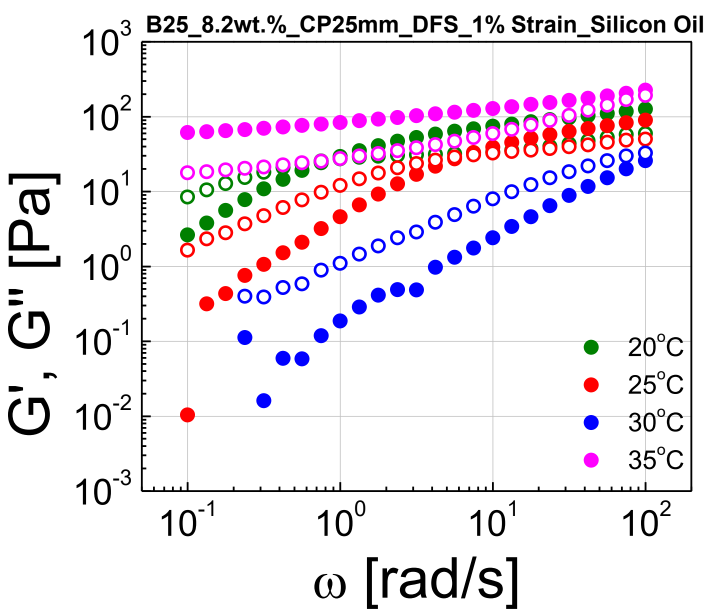

128/80 Squalene θ=150° VV T=20°C
right after shearing
15000s after shear
C(q,t)
t / s


Motor
Cone
Cuevette
Index Matching Bath
Sample
Laser Beam

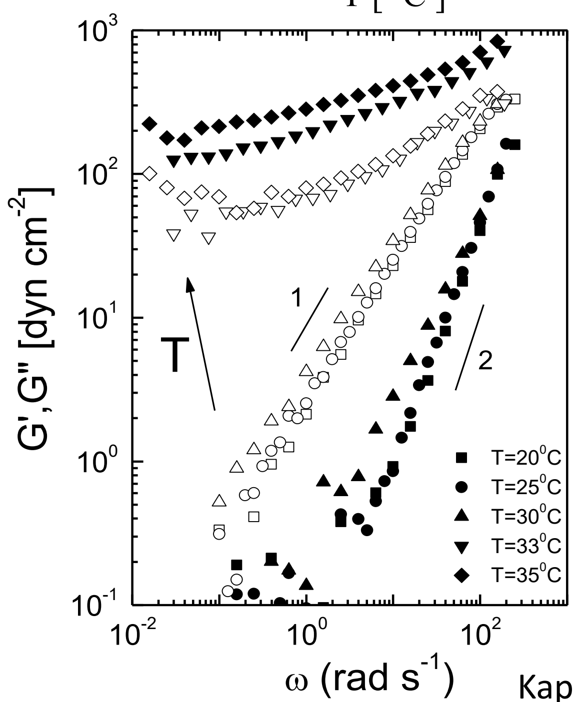
Temperature as control parameter





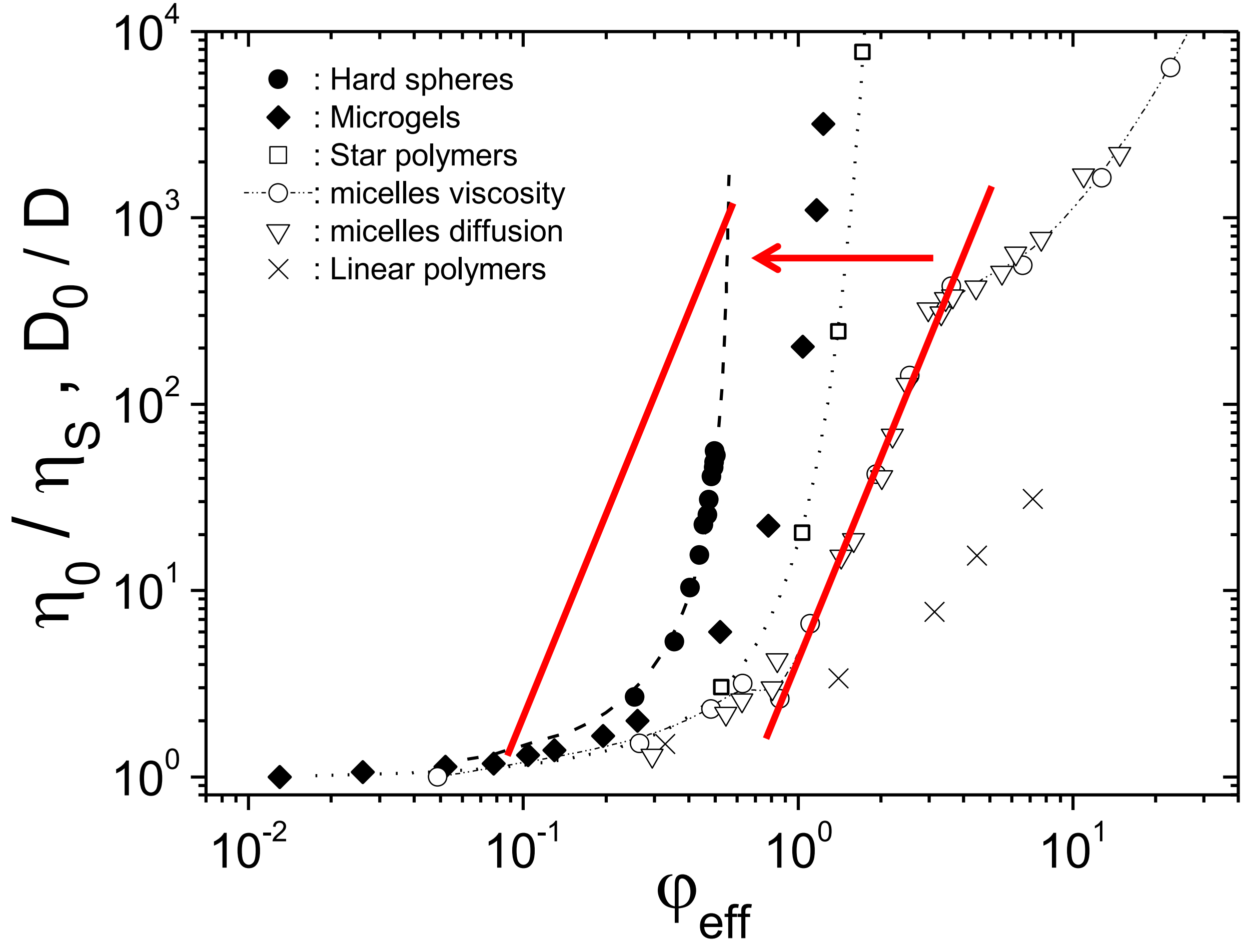


see P. Schurtenberger et al.



Kapnistos et al. PRL 2000

Some consequences of softness: viscosity & self-diffusion

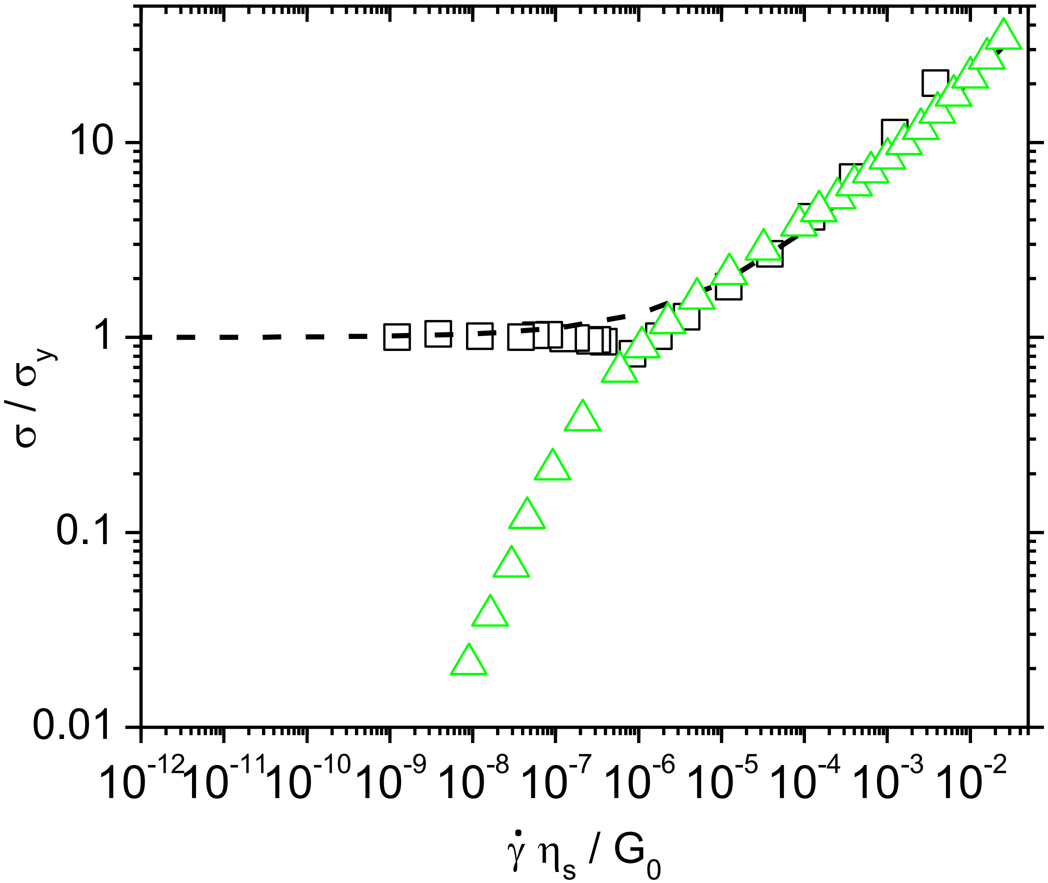


scale with R_h

$\phi_{eff}=c/c^*_h$

fragile vs strong analogy:
Mattsson et al. Nature 2009
van der Scheer et al. ACS Nano 2017

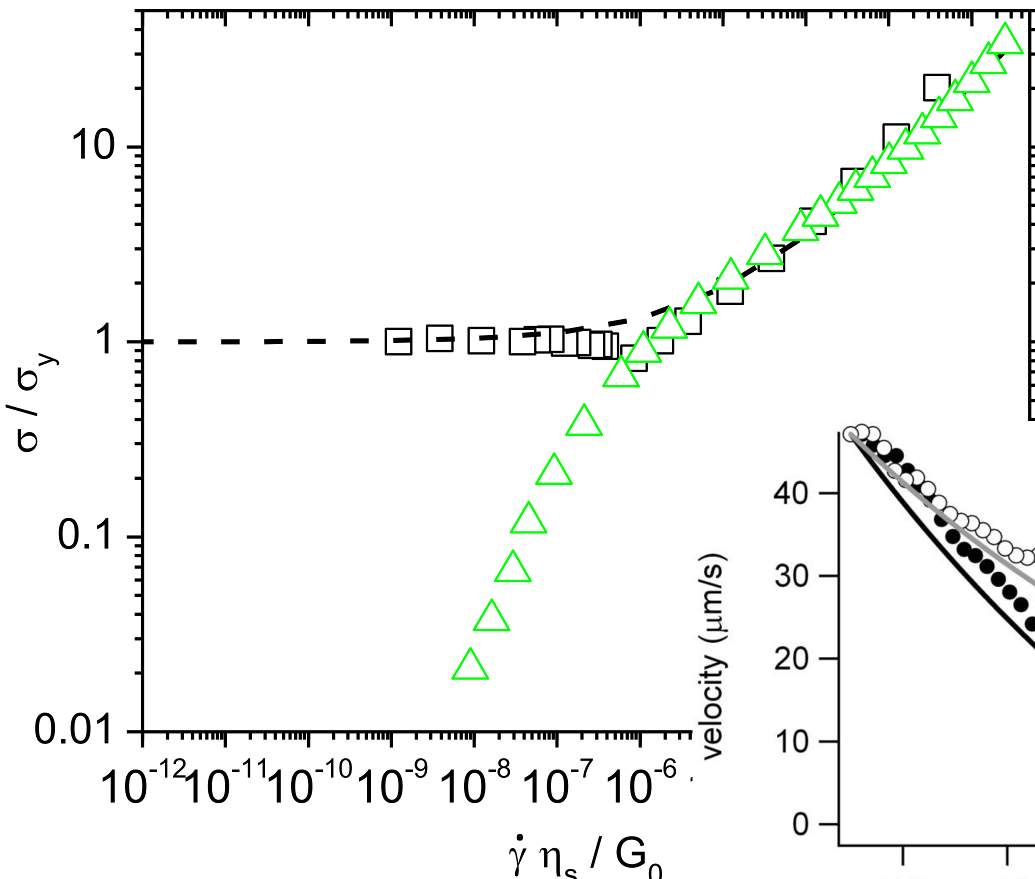
Some consequences of softness: flow curves

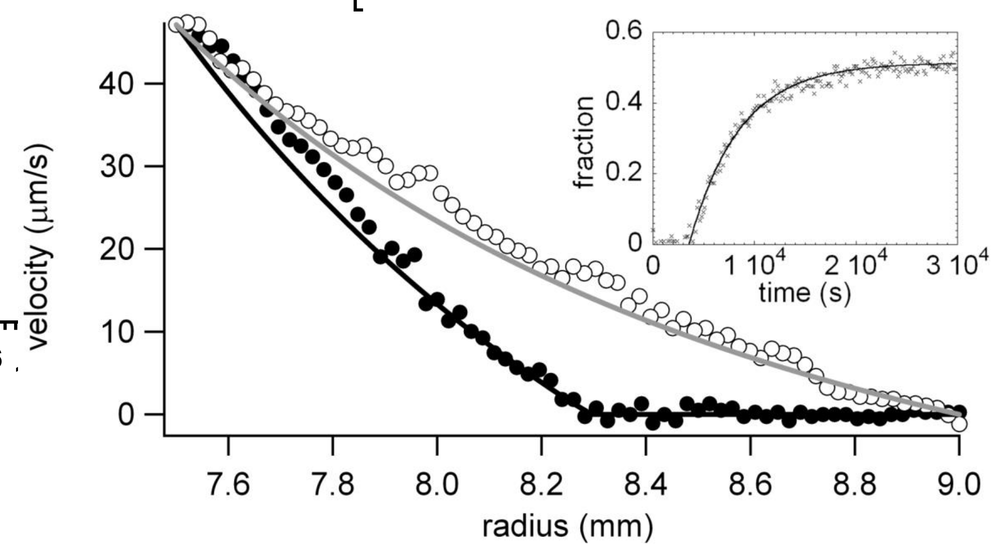


$$\sigma/\sigma_{\mathrm{y}} = 1 + k\dot{\gamma}^{1/2}$$

Cloitre et al. PRL 2003
Seth et al. Nat. Mat. 2011

Some consequences of softness: flow curves

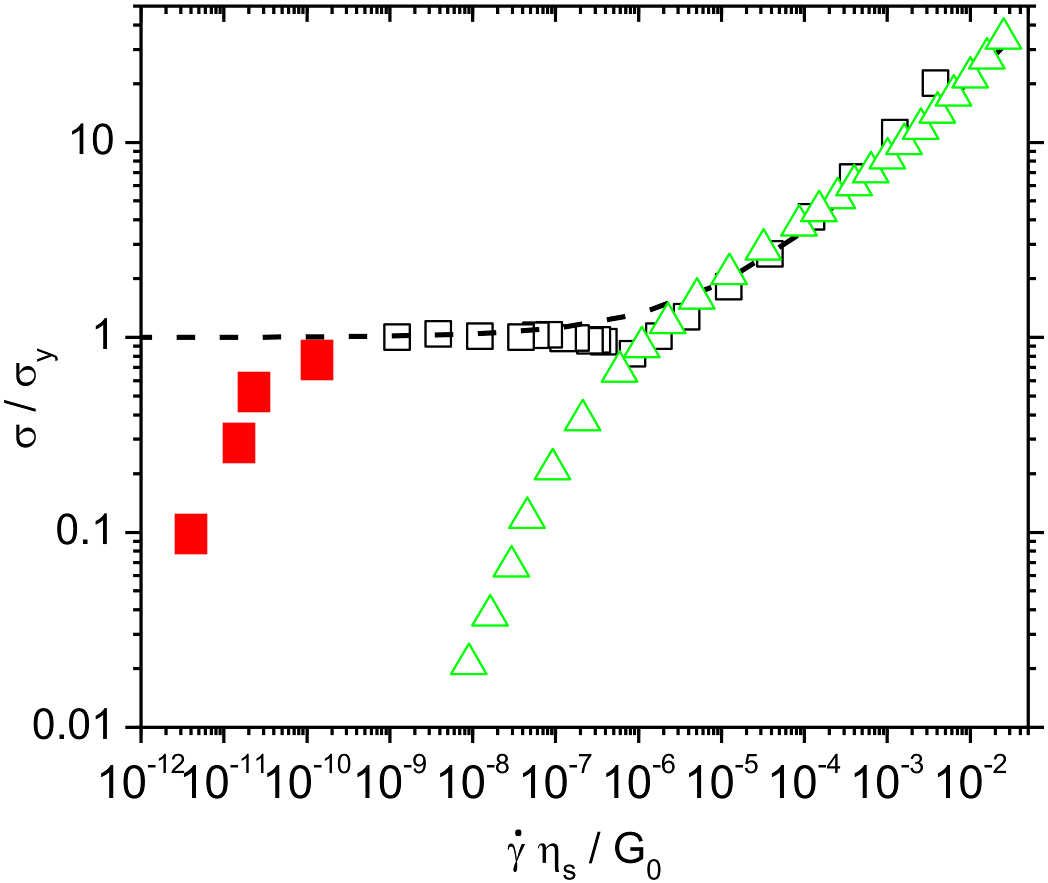




Rogers et al. PRL 2008, JOR 2010

Some consequences of softness: flow curves

Also, Sid Yip:
simulations on metallic glasses

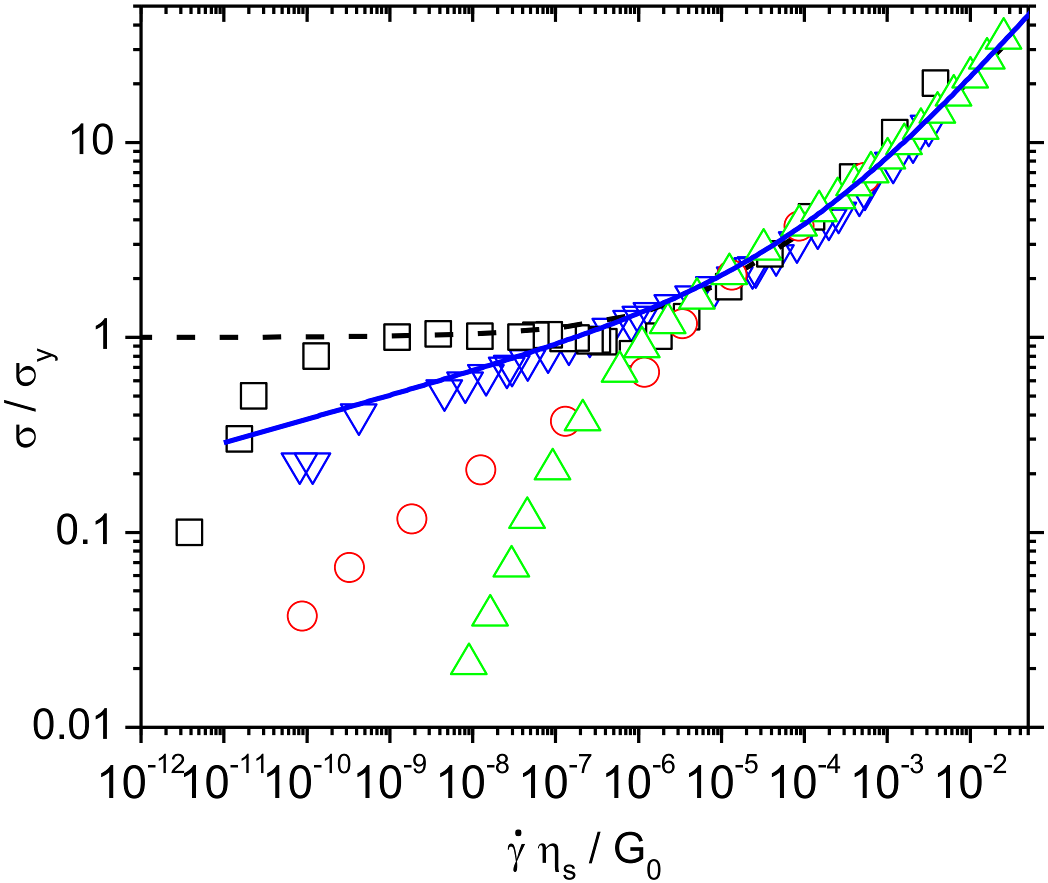


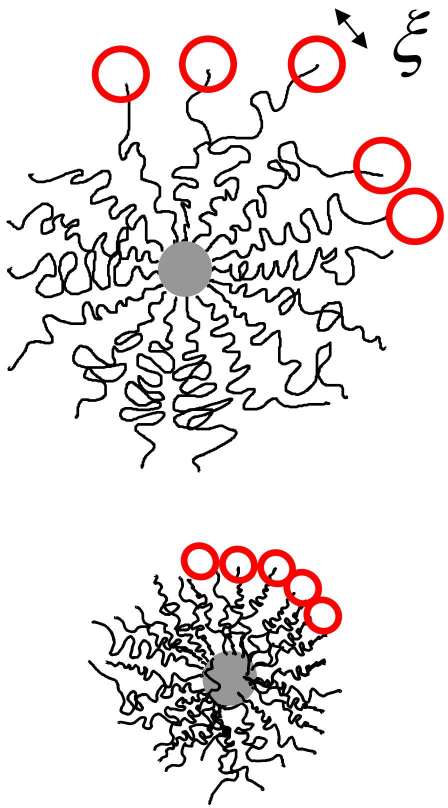
Soft glasses with detectable alpha relaxation

