NanoPaInt Marie Skłodowska – Curie ITN Network

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Fundamentals of rheology of capillary nanosuspensions: Effect of surfactants

Theme
for the PhD Thesis of ESR8

Supervisors:
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Duration of the PhD period:
36 months as of 1 January 2021
(starting date of the action)

Sofia University
Faculty of Chemistry
and Pharmacy

ESR8:
Fundamentals of rheology of capillary nanosuspensions: Effect of surfactants

The goal of the thesis will be to investigate the effect of surfactants on the rheological properties of capillary nanosuspensions such as

- **yield stress,**
- **viscosity,**
- **storage and loss moduli, *G‘* and *G“*.**

The surfactants can influence the nanosuspension rheology (at least) in three ways:

(i) by lowering the interfacial tension;
(ii) by increasing the elasticity of the oil/water interface, and
(iii) by affecting the three-phase contact angle particle/ water/ oil.

These effects will be investigated experimentally and interpreted theoretically by development of a model and computational procedure.

ESR8:
Fundamentals of rheology of capillary nanosuspensions: Effect of surfactants

Expected Results:

– The effect of water- and oil-soluble surfactants on the rheology of capillary nanosuspensions with aqueous and oily capillary bridges will be investigated at surfactant concentrations below and above the critical micellization concentration;

– For the used systems, the oil/water interfacial tension and dilatational elasticity, as well as the three-phase contact angle will be determined by means of appropriate experimental methods;

– Theoretical model and computational procedure for analysis of the state of capillary nanosuspension and its rheology will be developed; the quantitative interpretation of the experimental data will allow prediction and control of the nanosuspension rheology.

ESR8:
Fundamentals of rheology of capillary nanosuspensions: Effect of surfactants

An Introduction to the Theme:

The study will be an upgrade and extension over two previous works, where

- **No surfactants have been used;**
- **The studies were focused mostly on the yield stress.**

As an introduction, the next slides present two previous papers (see below). These slides may help the potential candidates to get impression about the research field of the project.

Previous papers:

K.D. Danov, M.T. Georgiev, P.A. Kralchevsky, G.M. Radulova, T.D. Gurkov, S.D. Stoyanov, E.G. Pelan, *Adv. Colloid Interface Sci*. **251** (2018) 80–96.

M.T. Georgiev, K.D. Danov, P.A. Kralchevsky, TD. Gurkov, D.P. Krusteva, L.N. Arnaudov, S.D. Stoyanov, E.G. Pelan, *J. Colloid Interface Sci*. **513** (2018) 515–526.

Presentation of previous results:

1) **Introduction**

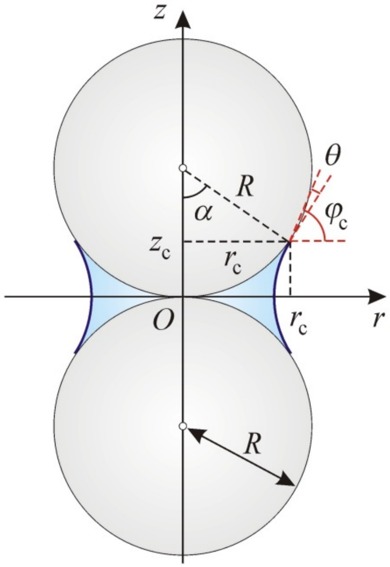
2) **Experimental data for capillary suspensions**

3) **Physical origin of the yield stress and quantitative model**

4) **Oily capillary bridges in water (theory vs. experiment)**

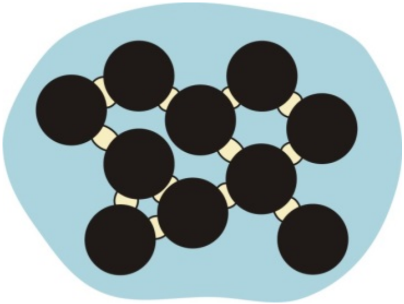
5) **Water capillary bridges in oil (theory vs. experiment)**

6) **Conclusions**

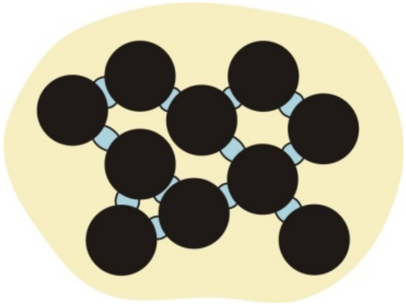


capillary bridge
(pendular ring)
between
two particles

Three phase dispersions
particles/water/oil:

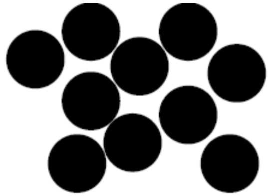
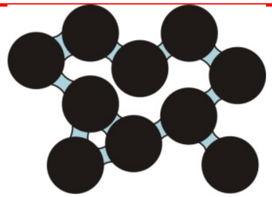
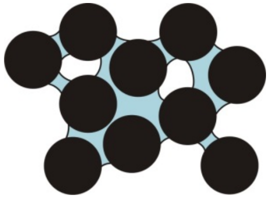
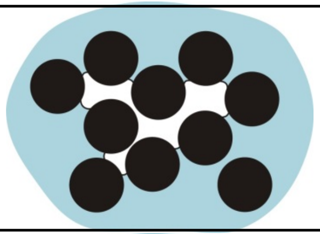
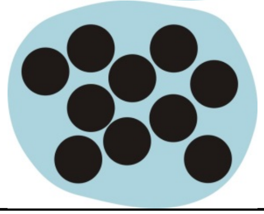