Erwin et al. JOR 2010

Some consequences of softness: flow curves

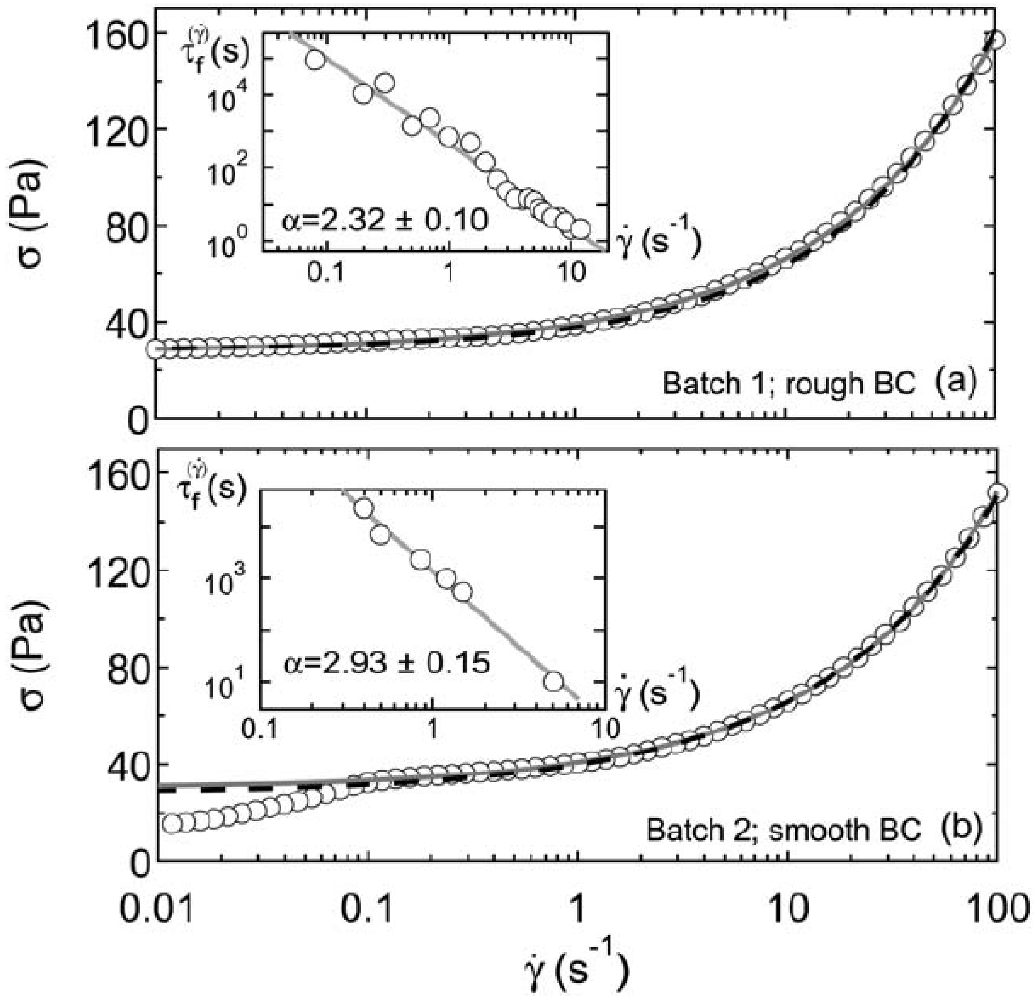
$$\frac{\sigma(\dot{\gamma})}{\sigma_y} = 6\left(\frac{\dot{\gamma}\eta_s}{G_0}\right)^{0.12} + 182\left(\frac{\dot{\gamma}\eta_s}{G_0}\right)^{0.5}$$





$$\Pi \approx kT\xi^{-3}$$

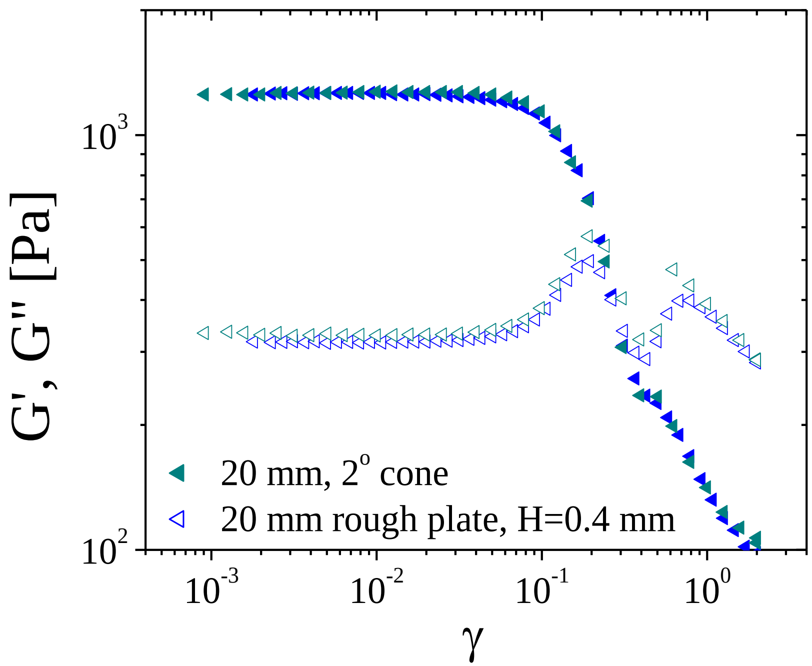
Erwin et al. SM 2010

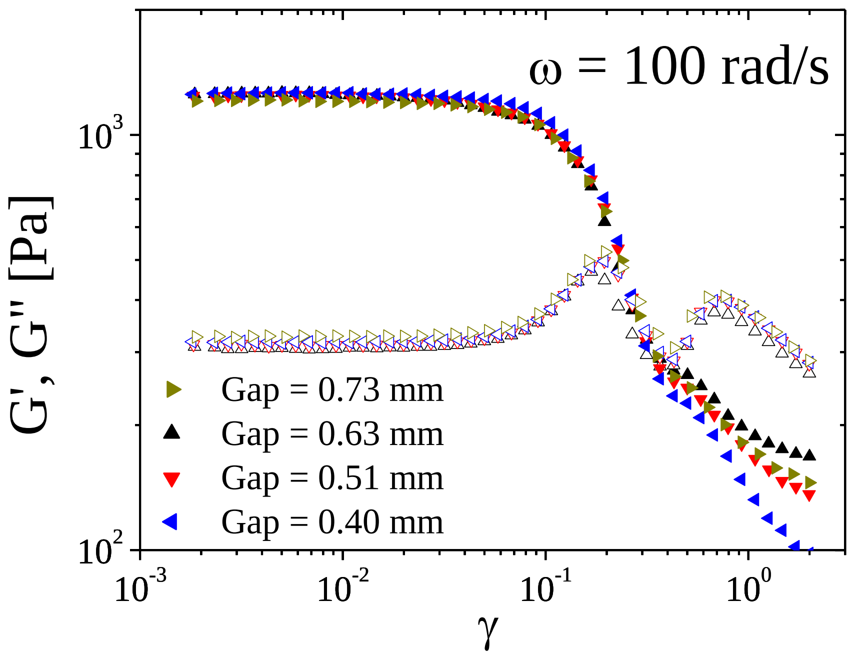


Divoux et al. SM 2011
Ovarlez, Manneville

carbopol slips

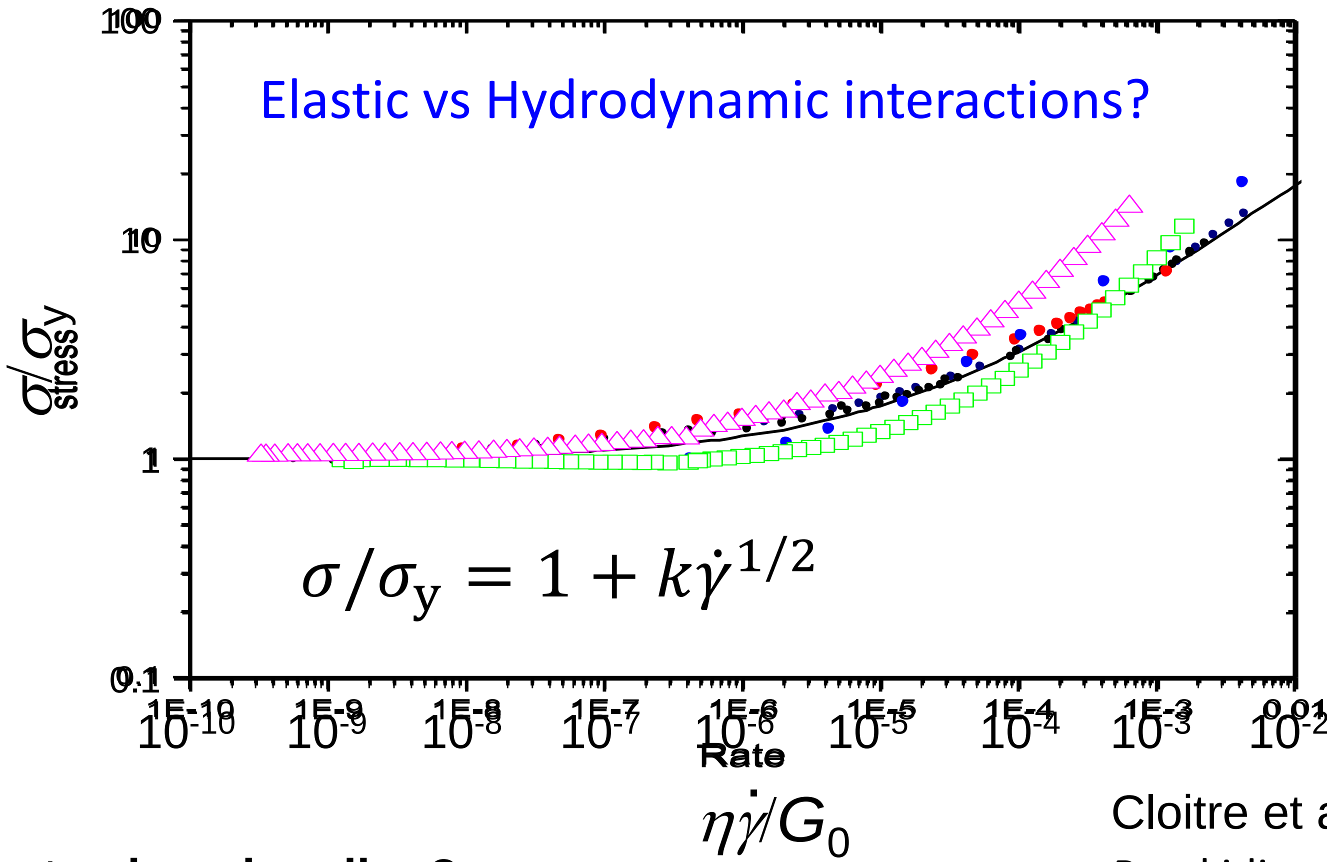
PBD stars in squalene do not slip @ stainless fixtures





M. Helgeson

Similar scaled flow curves: microgels, micelles, stars, but not hard spheres?



Cloitre et al., PRL 2003

Petekidis et al. JPCM 2004

Connection to shear banding?

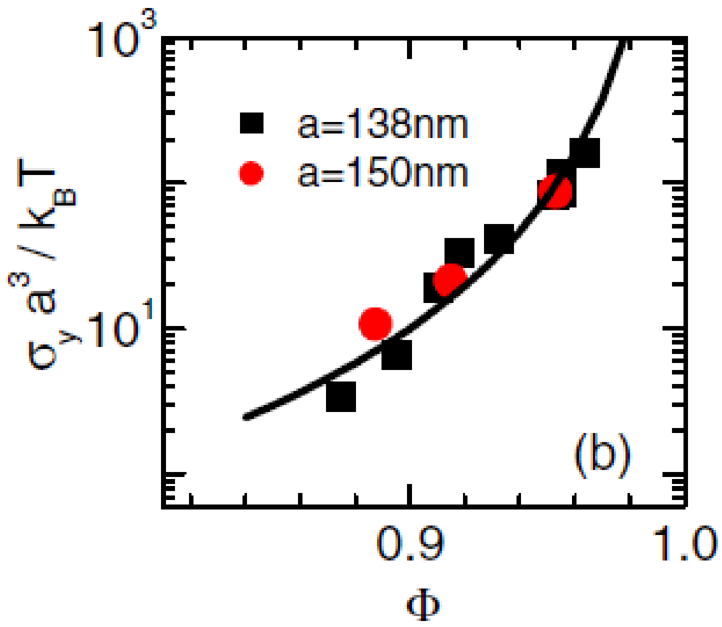
Hard spheres band – when they do not slip ; repulsive, attractive (Poon, Cates, Petekidis, Dhont)

Stars may band -- role of transient forces ? (Briels, Dhont, JCP 2010; PRF 2017 ; Rogers et al. PRL 2008)

Repulsive microgels do not band, attractive do (Cloitre)

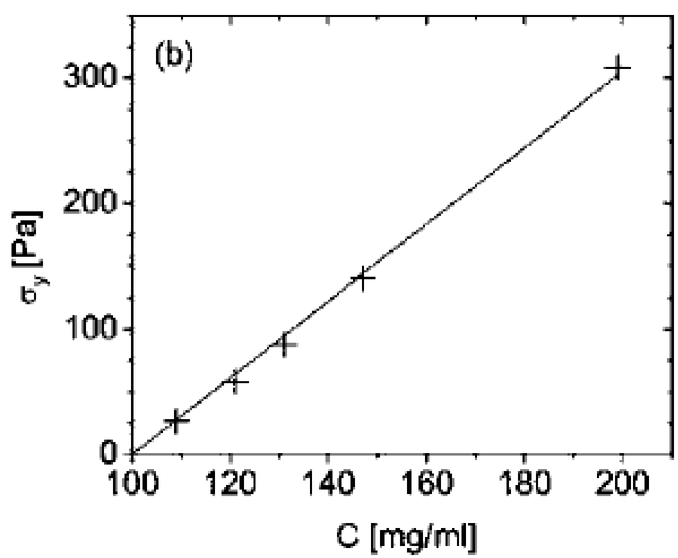
Yield stress and gradient banding scenario

Hard spheres
Strong dependence
Flow-concentration coupling



Besseling et al. PRL 2010

Stars
Weak dependence
Strong shear thinning



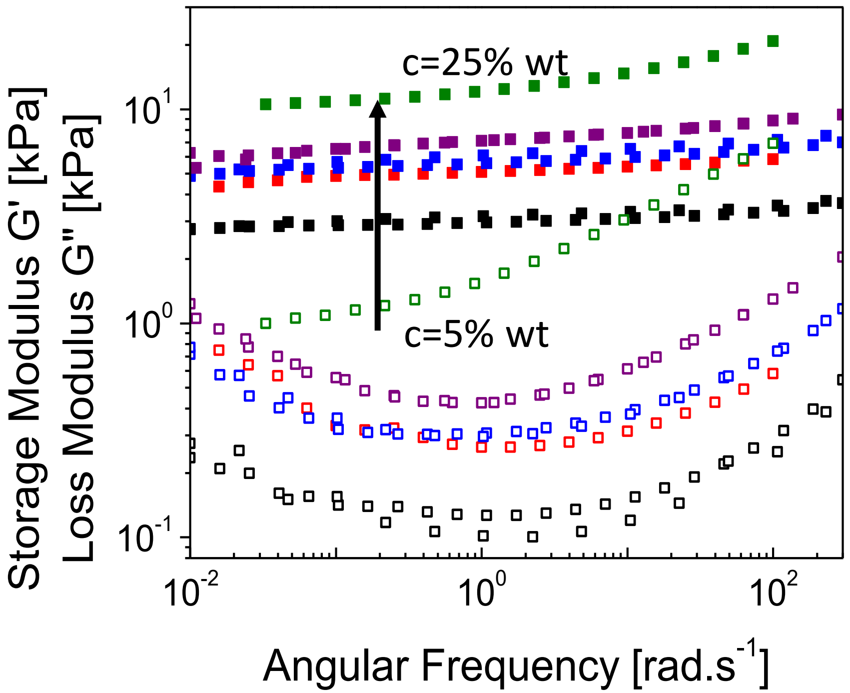
Erwin et al. SM 2010

Repulsive microgels do not band
Attractive mirogels band (Cloitre)
Link engagements of arms to attractions