oily capillary bridges
in water



water capillary bridges
in oil

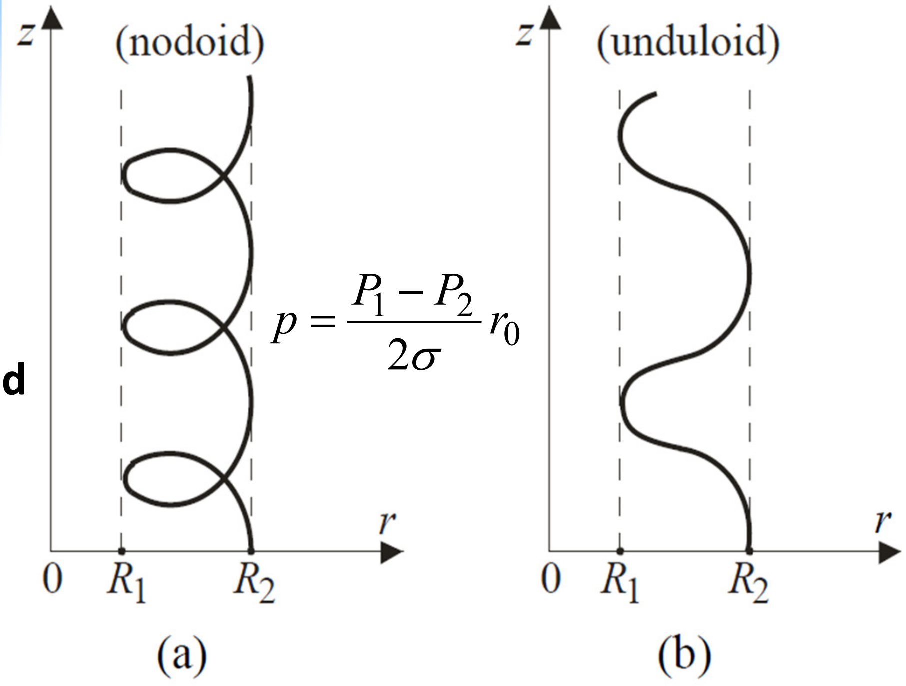
Classification of Wet Granular Materials (solid / liquid / gas)

Liquid content	State	Morphology	Physical description / topology
No	Dry		Granular materials – High particle volume fraction. Cohesion between the grains is weak.
Small	Pendular		Liquid capillary bridges (concave pendular rings) are formed; liquid – disperse phase; gas – continuous phase.
Middle	Funicular		Merging of capillary bridges; attractive capillary forces between particles. Bicontinuous (both liquid and gas phases are continuous.
High	Capillary		"Islands" of gas are present; the capillary menisci connect the particles; liquid – continuous phase; gas – disperse phase.
More	Slurry		The particles are completely immersed in the liquid; weak cohesion between the grains.

See: Mitarai, Nori, *Adv. Phys.* 55 (2006) 1-45.

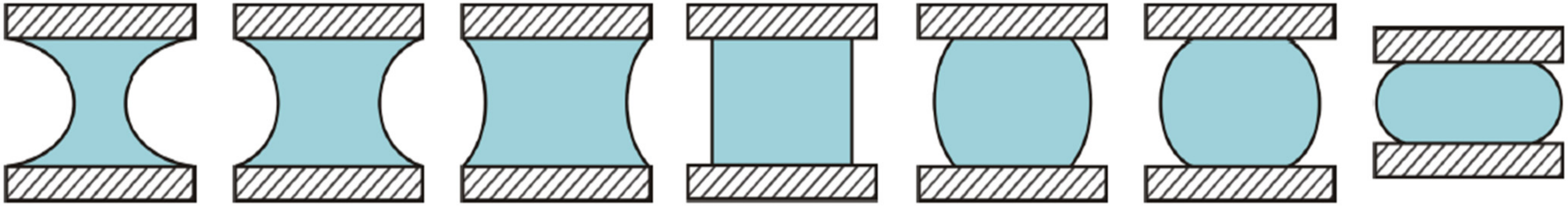
Classification of the capillary bridges

The capillary bridge profile can be a part of
(a) nodoid at $p < 0$ and $p > 1$ or
(b) unduloid at $0 < p < 1$. These curves are confined between two vertical lines at $r = R_1$ and $r = R_2$. →



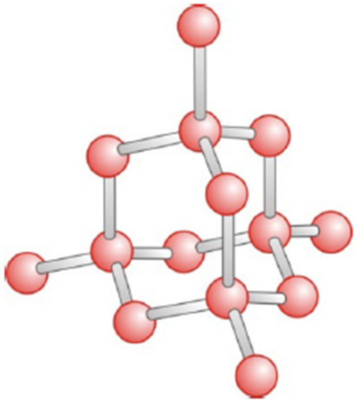
Sequence of capillary bridge profiles for increasing dimensionless capillary pressure, *p:*

← Concave capillary bridges → ← Convex capillary bridges →

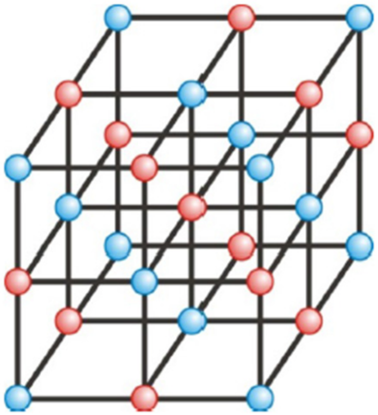


$-\infty < p < 0$	$p = 0$	$0 < p < 0.5$	$p = 0.5$	$0.5 < p < 1$	$p = 1$	$1 < p < +\infty$
concave nodoid	pseudo-sphere	concave unduloid	cylinder	convex unduloid	sphere	convex nodoid
Attractive capillary-bridge force, F_{cap}					$F_{cap} = 0$	Repulsion

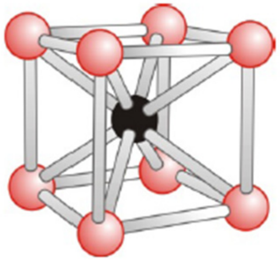
Regular crystal lattices with different number of closest neighbors (coordination number), *n*.