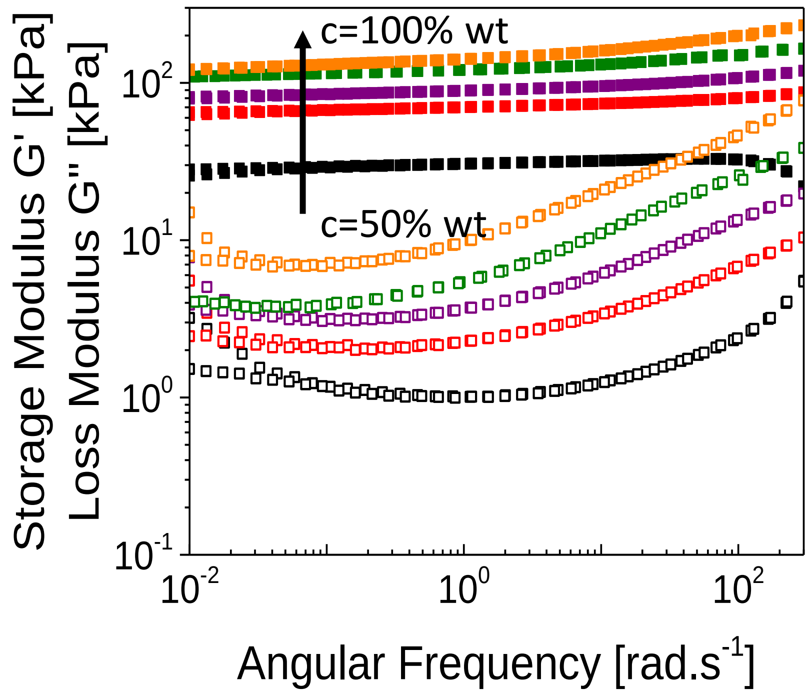
Banding: Olmsted, Fielding, Dhont

Linear viscoelastic spectra

Microgels (c*=1% wt)



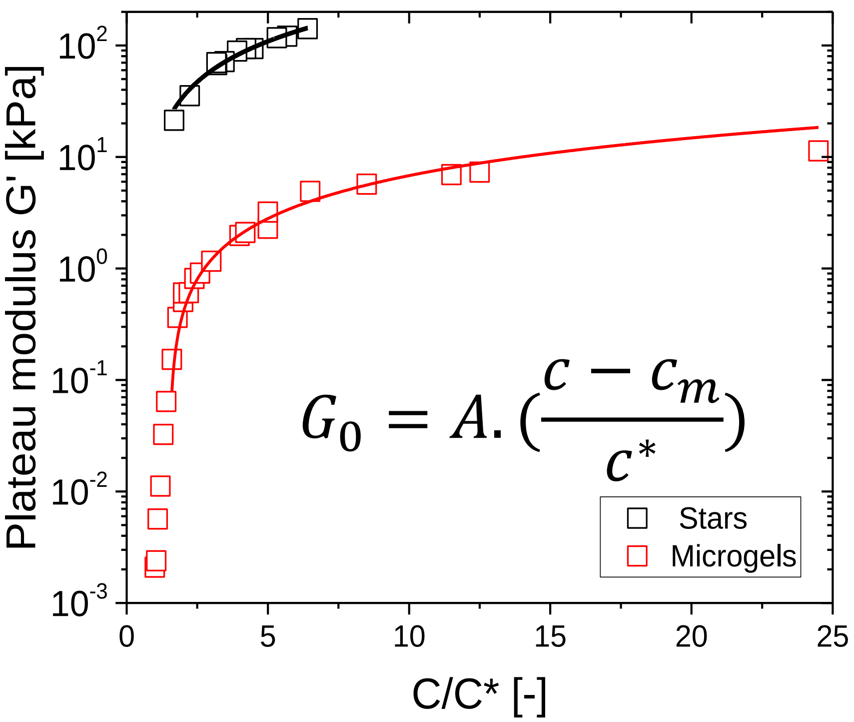
Stars (c*=16.5% wt)



Moduli compare to HS glasses
(which exhibit stronger ϕ–dependence)
Higher for stars

can reach melt!

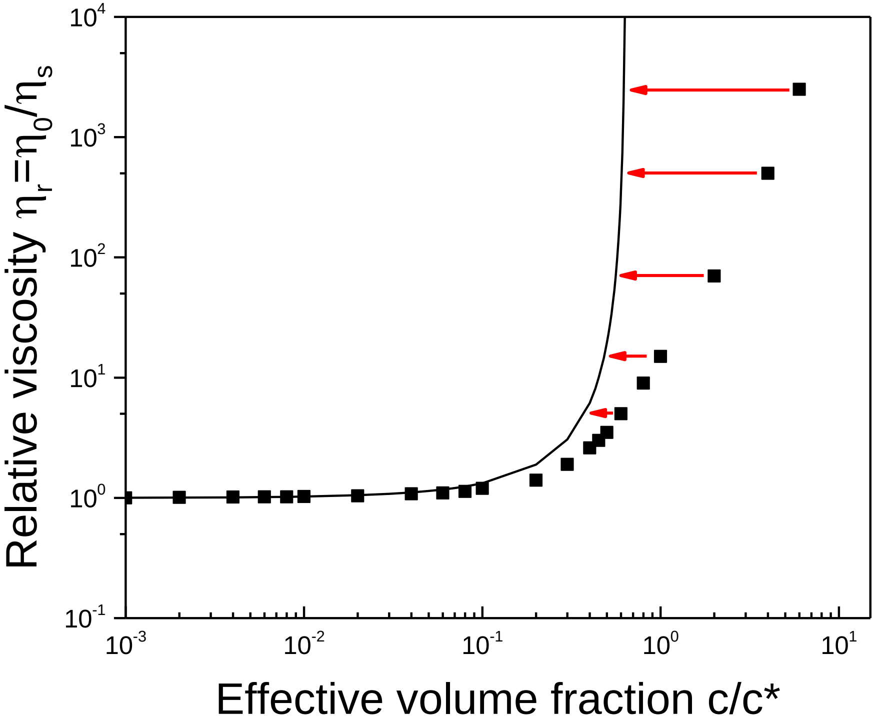
Plateau modulus

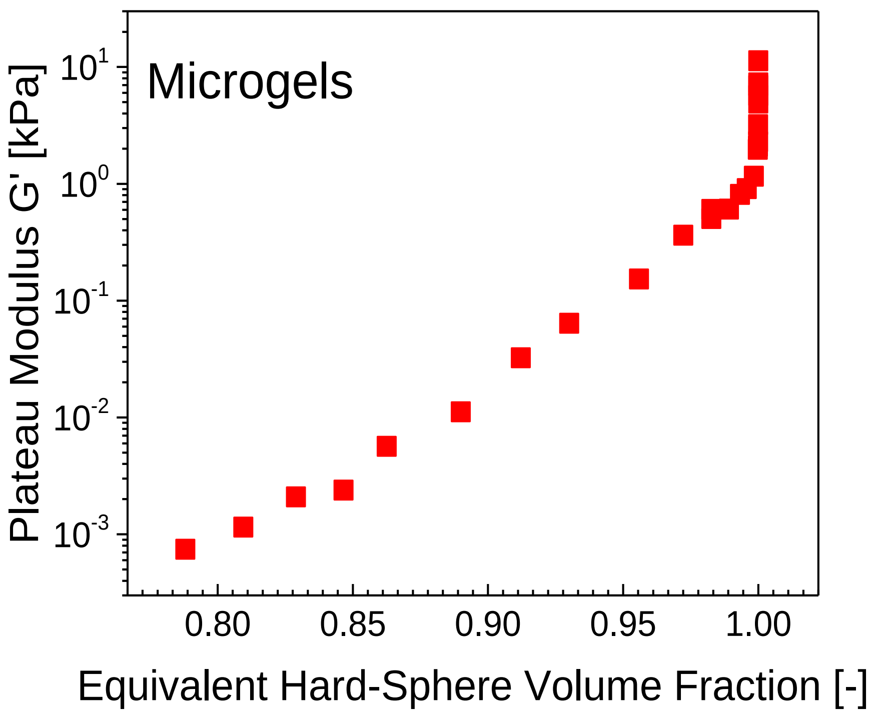


$$G_0 = A.\left(\frac{c - c_m}{c^*}\right)$$

	A [kPa]	C* [%wt]	C_m [%wt]
Stars	24.7	15.6	9.2
Microgels	0.8	1	1.5

Plateau modulus





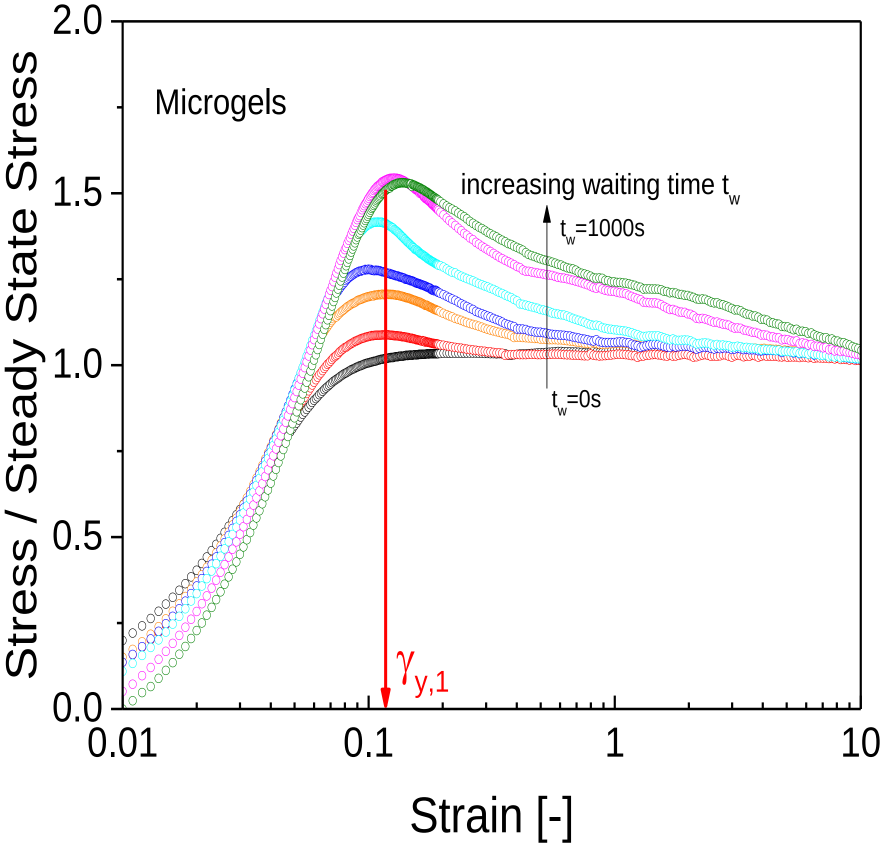
$$\varphi = \tanh(\frac{c}{c^*})$$

(Eq. HS volume fraction=1 corresponds to the close packing)

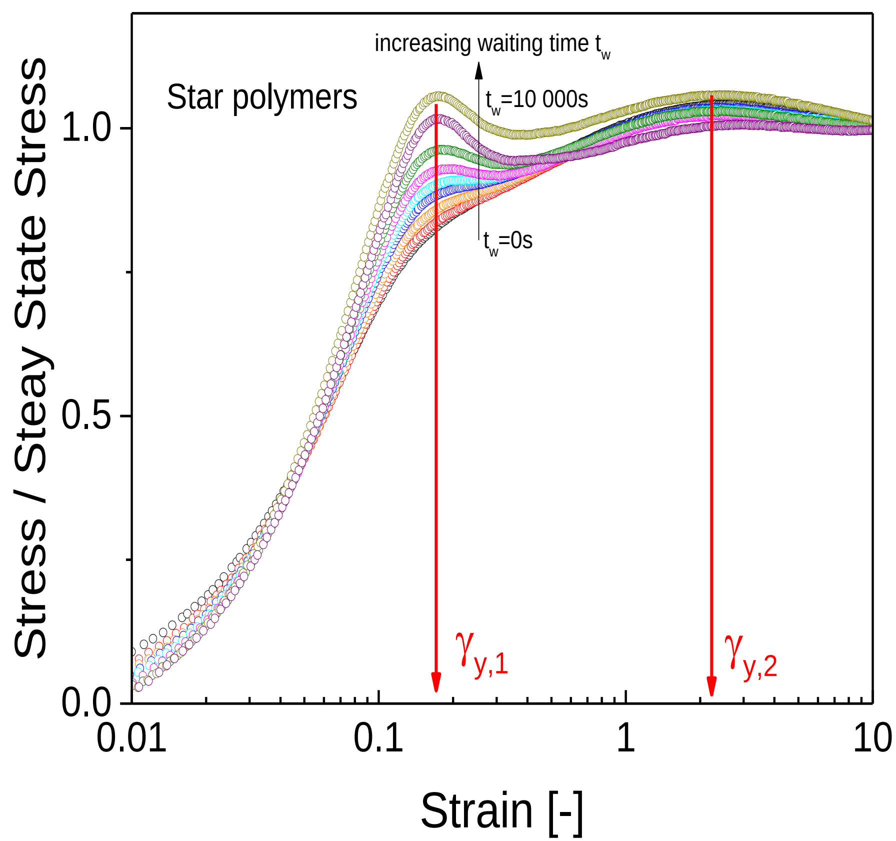
Yielding: start-up in simple shear

Influence of waiting time (at $0.2s^{-1}$)

Microgels 5% wt (5c*)



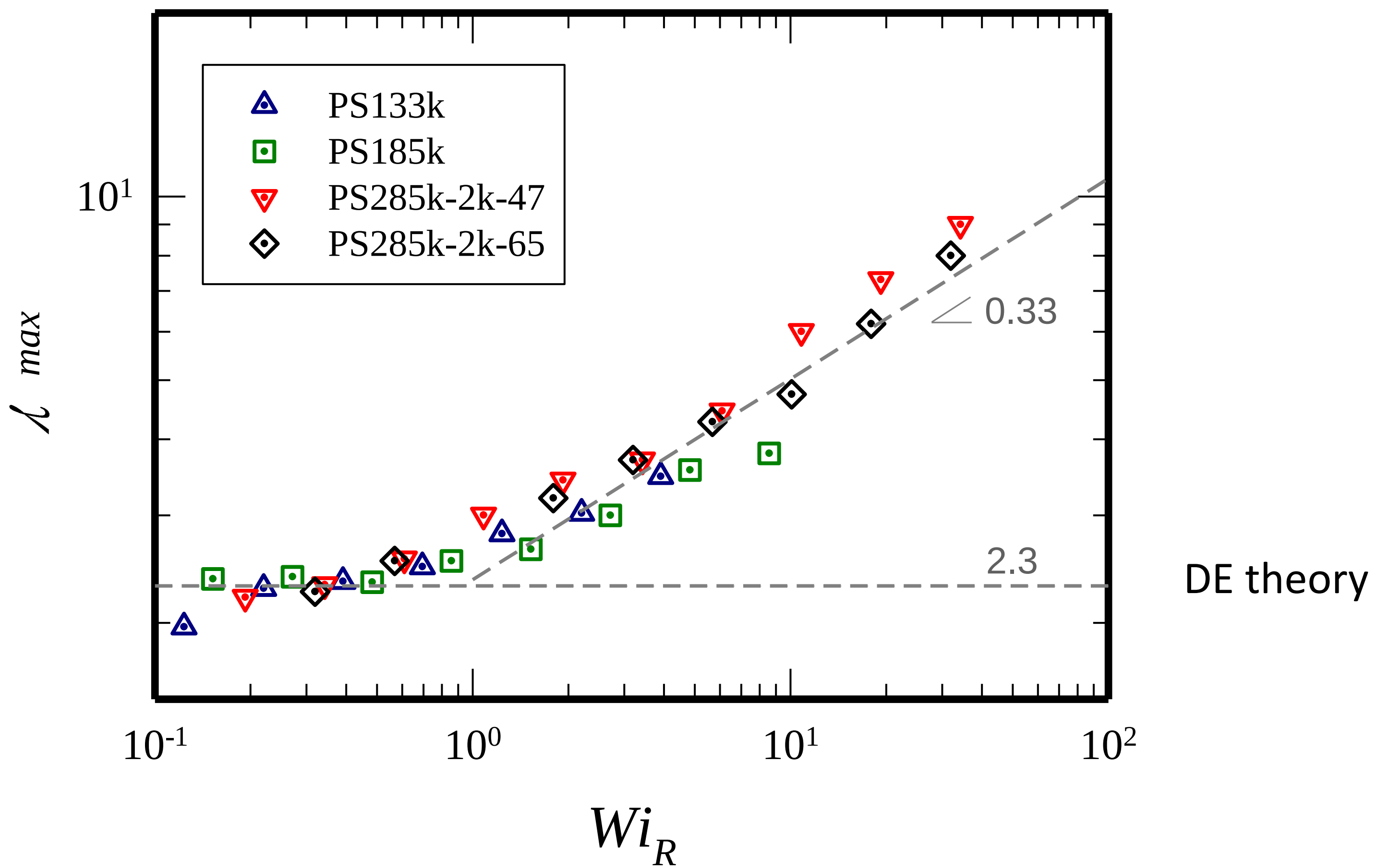
Stars 75% wt (4.5c*)



Stars exhibit two peaks: gradual yielding

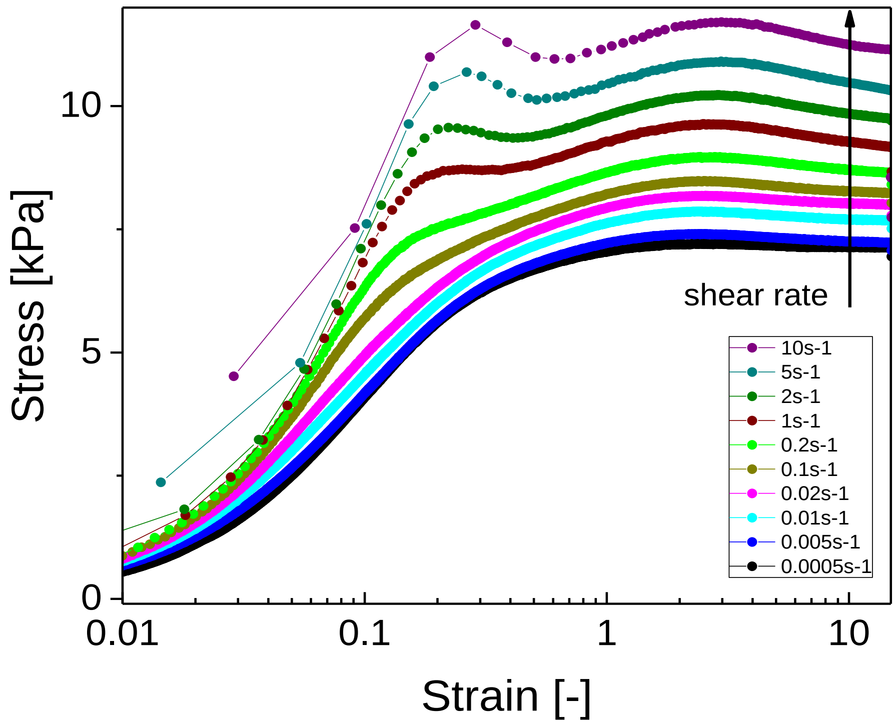
Helgeson et al. JOR 2007
Pham et al. EPL 2006, JOR 2008
Koumakis and Peterkidis, SM 2011

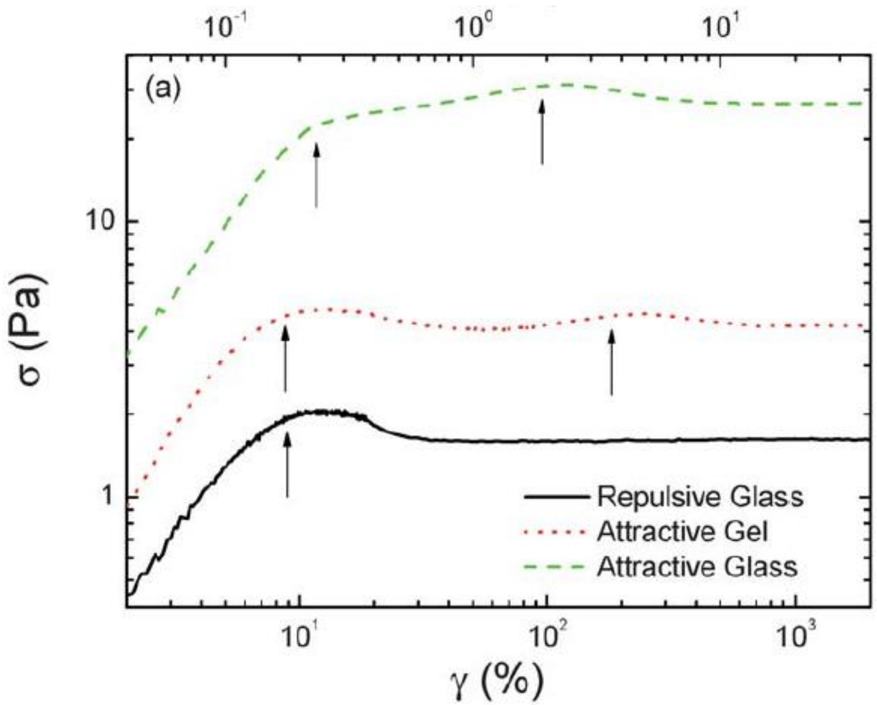
Peak strain in entangled polymers



Costanzo et al., Macromolecules 2016

Yielding: start-up in simple shear
Influence of shear rate for stars c=75% wt



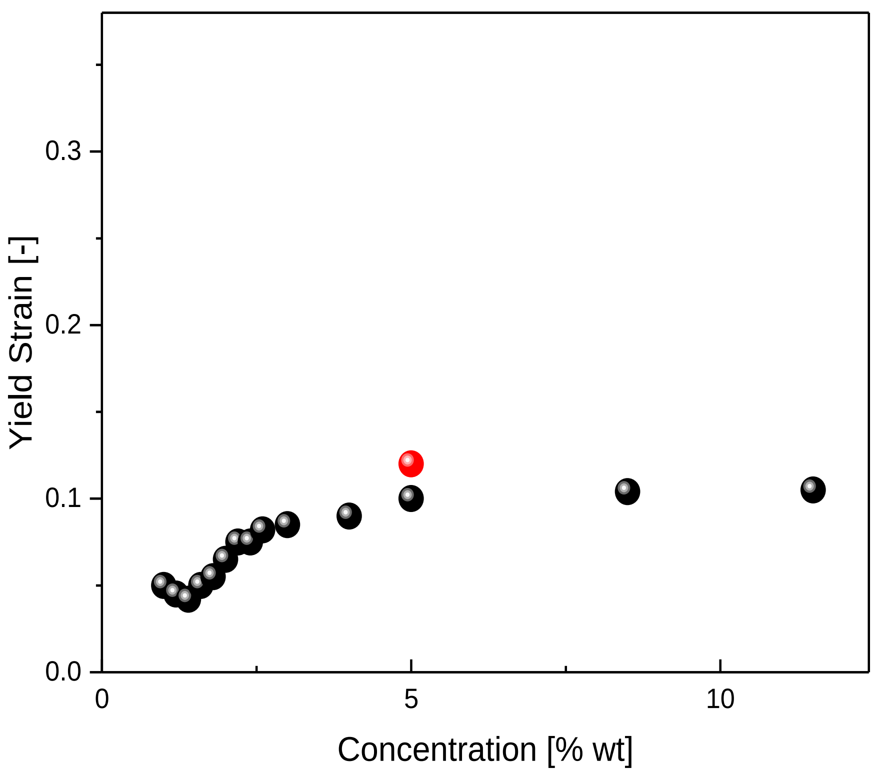


Yield stress peaks reflect dual nature of particles (colloidal, polymeric)?

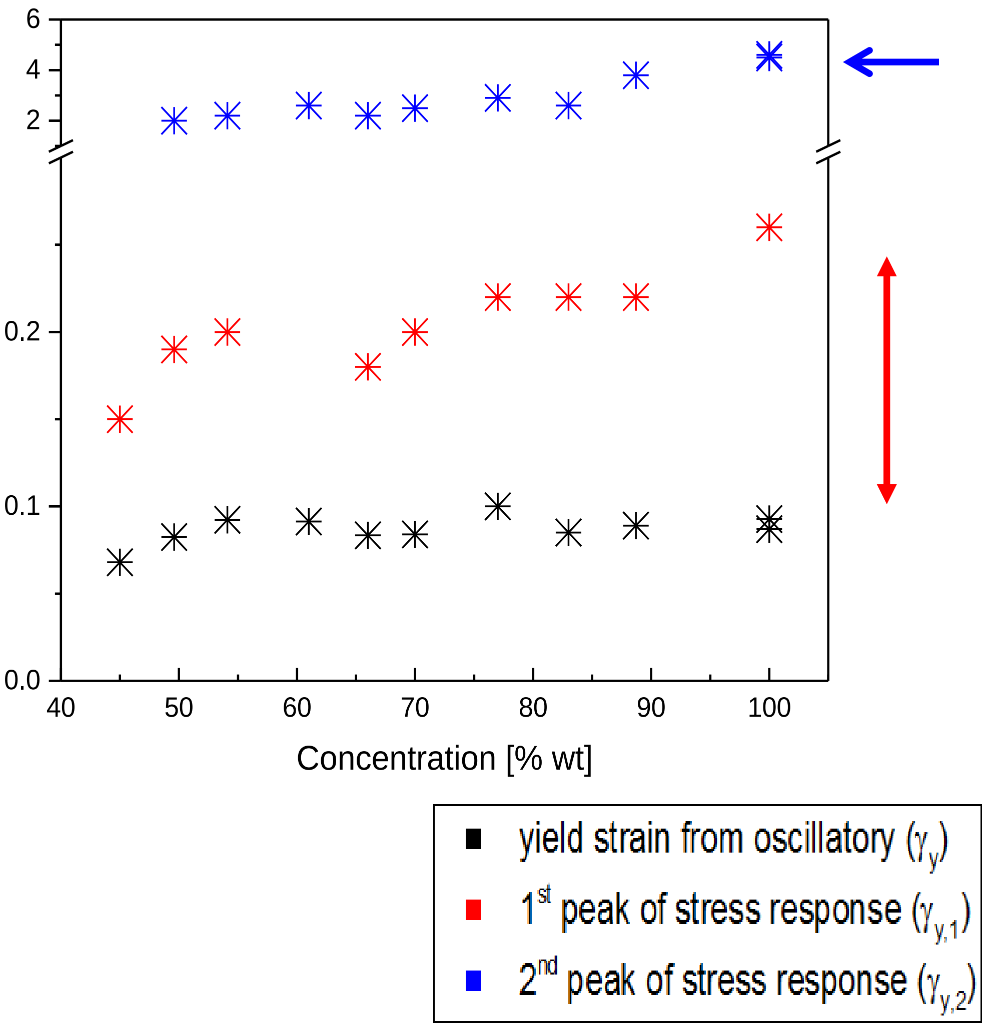
Koumakis et al. SM 2011
Helgeson et al. SM 2014
Kim et al. JOR 2014

Yield strain for microgels and stars

Microgels

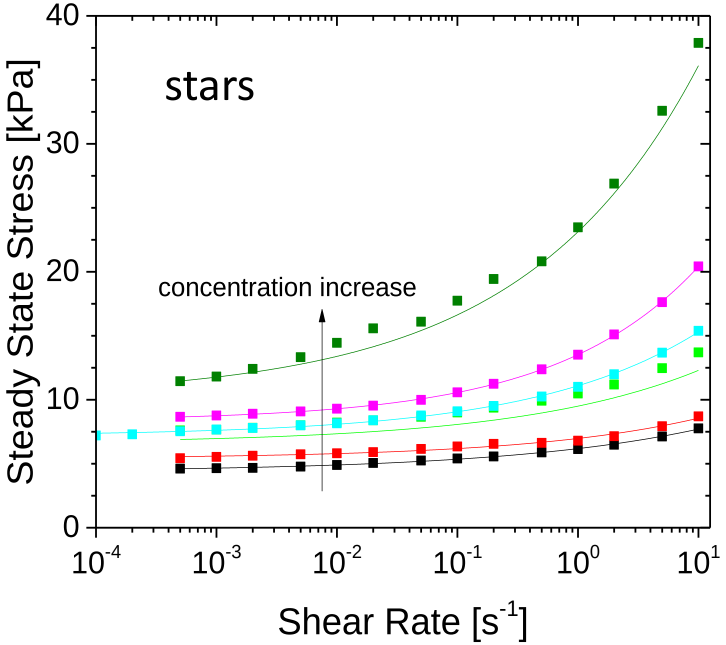


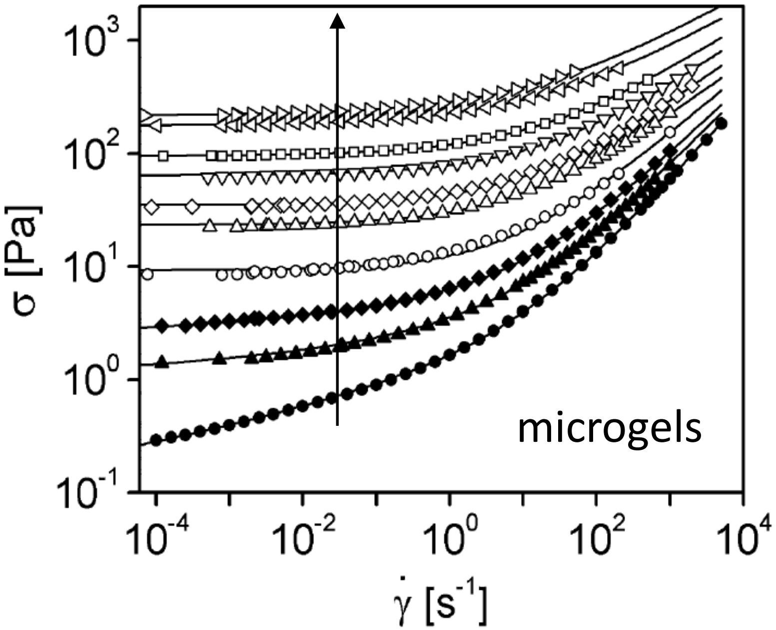
Stars

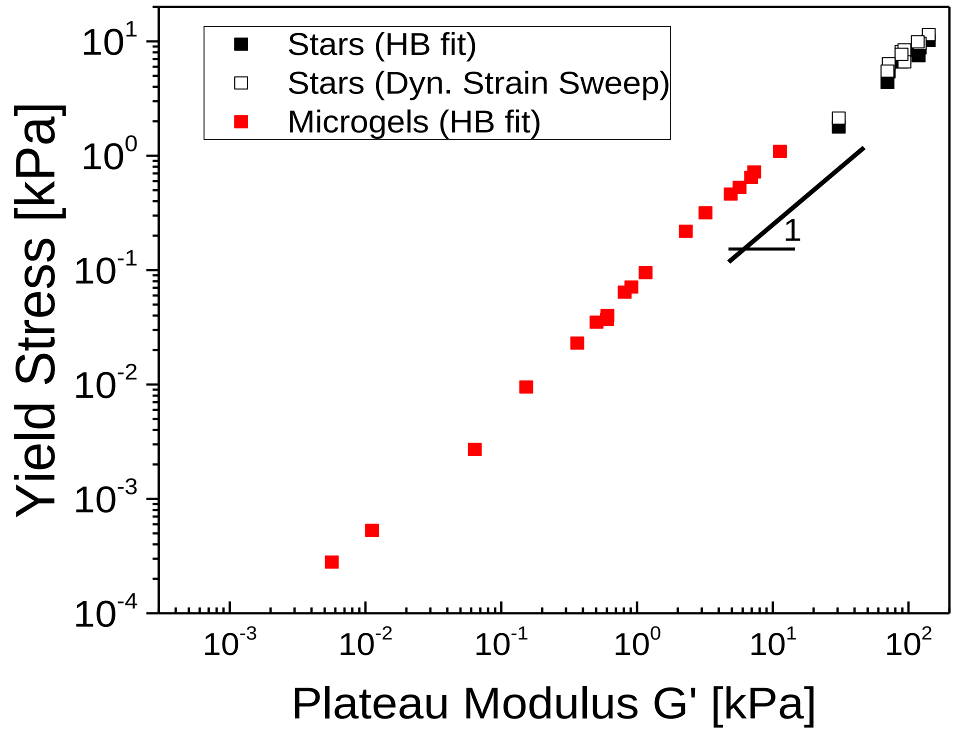


Dhont et al. PRF 2017

Star and microgel flow curves: yield stress

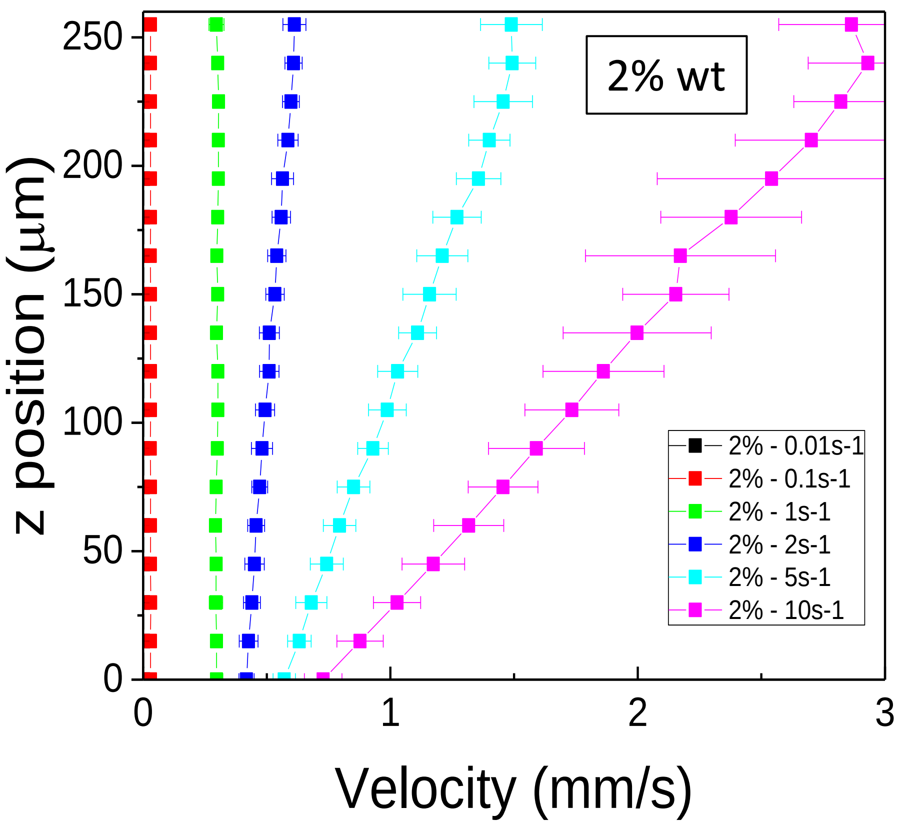


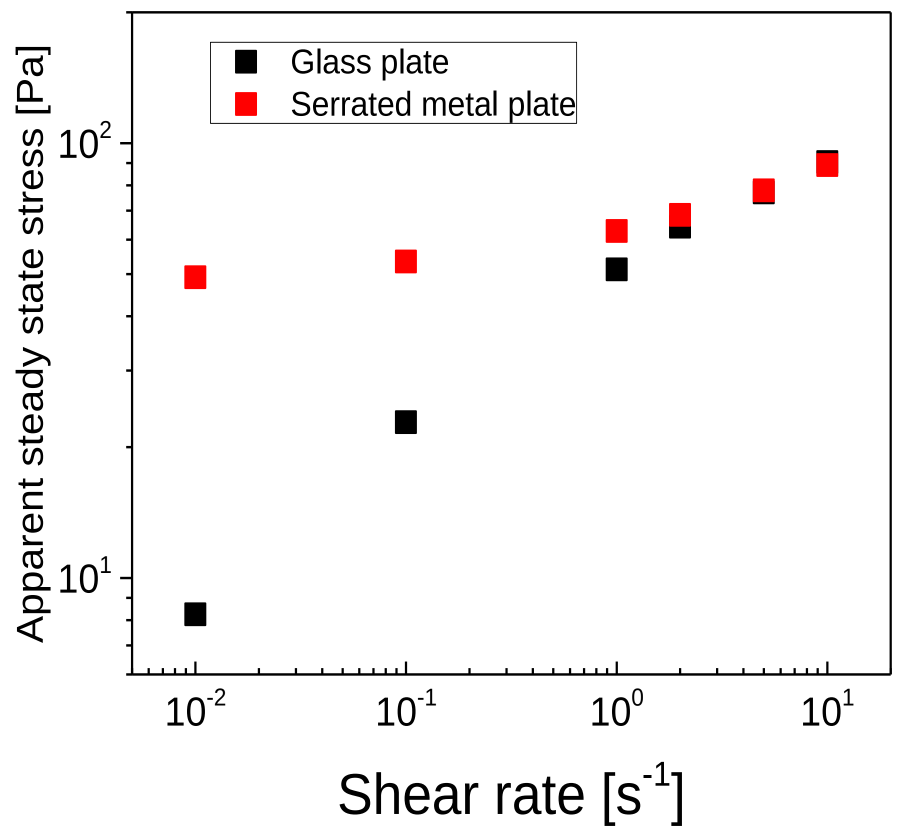




Pellet, Cloitre, *Soft Matter* 2016

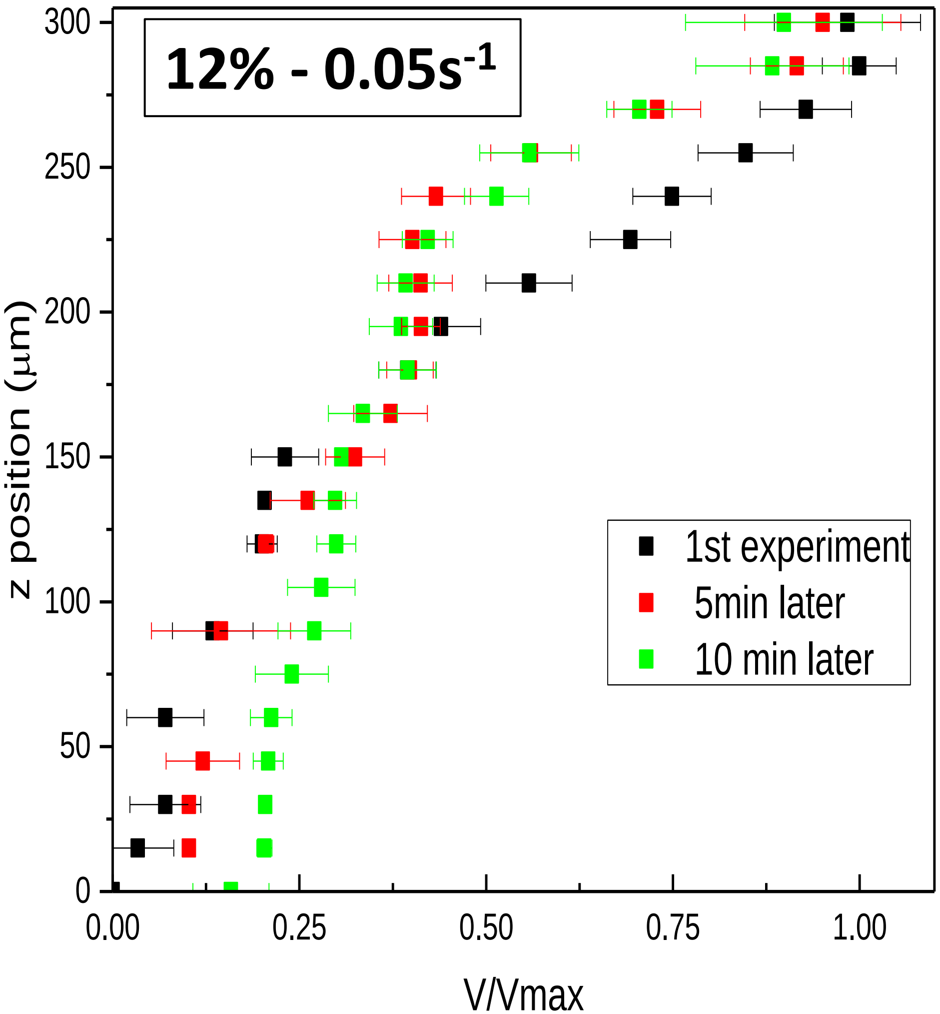
Velocity profiles in microgel suspensions: wall slip