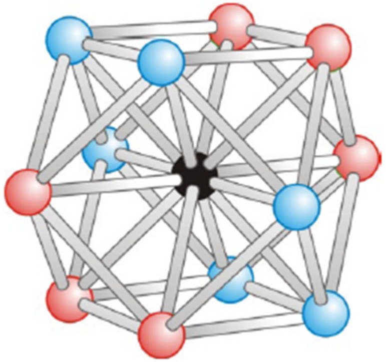
Diamond
$n = 4$, $\phi_p = 0.340$



Simple cubic
$n = 6$, $\phi_p = 0.524$



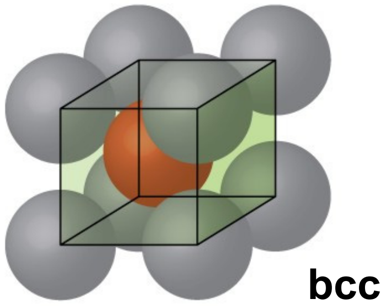
Body centered cubic
$n = 8$, $\phi_p = 0.680$

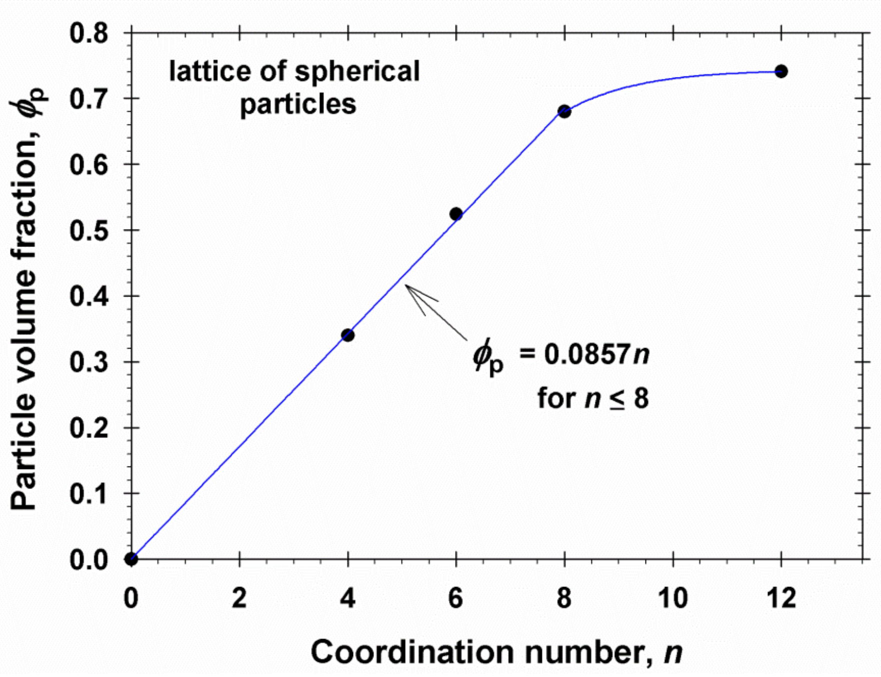


Face centered cubic
$n = 12$, $\phi_p = 0.740$

Estimate of the number of capillary bridges per particle, *n*.

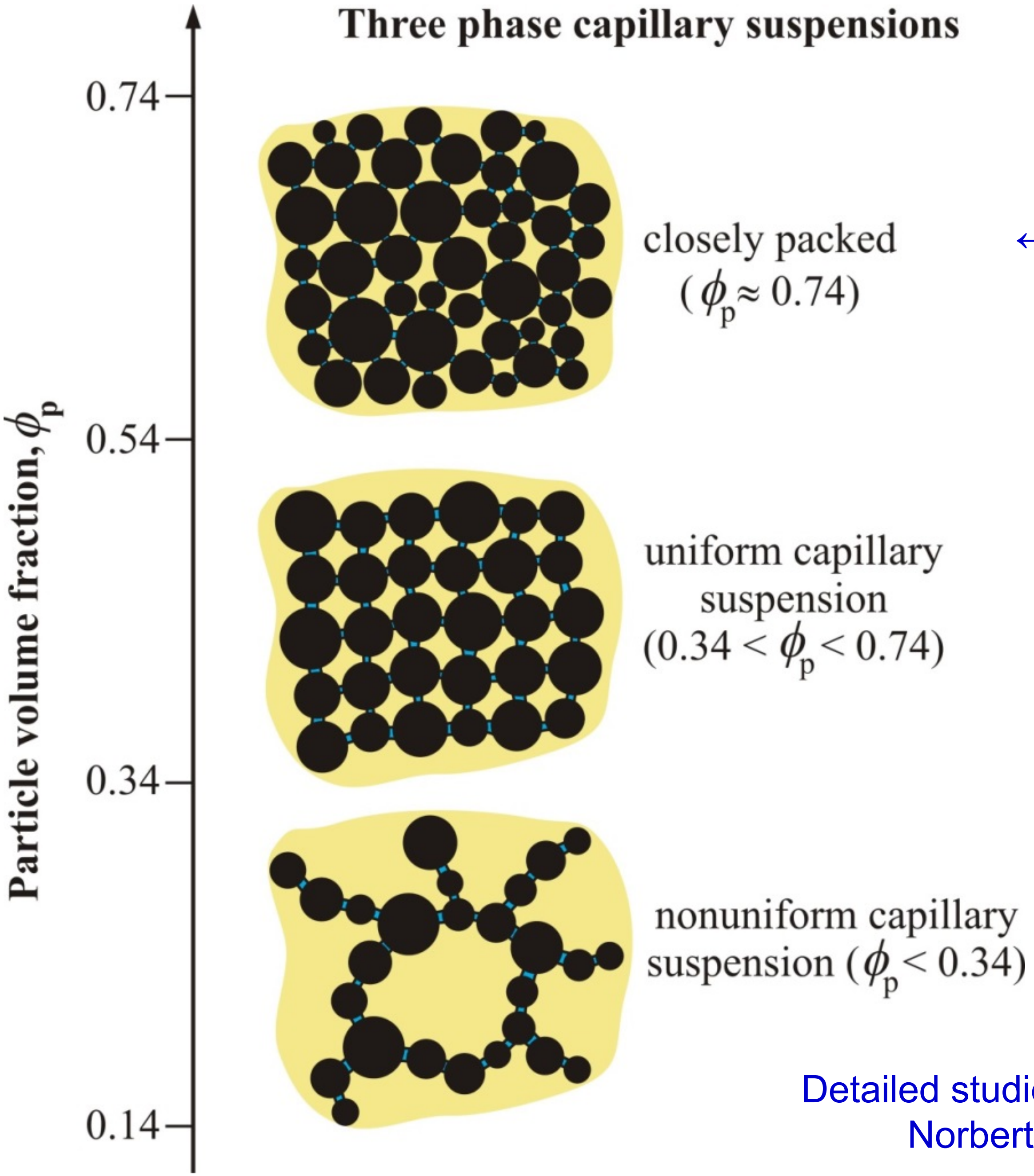
ϕ_p – particle volume fraction if the particles touch each other





Capillary-bridge bonds: φ_p and *n* continuously vary and are related:

$$\boxed{n = \frac{\phi_p}{0.0857} \quad \text{for } n \leq 8}$$



← granular materials,
$\phi_p \approx 74$ %

← **our study**

← particle networks
$\phi_p = 10 – 34$%

Detailed studies by Erin Koos and
Norbert Willenbacher

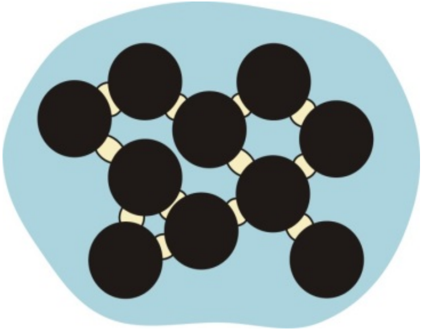
Objective of the study

Investigate uniform oil/water/solid dispersions, which solidify upon the addition of minimal amount of the "inner" liquid, and study their rheology.

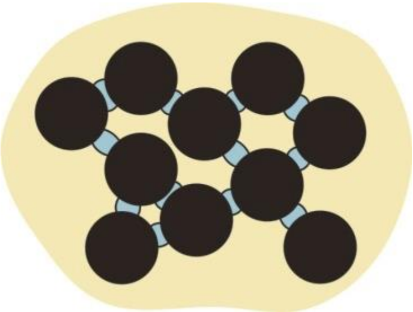
"inner" liquid is that, which forms the capillary bridges.

Two "mirror" systems:

- **(i) Water bridges; hydrophilic particles;**
- **(ii) Oily bridges; hydrophobic particles.**



water-continuous suspension with hydrophobic particles and oily capillary bridges



oil-continuous suspension with hydrophilic particles and water capillary bridges

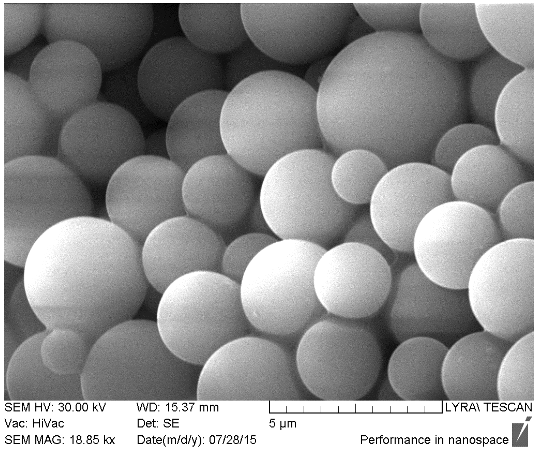
Applications: Foods – creams; chocolade, etc.; Construction materials, etc.

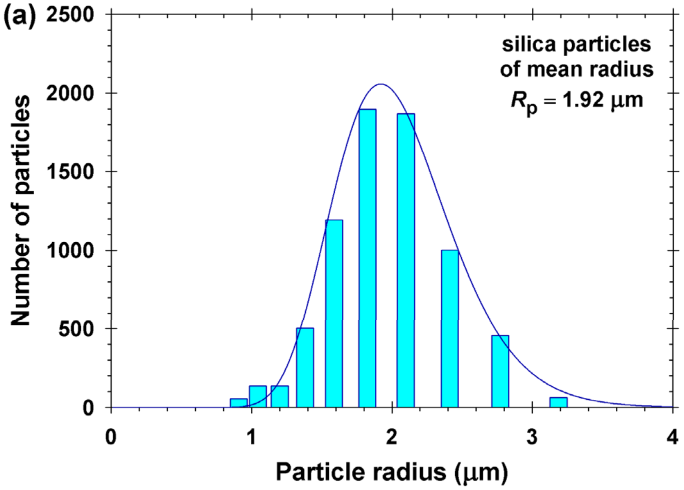
Solidification is observed at fraction of the inner liquid below 1 vol%!