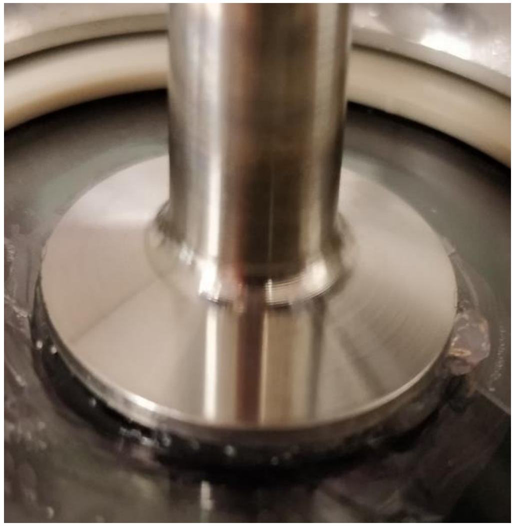




To avoid need surface treatment: Seth et al. SM 2012 ; Cloitre and Bonnecaze, Rheol. Acta 2017

Flow instabilities at higher concentrations: microgels





Conclusions I: soft colloids are tunable

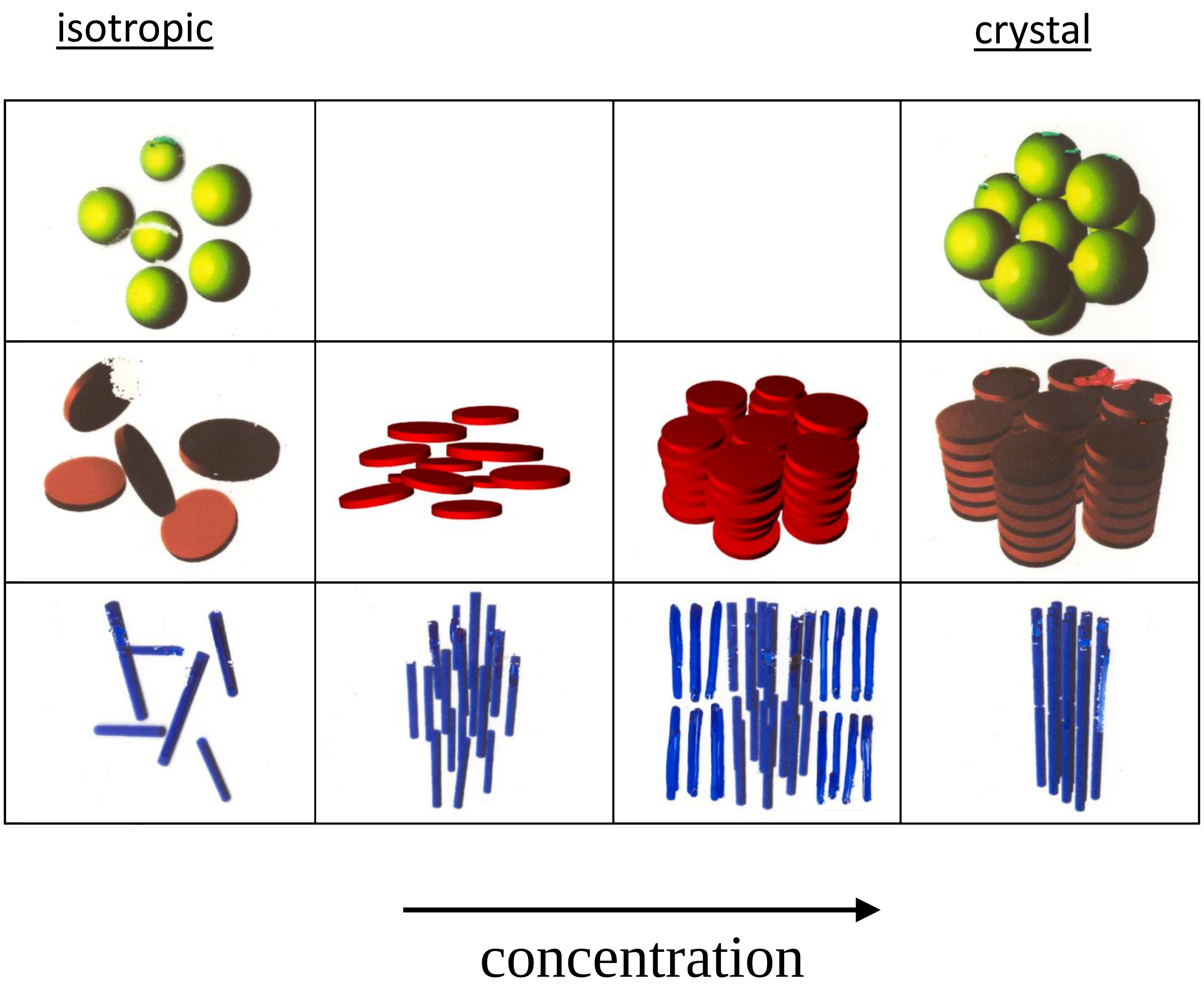
Soft (stars, microgels) vs Hard (HS) colloids in glassy state:

Jamming ambiguous in soft ; elastic interactions important
Yielding is gradual, depends on internal microstrure
Shear banding: present in HS and stars, not in microgels
Wall slip: mainly microgels, HS (can control)
Flow curves: universal scaling for soft (HB exponent of ½)
More than one time scale (η/G) (in stars)
Osmotic interactions control flow of mixtures:
particle compression and depletion

Expect weaker shear thickening
Explore analogies to molecular glasses

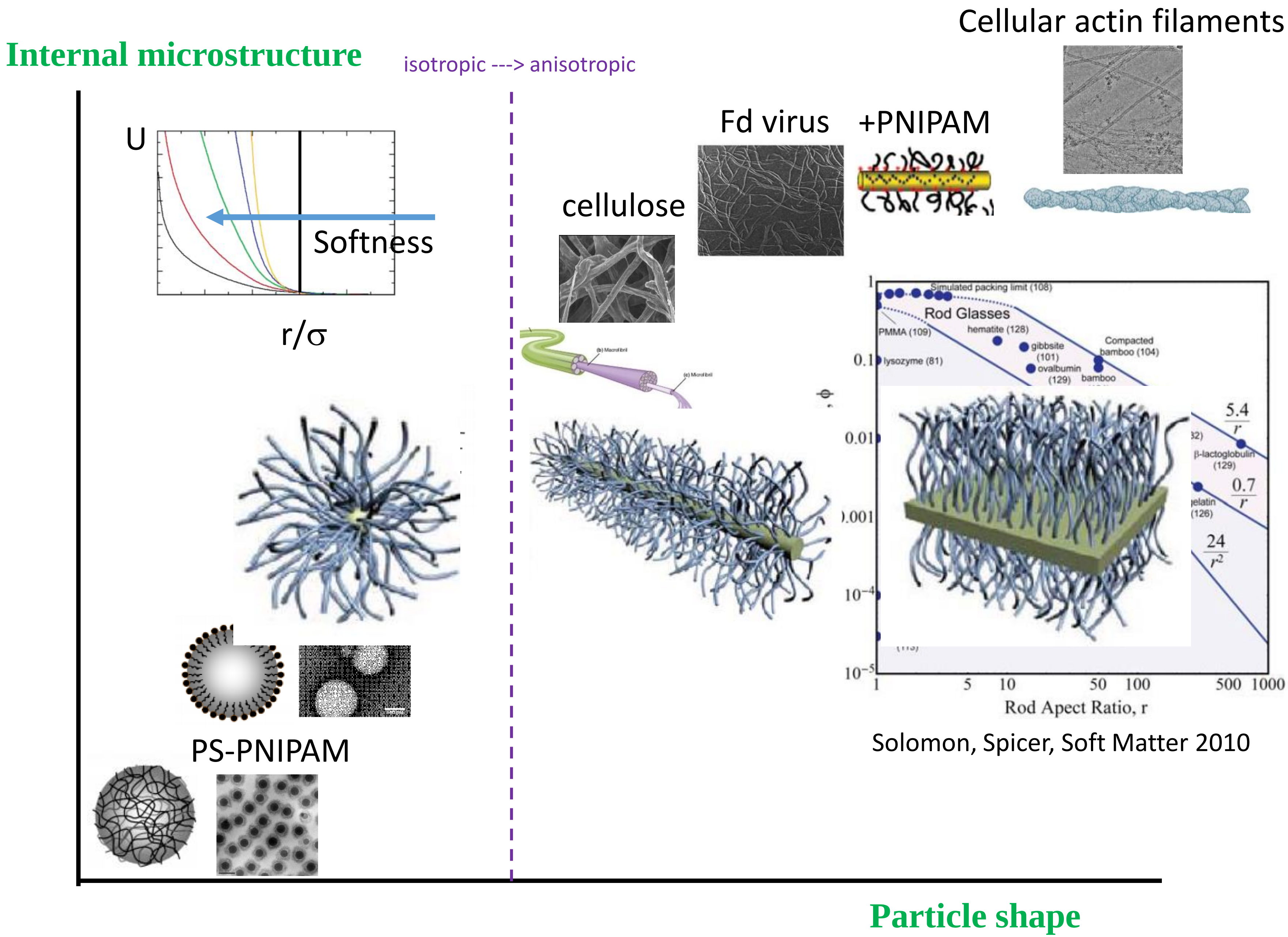
Soft particles at contact: engagements, facets, bonding
Hard particles at contact: friction
Hydrodynamics

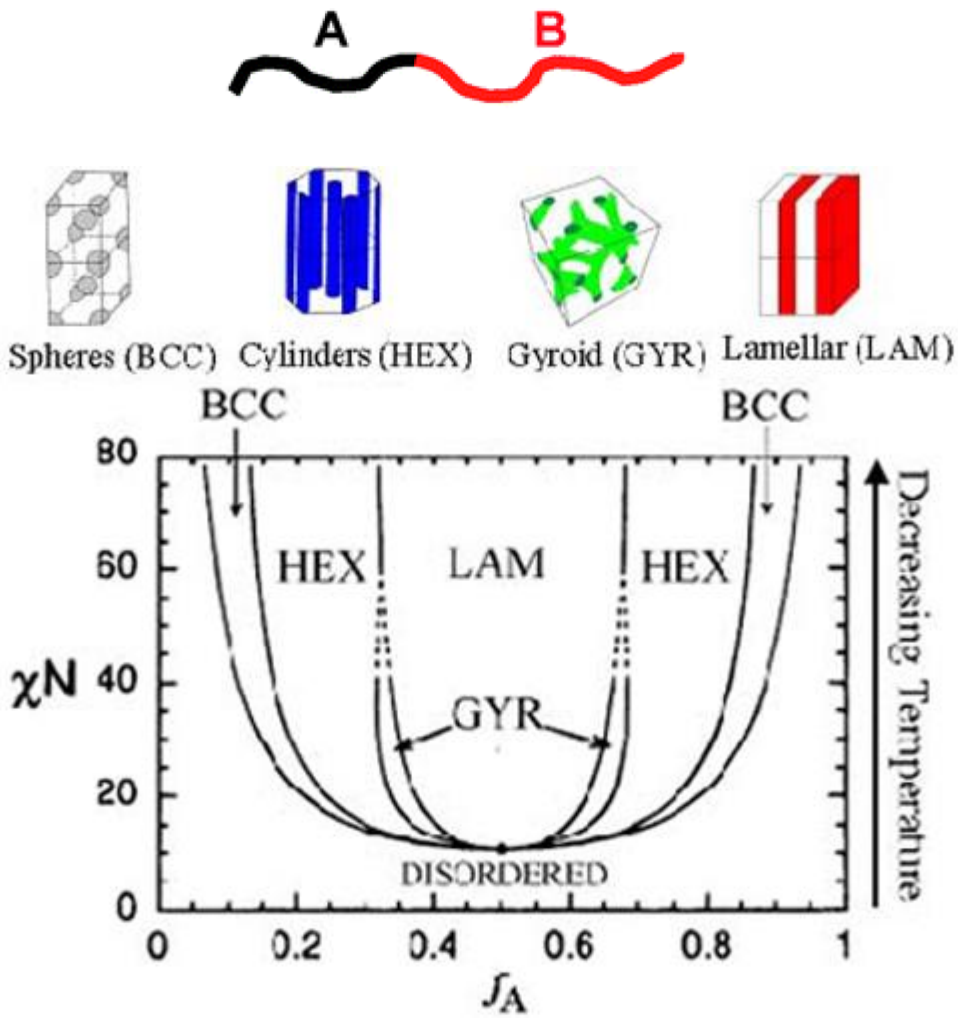
Shape matters



Alder, Pusey, Lekkerkerker, Frenkel, Dhont, Philipse, Fraden, Dogic

Soft colloidal systems of varying shape

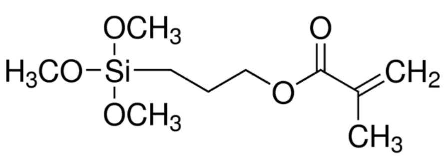




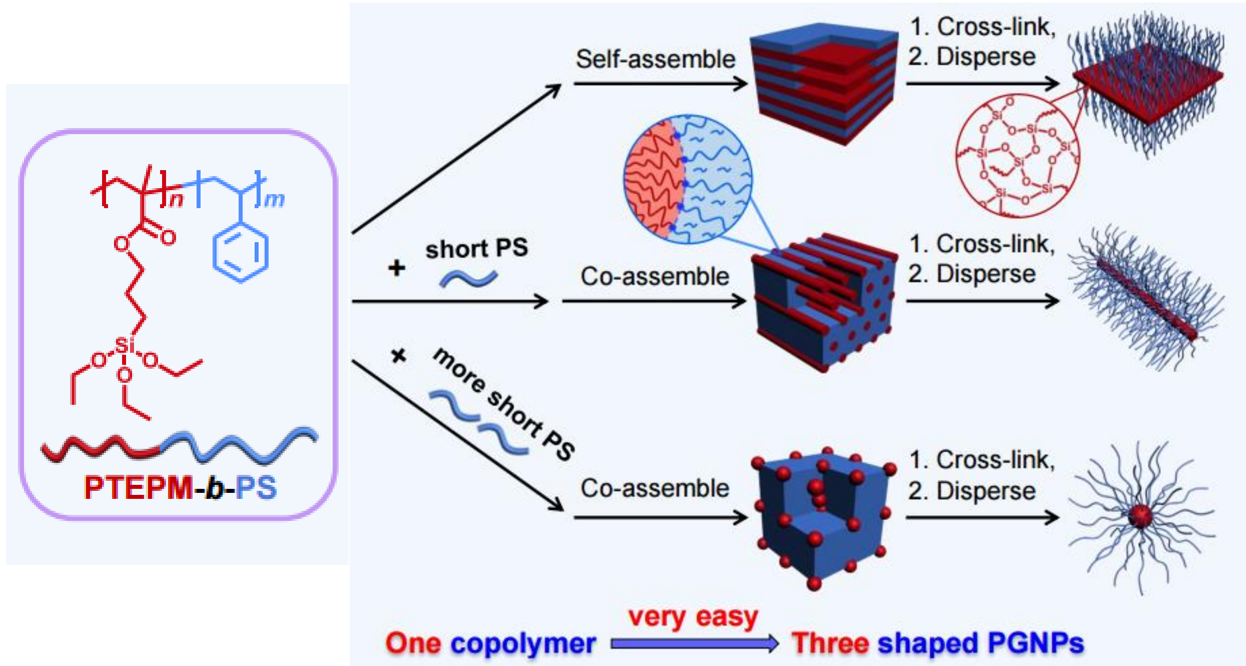
Leibler, Fredrickson, Matsen

Polymer Grafted Nanoparticles with controlled microstructure

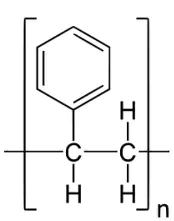
Core: PTEMP



poly(3-(Triethoxysilyl)propyl methacrylate)



Shell: PS



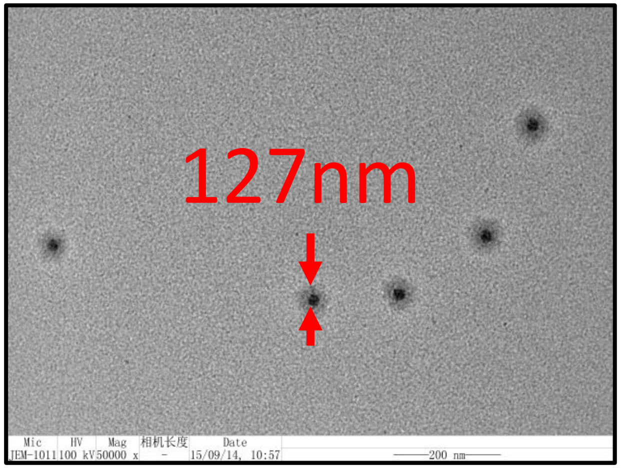
PGNOs	core			M_n of PS hairs (kg/mol)	graft density (chains/nm^2)
	shape	size[a] (nm)	wt% core		
lam-PS111k	lamella	16.0	21.1	111	0.118
cyl-PS111k	cylinder	27.0	21.1	111	0.101
sph-PS111k	sphere	30.0	21.1	111	0.075

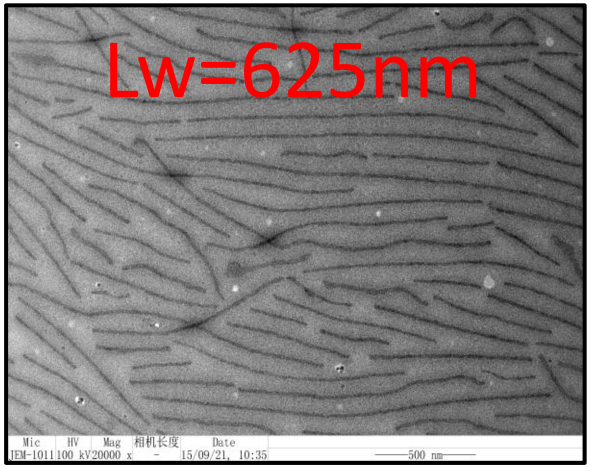
Same Mw per arm

Similar grafting density

Ruan et al. ACS Macro Lett., 2015

TEM and Light Scattering characterization





R_H=49 nm (Light Scattering)
PDI=1.04 (TEM)
Mw=3x10^7 g/mol
f=212
C*(R_H)=0.10 g/mL