Increasing solidification is observed with the rise of the fraction of inner liquid.

Materials and Methods

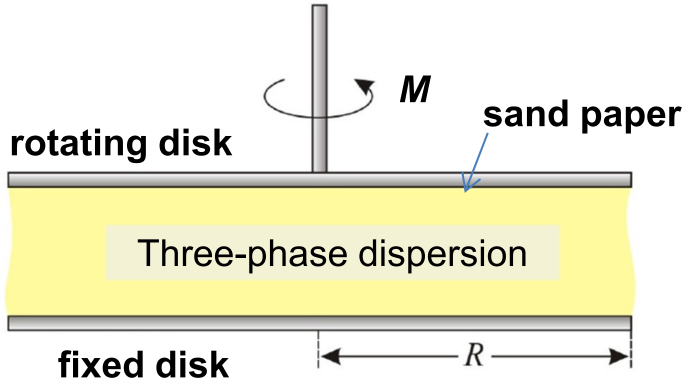
Tokuyama Corporation (Japan) <u>spherical</u> hydrophilic particles of <u>fused quartz</u> (density = 2.2 g/cm^2) with low surface roughness (EXCELICA®)





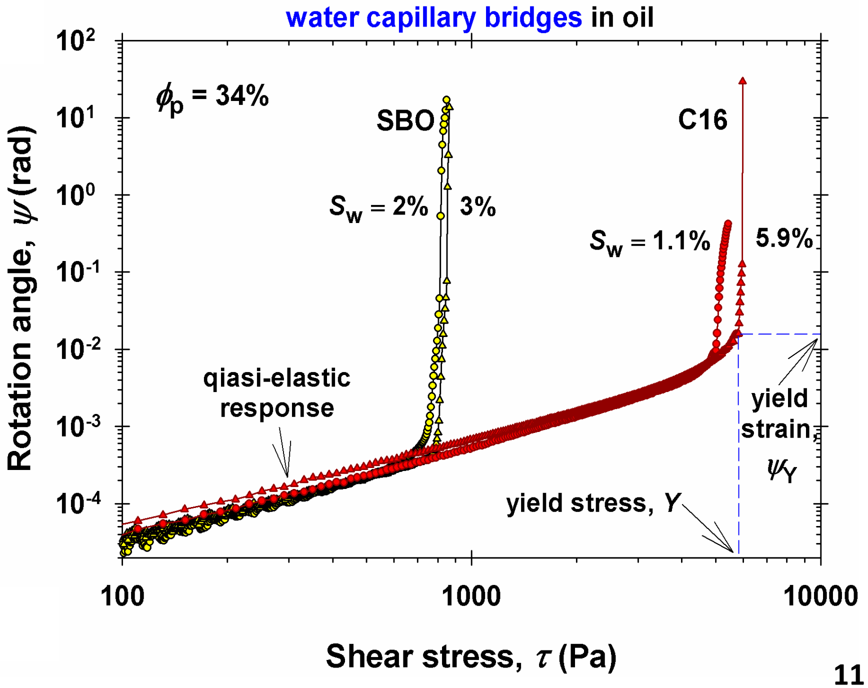
Hydrophilization by NaOH; hydrophobization by HMDS

<u>Rotational rheometer: two parallel disks</u>

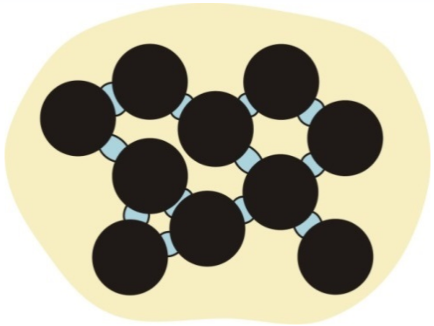


<u>Oil phase</u>: soybean oil (SBO) or hexadecane (C16).

<u>Material's hardness</u> is characterized by the <u>yield stress</u>.