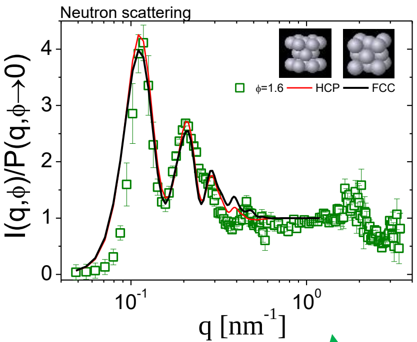
L_H=630 nm (Light Scattering)
L_p=775 nm (Light Scattering)
Aspect ratio (L/D)= 8
PDI_{length}=1.3 (TEM)
Mw=6x10^9 g/mol
f=3.6E4
C*(L_H)=0.026 g/mL

Polymer-grafted nanoparticles in diethyl phthalate (good solvent) at 13%wt

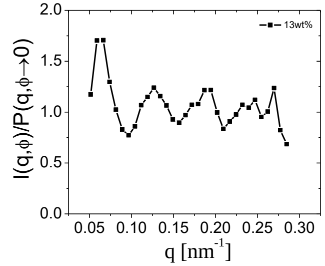
$$\varphi_{eff} = \frac{c}{c^*} = 1.3$$

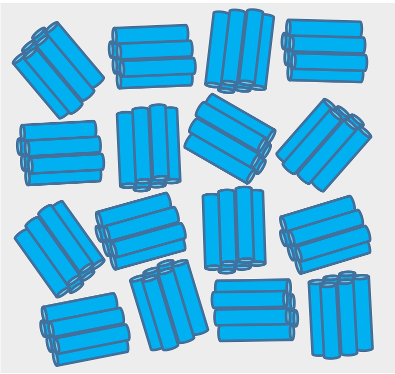
$$\varphi_{eff} = \frac{c}{c^*} = 5.0$$

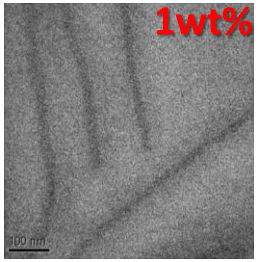
SAXS & SANS at the same mass fraction (13wt%)

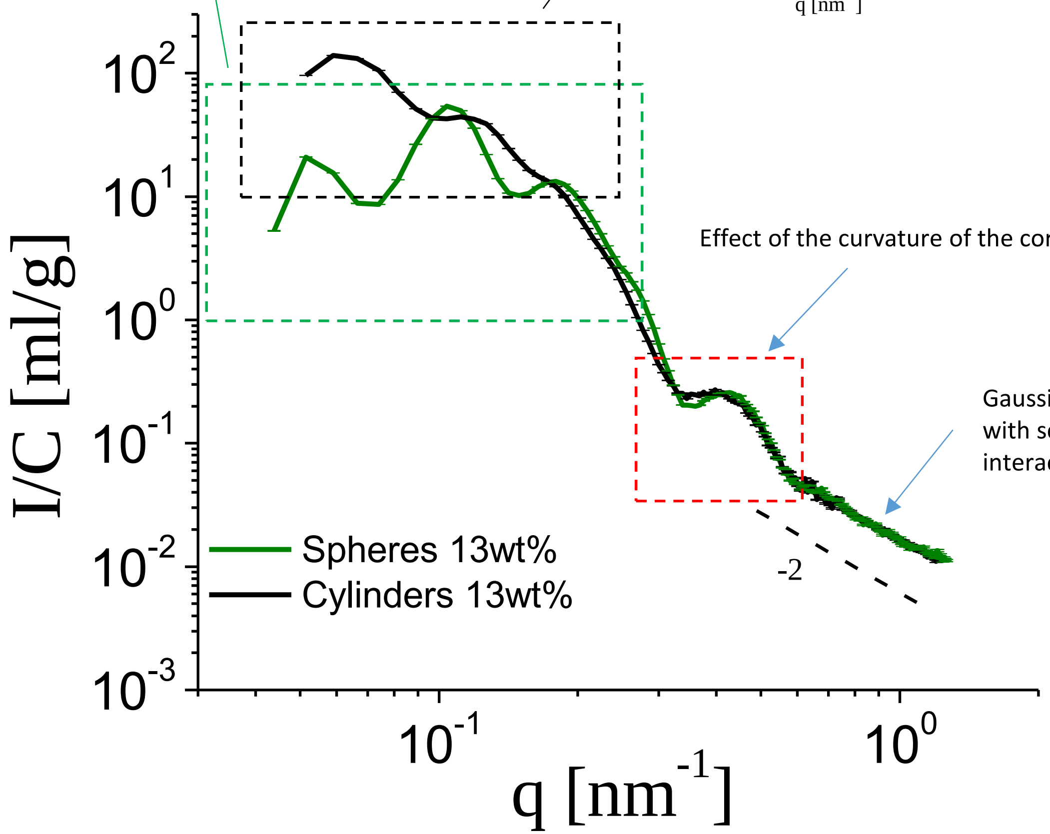


Orientational order: cubatic phase









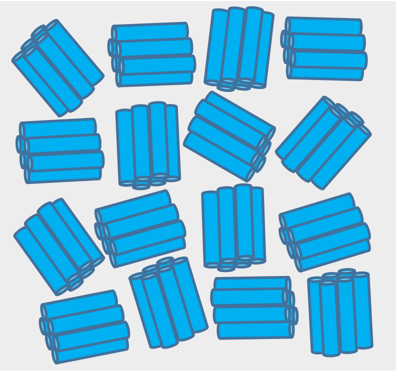
Effect of the curvature of the core

Gaussian chains in good solvent with screened exlcuded volume interactions

$$q^{-\frac{1}{\nu}=-2}$$

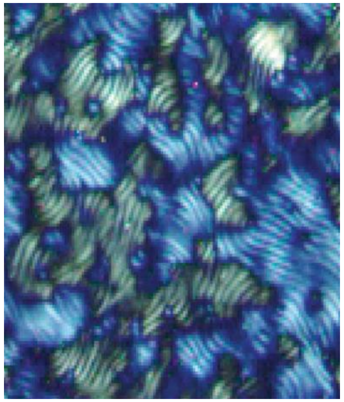
Pusey et al., PRL 1989
Blaak et al., JCP 1999
Junaid et al., J. Coll. Int. Sci. 2010
Likos, Phys. Rep. 2001

short rods, AR~6



Cubatic phase - glass

long rods, AR~100

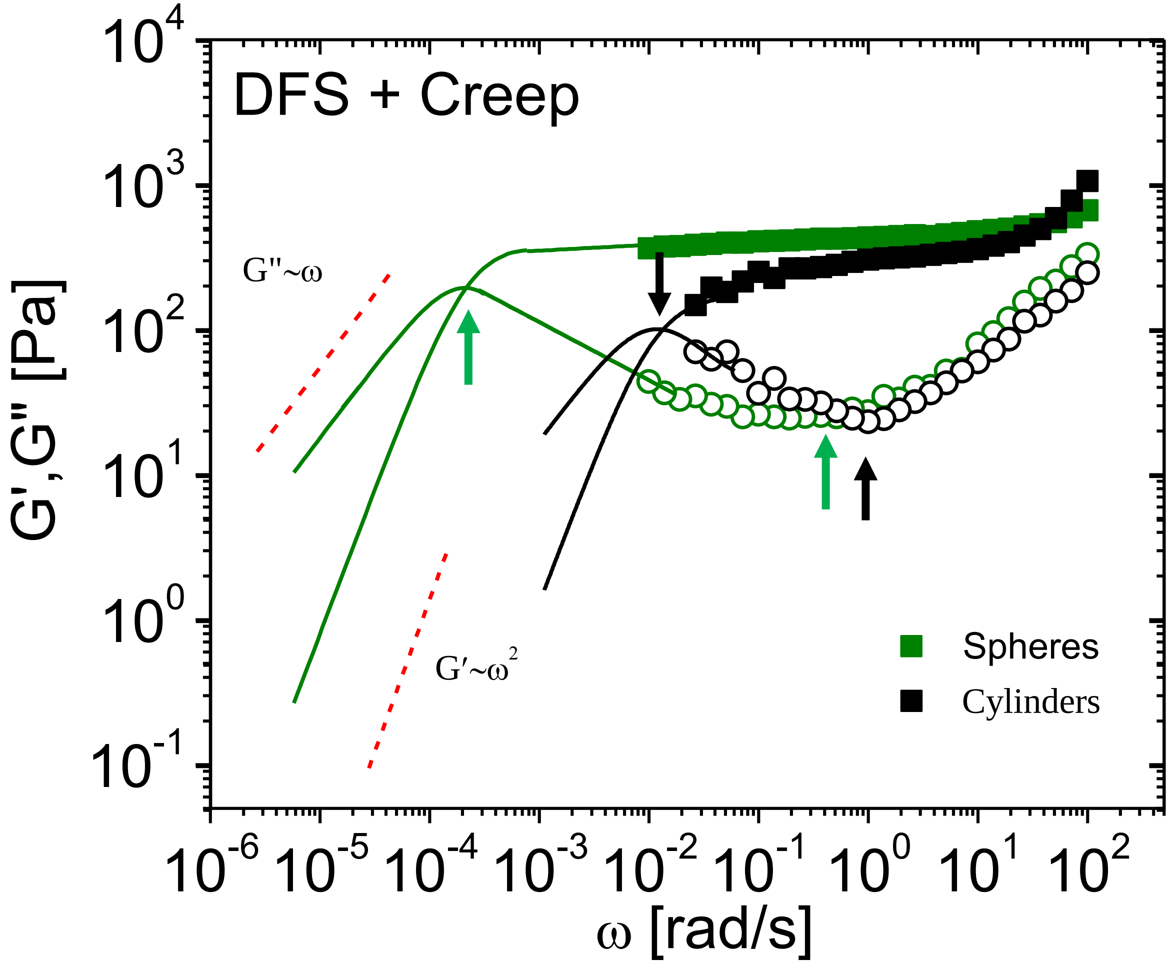


Nematic glass – orientational texture

Dhont, Kang PRL 2013 ; SM 2013

LVE spectra at the same mass fraction (13wt%)

T=25°C



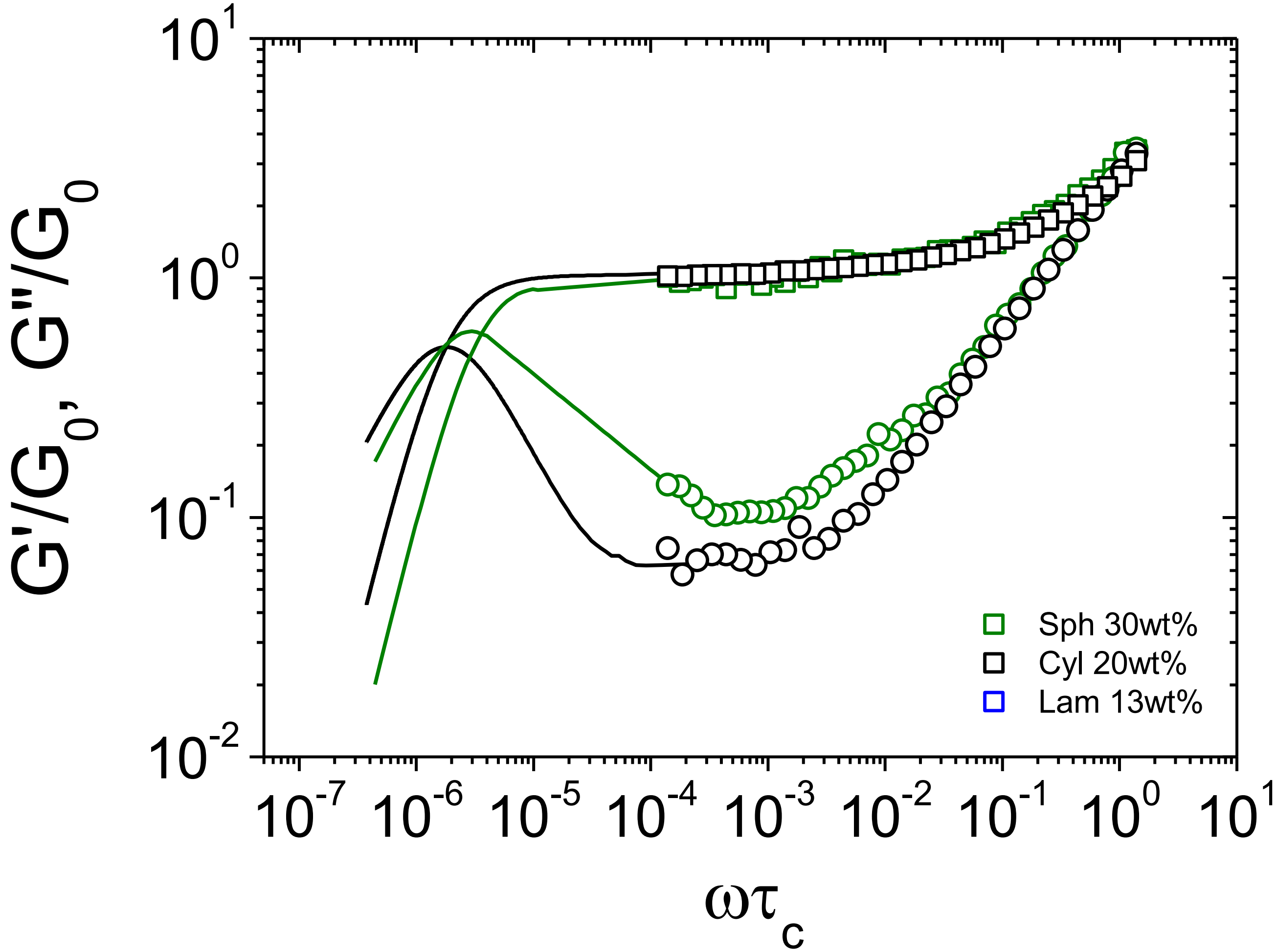
$\varphi_{eff} = \frac{c}{c^*} = 1.3$

$\varphi_{eff} = \frac{c}{c^*} = 5$

Soft glasses with detectable alpha relaxation

8mm Cone +Peltier on Ares Solution (LVE-NLVE) and Anton Paar MCR 702 (Creep)
Rejuvenation (DSST) +aging (DtST 30 min) before any measurements

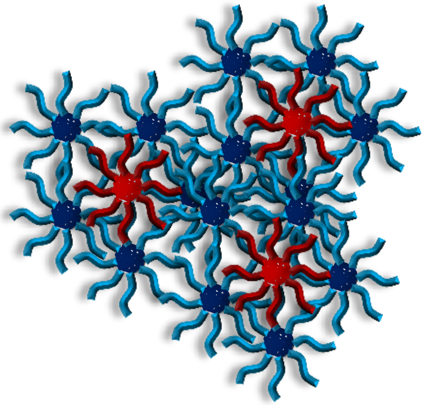
Shape-independent high-frequency dynamics



Trappe, Weitz, PRL 2000

Dynamics of spheres and lamellas: caging effect

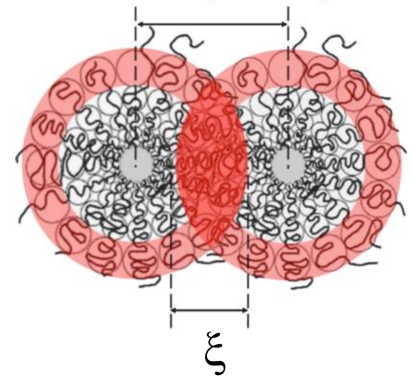
13wt%



$$\tau_{\beta}^{LVE} = \frac{1}{\omega(G''_{min})} = 2.8s$$

$$\tau_{\alpha}^{LVE} = \frac{1}{\omega(G_c)} = 5000s$$

$r = R_h\left(3 - \phi_{eff}^{1/3}\right)$ Brushes overlap

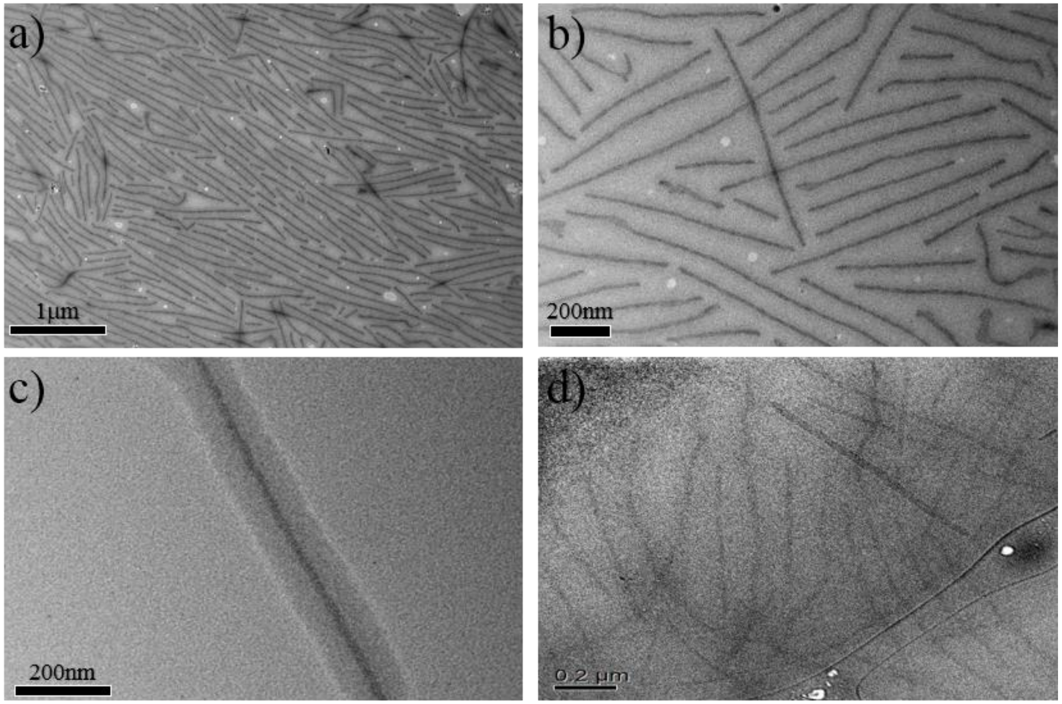


$$r < 2R_H$$

$$G_p = \frac{k_B T}{\xi^3}$$

$$\xi \approx 0.2r$$

Cylinders

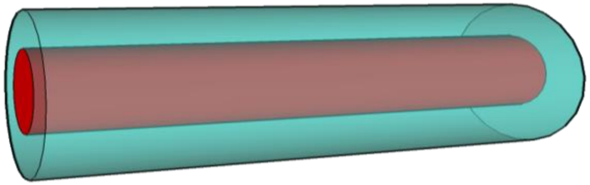


thickness: 104 nm

204 nm at 1wt%
106 nm at 13 wt%

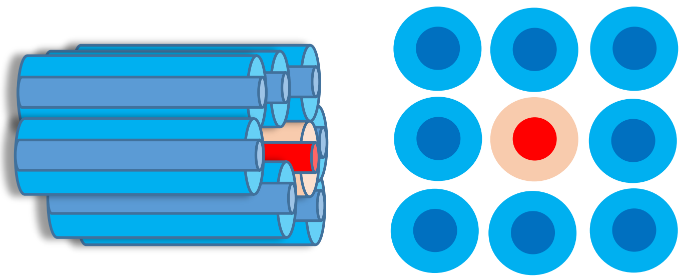
overlap

98 nm at 20wt%
83 nm in the melt state



Dynamics of cylinders: fluctuations and tube renewal

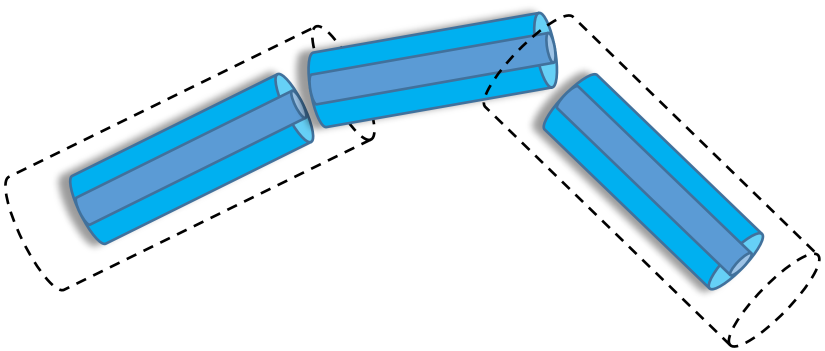
13wt%



Cylinder fluctuations inside the tube

$$\tau_{\beta}^{LVE} = \frac{1}{\omega(G''_{min})} = 1s$$

$$D_{\perp} = \frac{(R_{core+shell})^2}{\tau_{\beta}^{LVE}} = 4 * 10^{-15}\ \frac{m^2}{s}$$