Yield stress, Y, vs. the volume fraction of the inner liquid, S_{i}



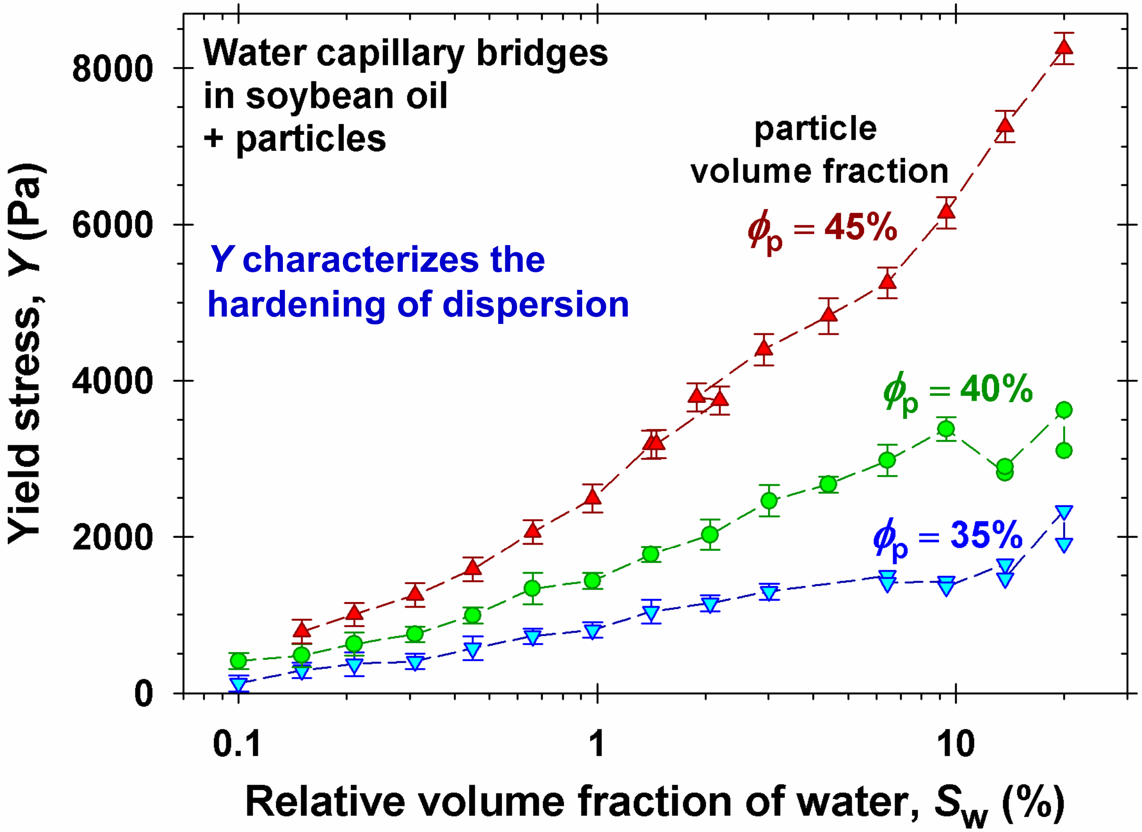
Experiment:

$$\boxed{Y \text{ vs. } S_{\mathrm{w}} = \frac{\phi_{\mathrm{w}}}{\phi_{\mathrm{oil}} + \phi_{\mathrm{w}}}}$$

ϕ_{w} – volume fraction of water

ϕ_{oil} – volume fraction of oil

ϕ_{p} – volume fraction of particles



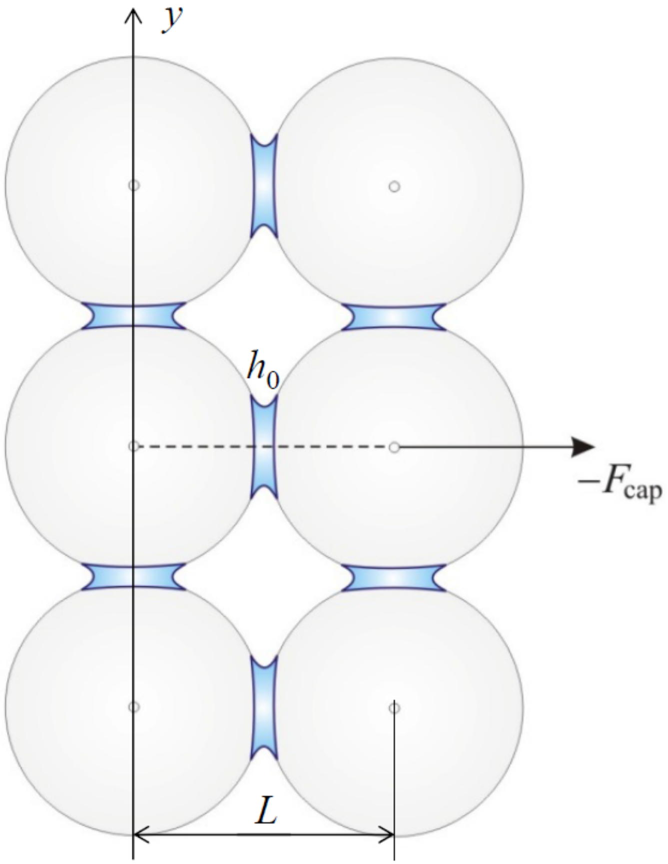
Goal: Understanding (quantitative theory) the dependence of *Y* on the system's parameters:

$$\boxed{Y = Y(S_{\mathrm{w}}, \phi_{\mathrm{p}}, \sigma, a, \alpha)}$$

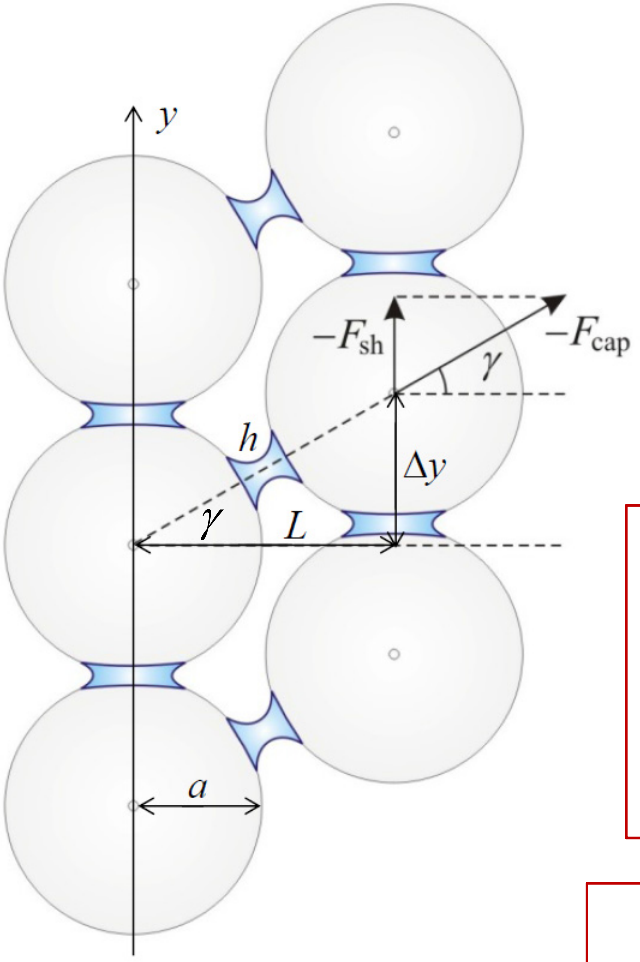
σ – o/w interfacial tension; a – particle radius;

α – s/w/o three-phase contact angle.