Tube renewal

$$\tau_{\alpha}^{LVE} = \frac{1}{\omega(G_c)} = 67s$$

$$D_{||} = \frac{(L_H)^2}{\tau_{\alpha}^{LVE}} = 6 * 10^{-15}\ \frac{m^2}{s}$$

Perpendicular and parallel diffusion coefficients are very similar at this concentration: weak/absent shell interpenetration

Edwards, Evans, J. Chem. Soc., Far. Trans. 1982

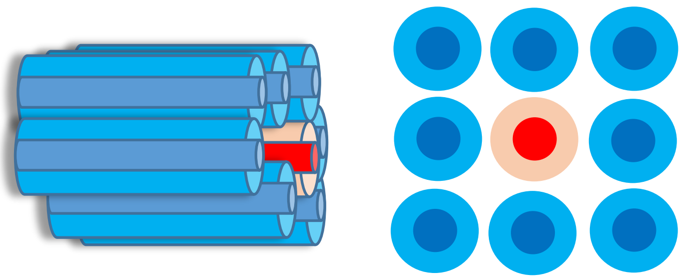
Doi, Edwards, The Theory of Polymer Dynamics, 1986

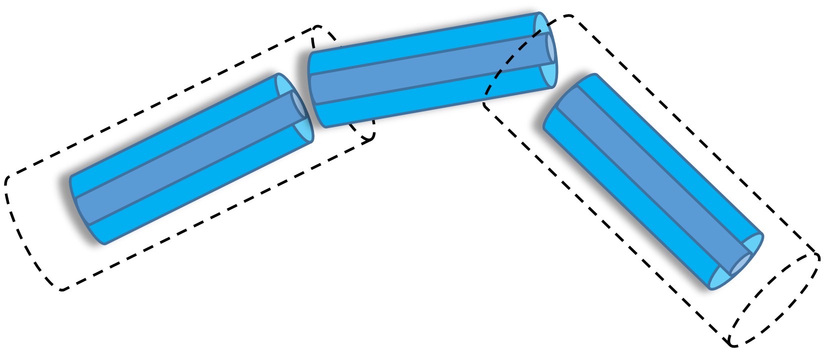
Teraoka, Hayakawa, JCP 1988

Zhao, Wang, Polymer 2013

Dynamics of cylinders: fluctuations and tube renewal

20wt%





Cylinder fluctuations inside the tube

$$\tau_\beta^{LVE} = \frac{1}{\omega(G''_{min})} = 12s$$

$$D_\perp = \frac{(R_{core+shell})^2}{\tau_\beta^{LVE}} = 2 * 10^{-16}\ \frac{m^2}{s}$$

Tube renewal

$$\tau_\alpha^{LVE} = \frac{1}{\omega(G_c)} = 7692s$$

$$D_{||} = \frac{(L_H)^2}{\tau_\alpha^{LVE}} = 6 * 10^{-17}\ \frac{m^2}{s}$$

The parallel diffusion coefficient is now slower: shell interpenetration

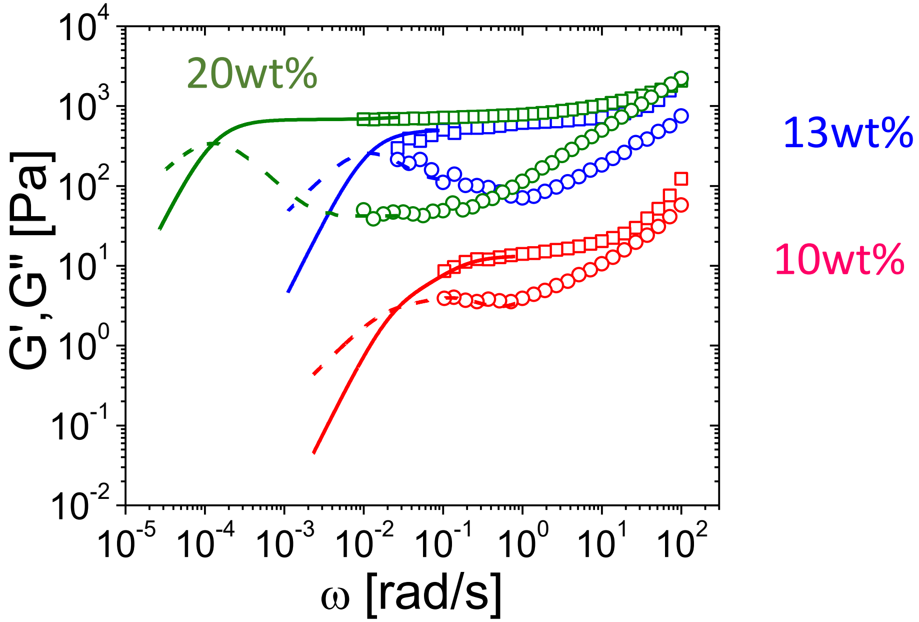
Edwards, Evans, J. Chem. Soc., Far. Trans. 1982

Doi, Edwards, The Theory of Polymer Dynamics, 1986

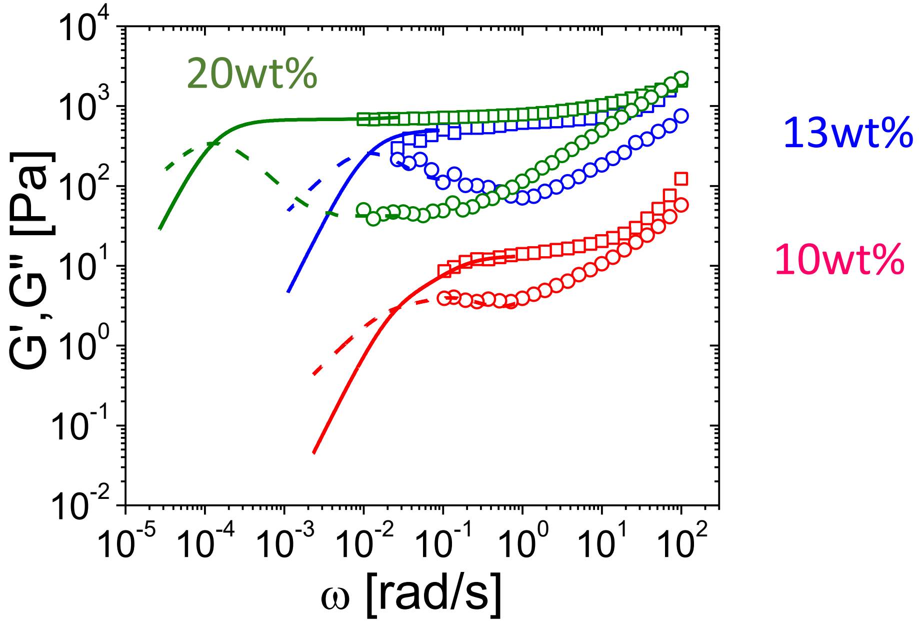
Teraoka, Hayakawa, JCP 1988

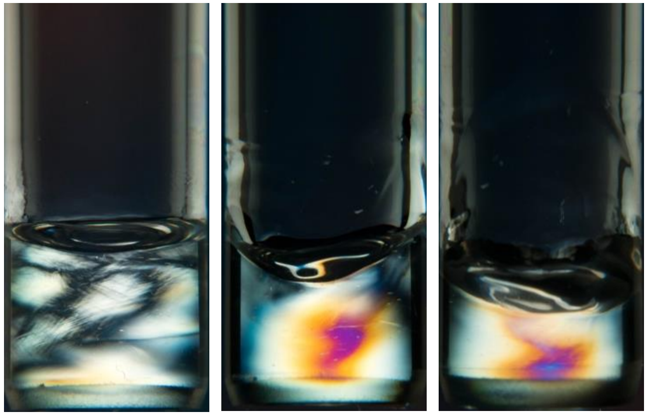
Zhao, Wang, Polymer 2013

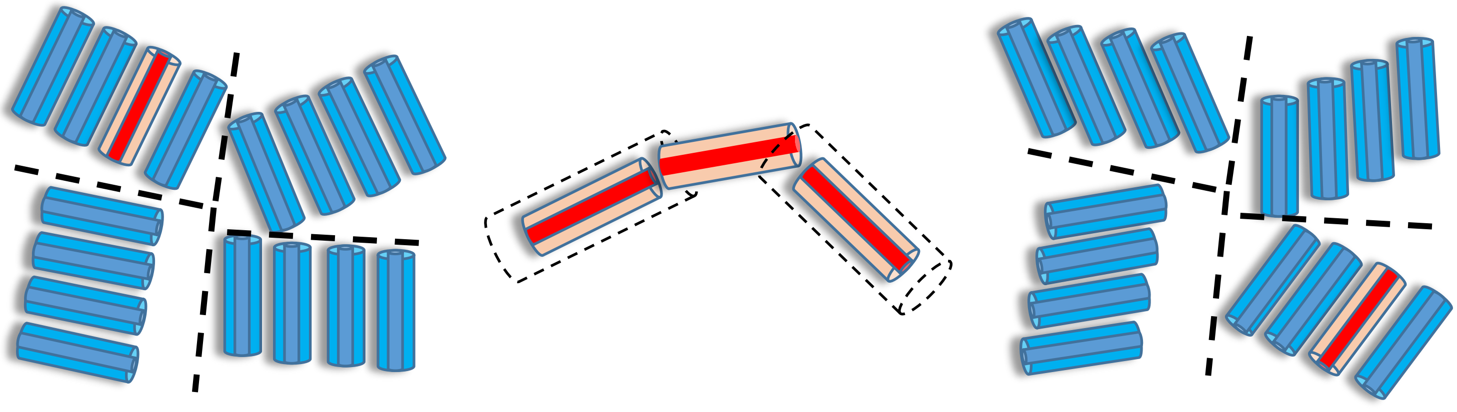
Cylinders: LVE from 10 to 13 to 20%wt.



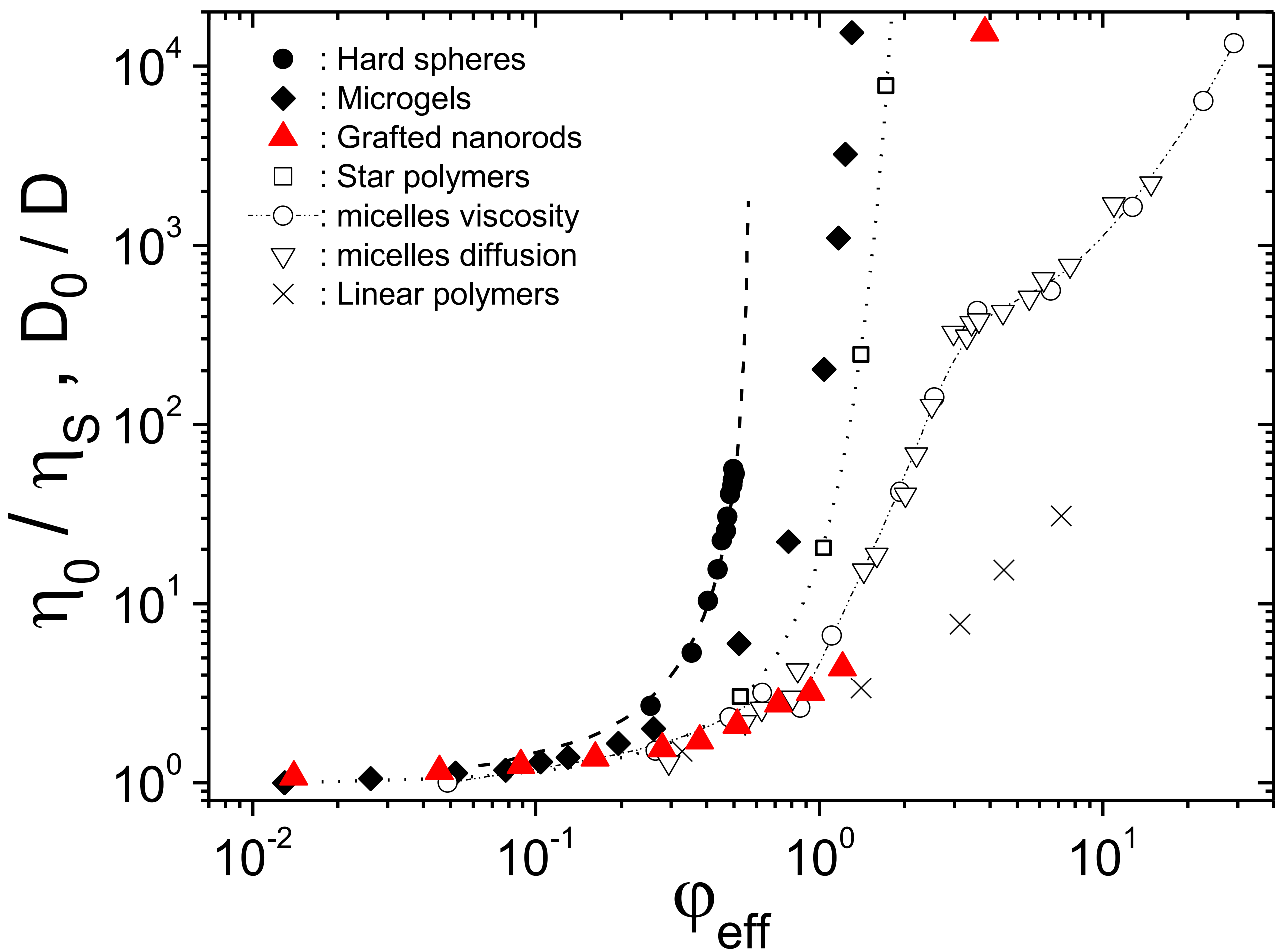
Cylinders: LVE from 10 to 13 to 20%wt.







Some consequences of softness: viscosity & self-diffusion

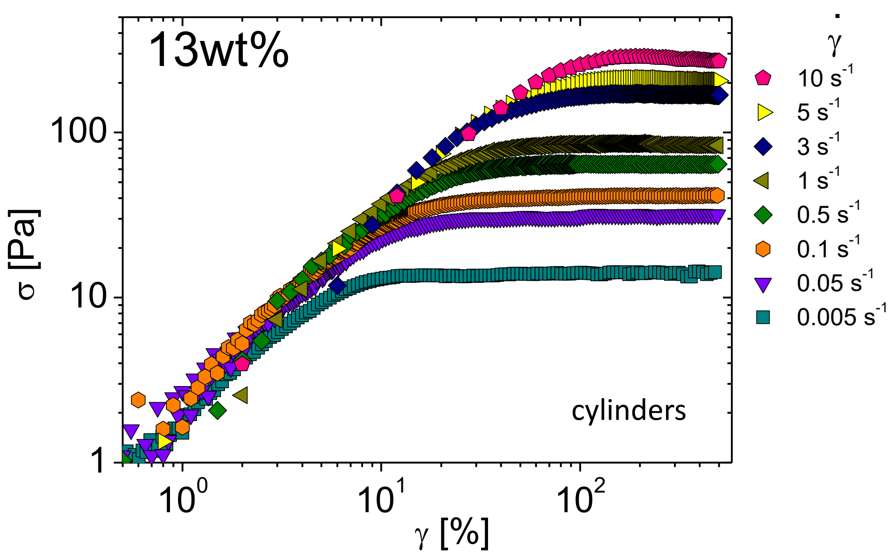


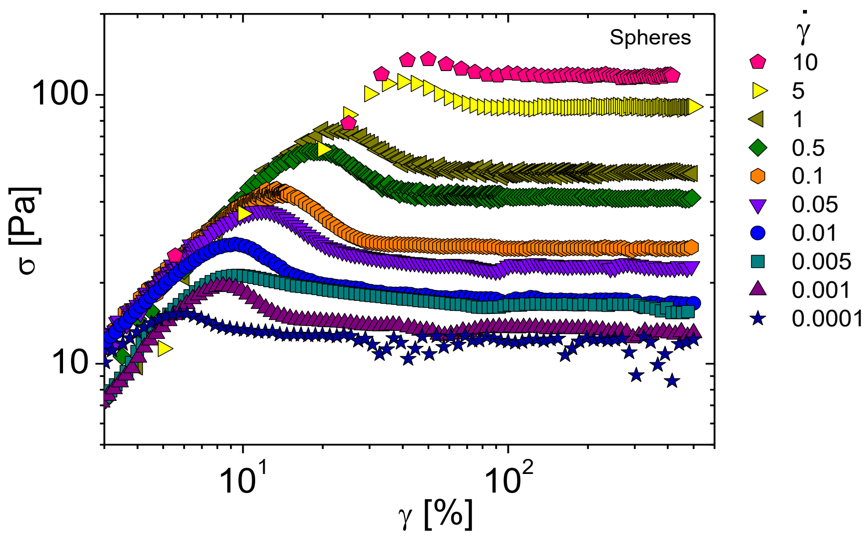
scale with R_h

$\phi_{eff} = c/c^*_h$

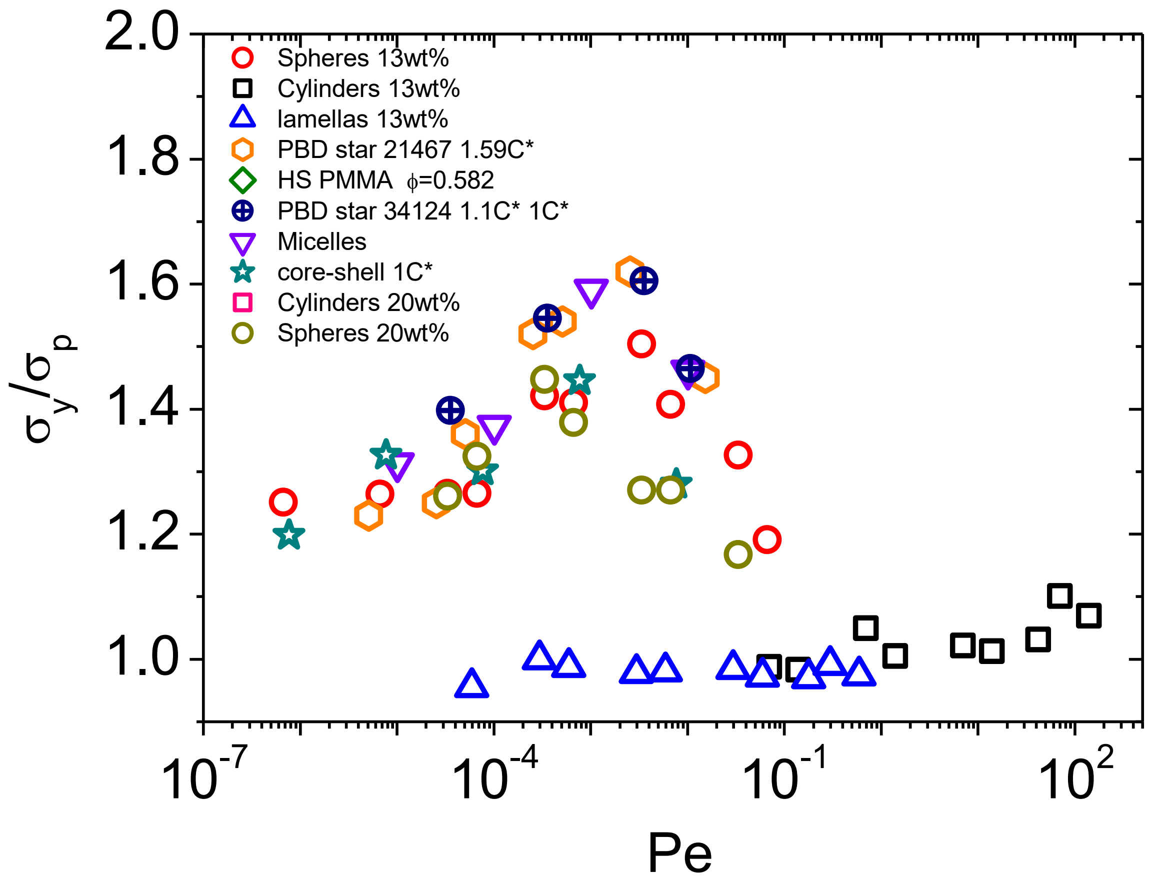
COCIS 2014 ; Adv. Polym. Sci. 2010 ; Phys. B 2001