Physical Origin of the Yield Stress in Capillary Suspensions



Initial state



After displacement Δy

shear strain

$$\varepsilon = \frac{\Delta y}{L} = \tan\gamma$$

capillary force

$$F = F_{\mathrm{cap}}$$

y-projection of F

$$F_{\mathrm{sh}} = F(h)\sin\gamma$$

$$= F(h)\frac{\varepsilon}{(1+\varepsilon^2)^{1/2}}$$

length of the bridge

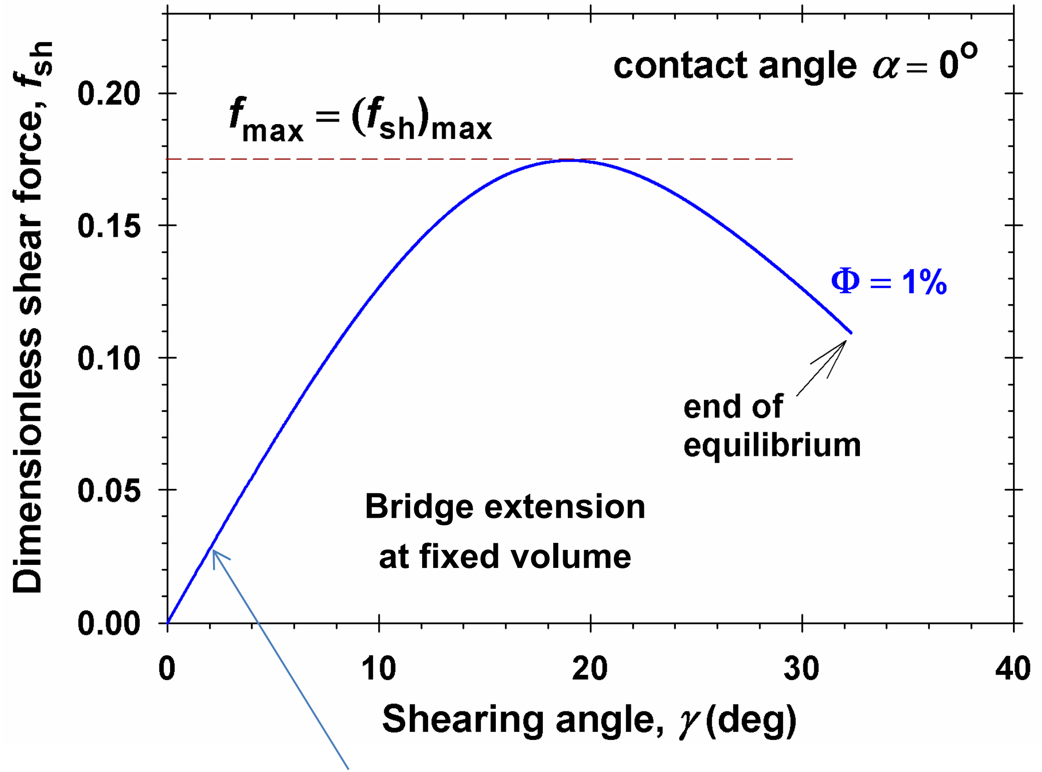
$$h = [L^2 + (\Delta y)^2]^{1/2} - 2R$$

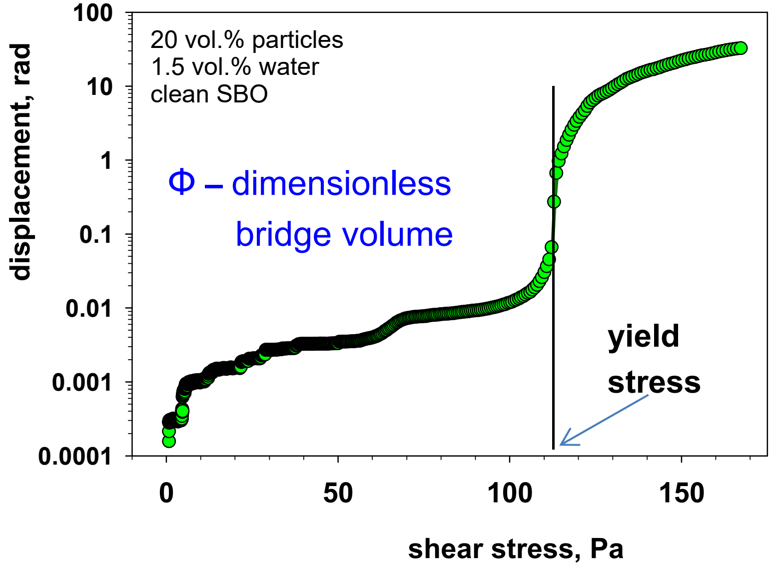
$$= h_0 + \frac{1}{2}L\varepsilon^2 + O(\varepsilon^4)$$

$$F_{\mathrm{sh}}(\varepsilon) = F(h_0)\varepsilon - \frac{1}{2}[F(h_0) + |F'_h|L]\varepsilon^3 + O(\varepsilon^5)$$

$f_{\mathrm{sh}}(\varepsilon)$ is a curve with maximum!