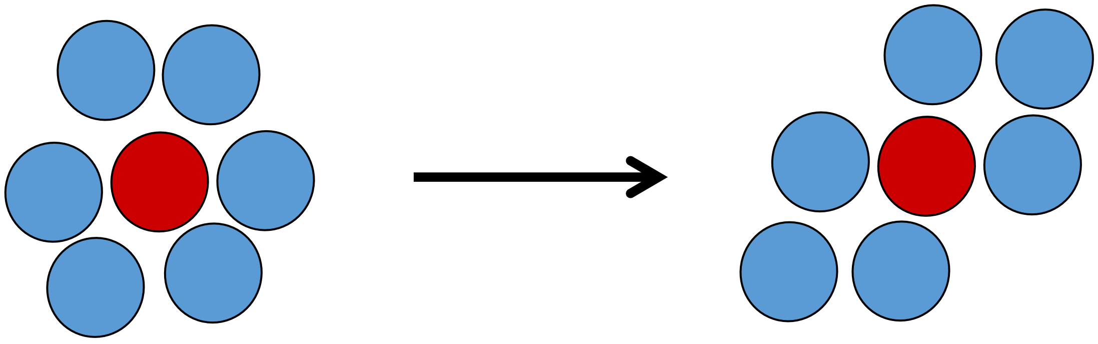
Nonlinear rheology: start-up shear



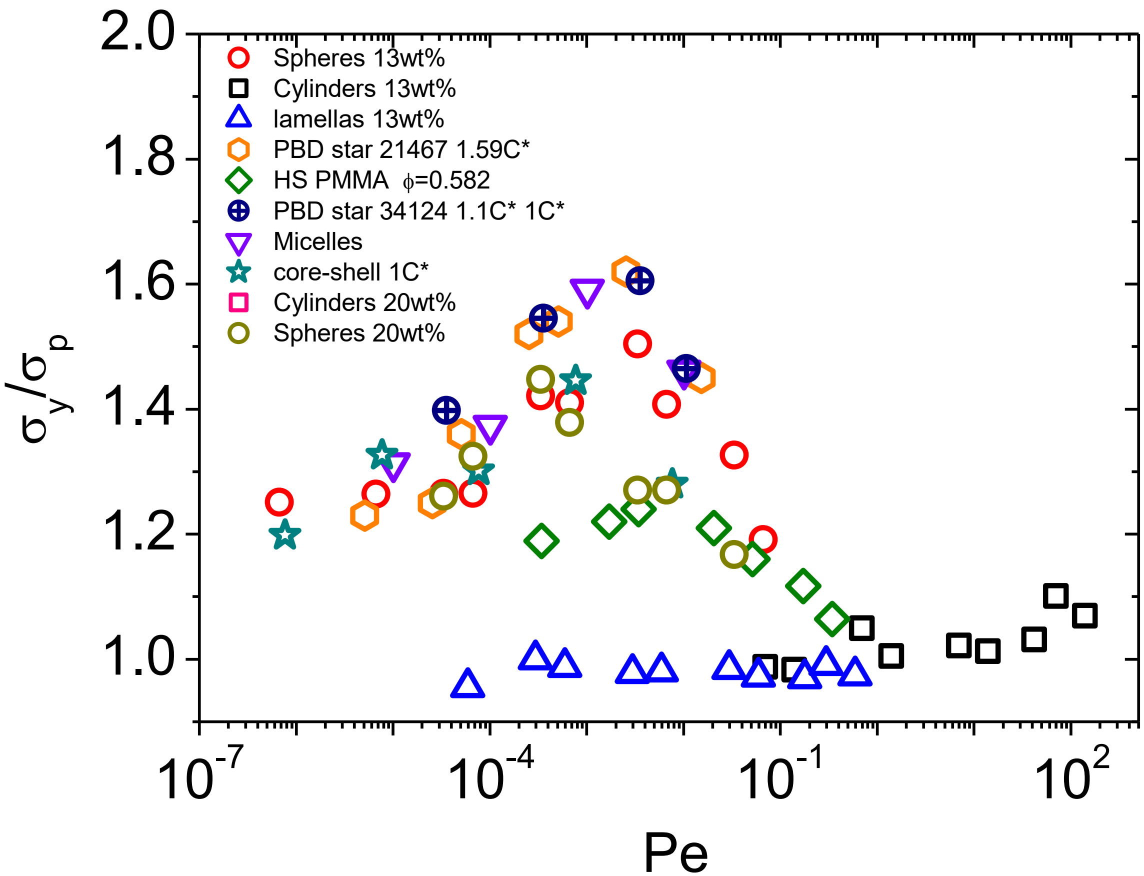


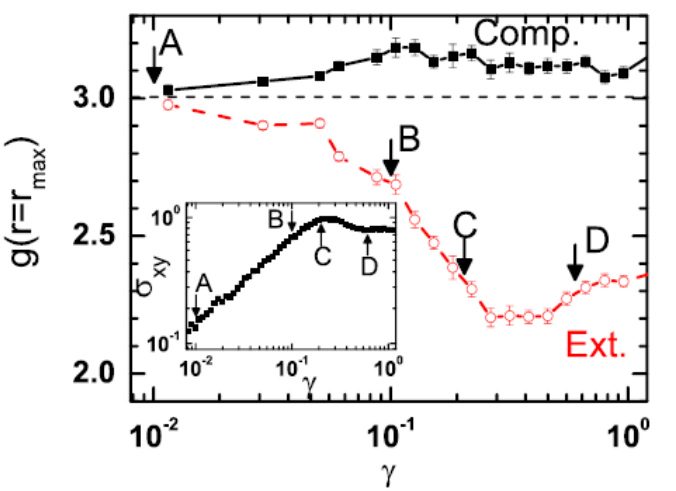
Yield stress





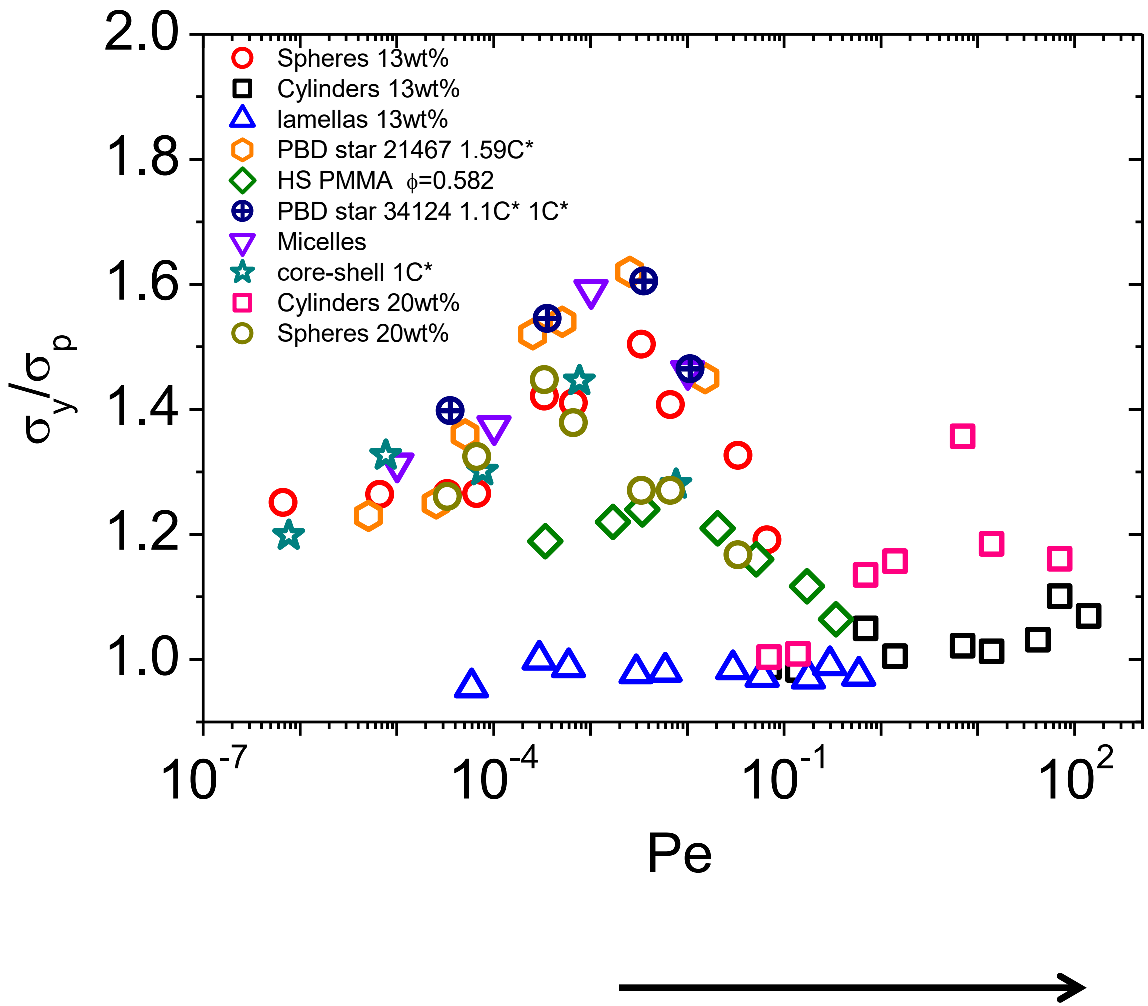
Yield stress





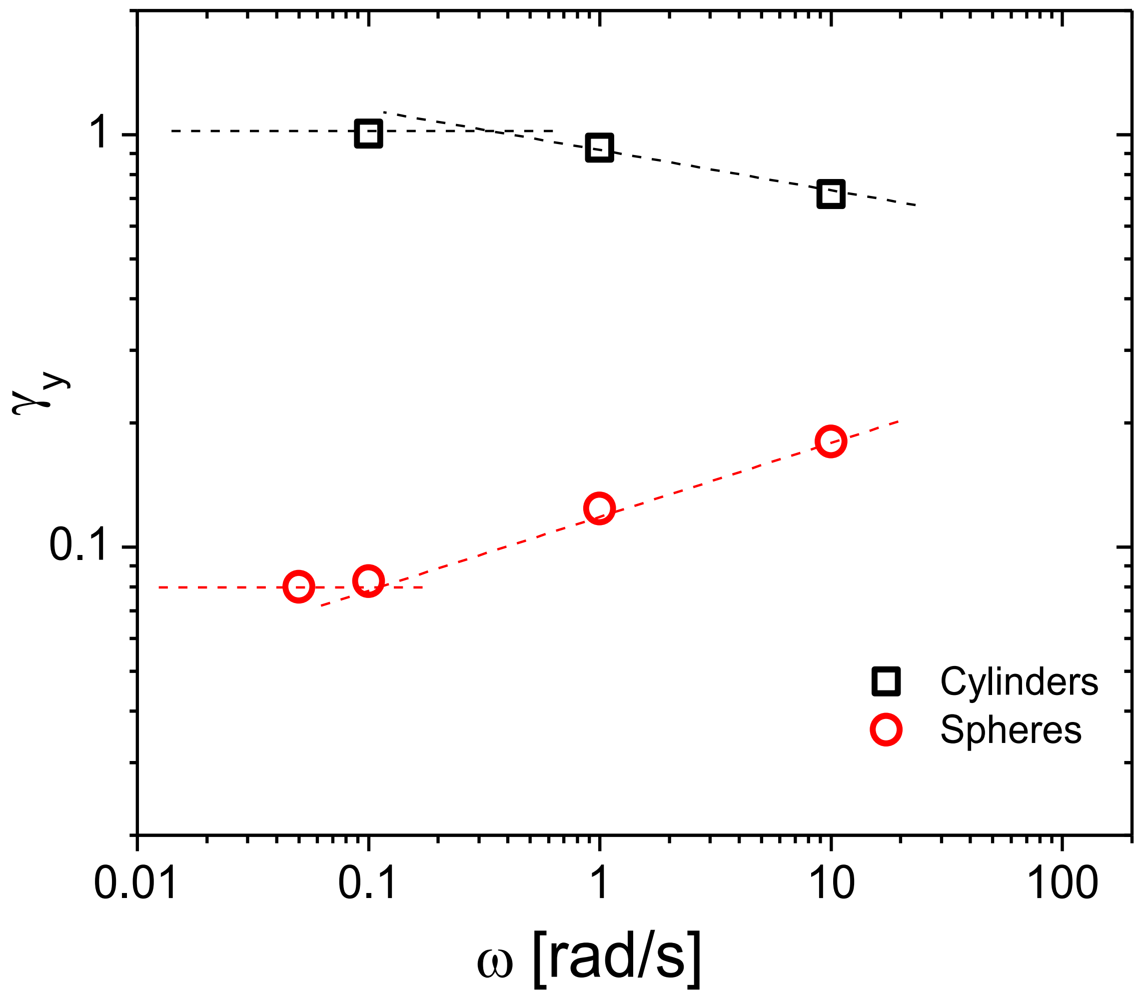
Koumakis et al. JoR 2017

Yield stress



Shape shifts pear to higher Pe

Yield strain: Comparison at 13wt%



2^{nd} peak of stars

all spheres (and rods)

$\gamma_y \sim \omega^m$

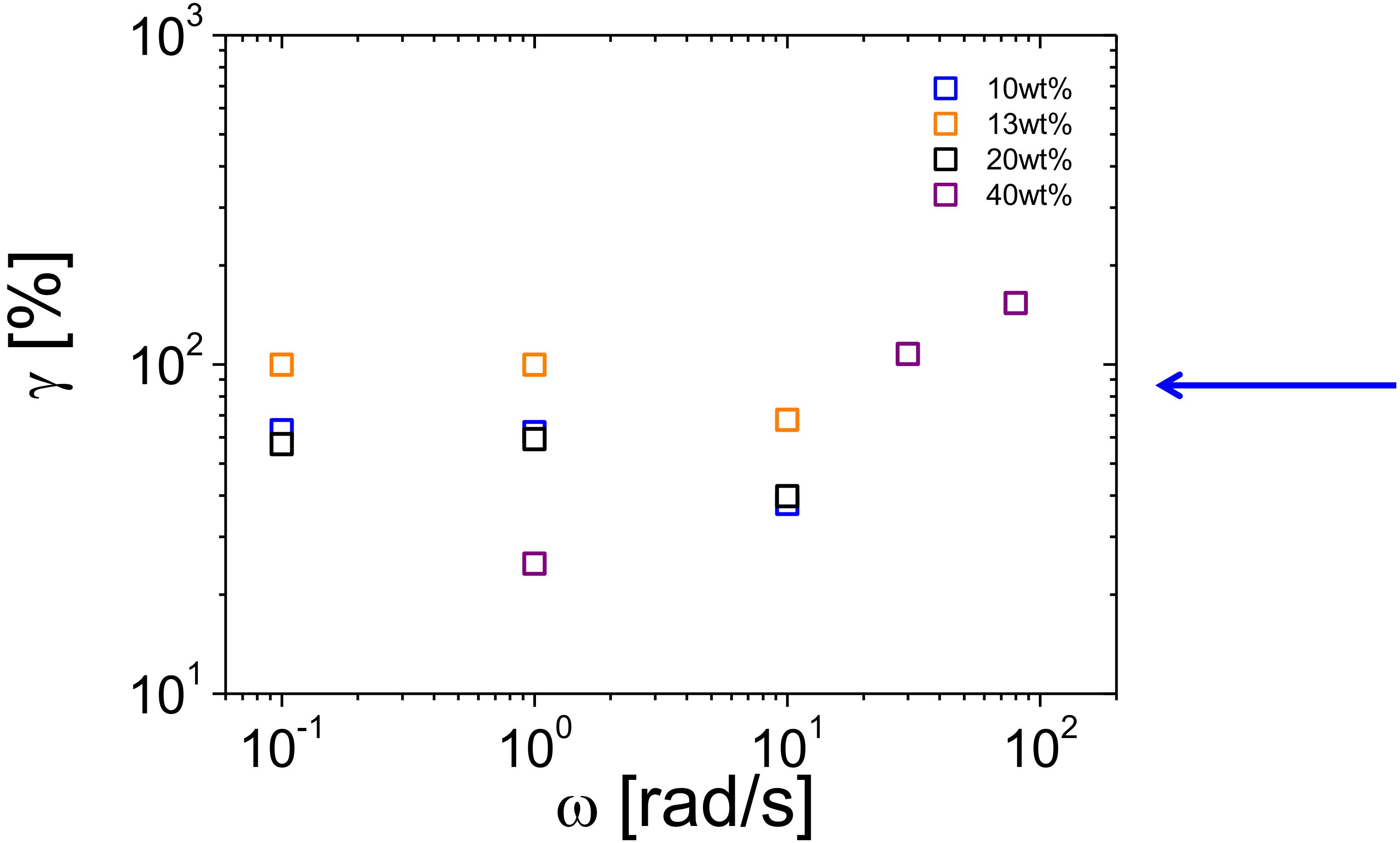
m= 0.14-0.2

Helgeson et al. JoR 2007

Koumakis et al. PRL 2013

Dhont et al. PRF 2017

Yield strain: Compare cylinders at different concentrations



2nd peak of stars

Conclusions II

Shape effects:

Grafted cylinders: tube-renewal and re-organization, 2 times
Yielding reflects different packing efficiency
(small aspect ratio)
Large yield strain

Measure N1 and N2
Elongational flows