Yield stress due to the maximum of the force of system's response





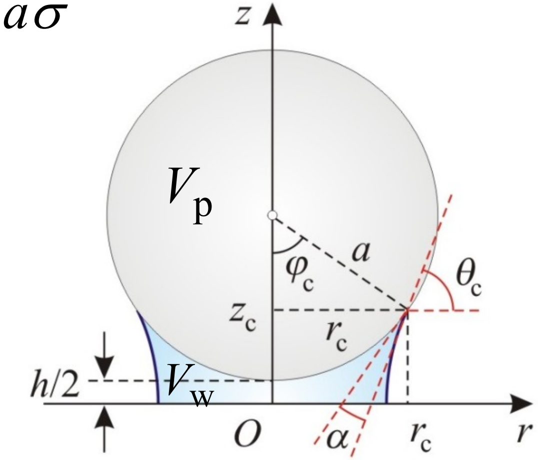
$$f_{\mathrm{sh}} = \frac{F_{\mathrm{cap}} \sin\gamma}{2\pi a \sigma}$$

$$\Phi = \frac{V_{\mathrm{w}}}{V_{\mathrm{p}}}$$

Exact theoretical curve (no series expansion)

There is a maximum in the system's response to shear deformation:

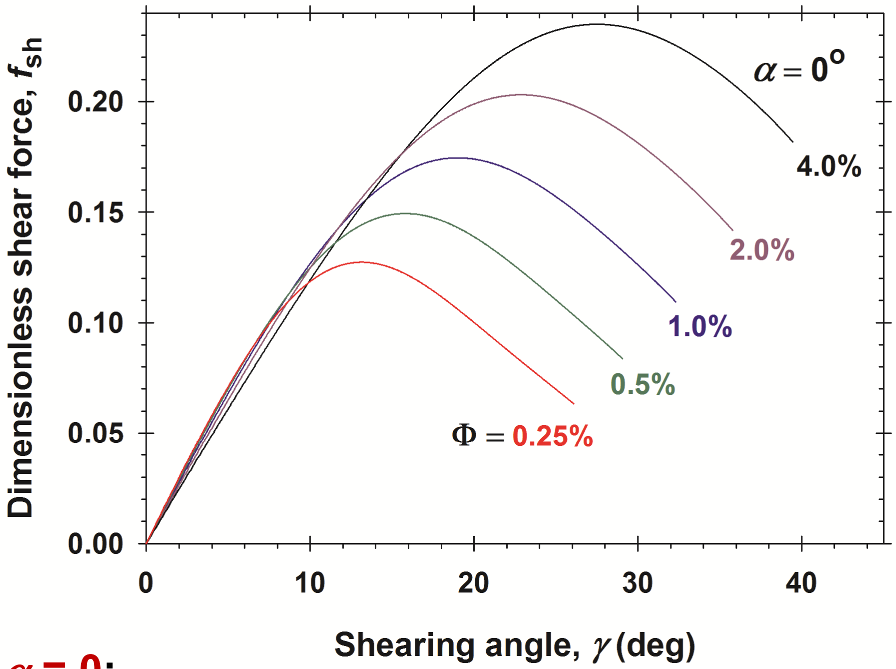
At {external force} > $f_{\max}$, <u>the capillary bridge breaks</u>!

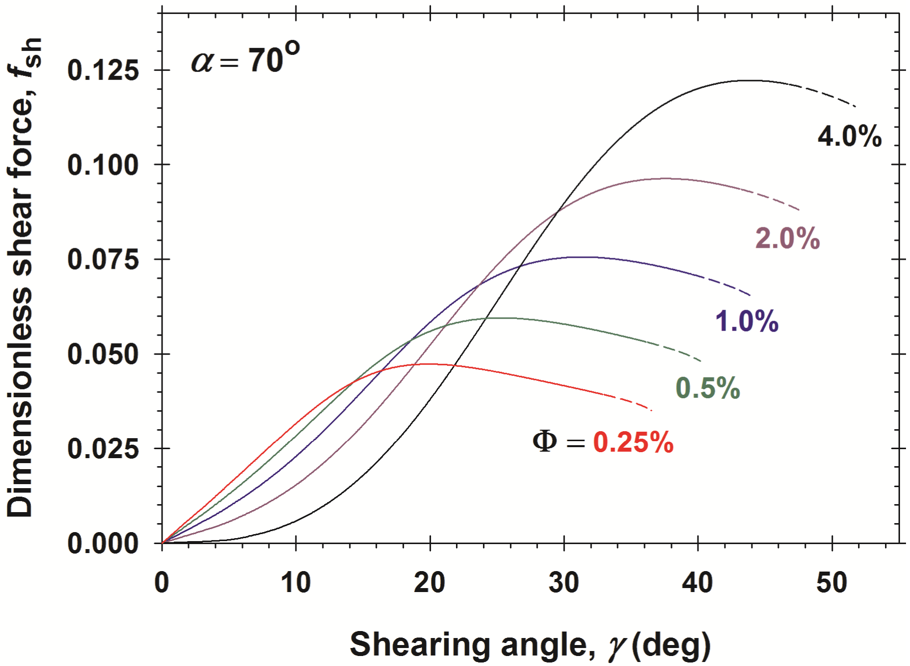


Yield stress: $\boxed{Y \propto f_{\max}}$

The bridge cannot withstand external force > $f_{\max}$

Shear response force f_{sh} vs. contact angle α and bridge dl volume Φ





$\alpha = 0$:

For all dimensionless bridge volumes, Φ, the f_{sh} vs. γ curves have a maximum.

All curves correspond to stable equilibrium, up to the end points (for greater γ, the governing system of equations has no solution for the given bridge volume, characterized by Φ).

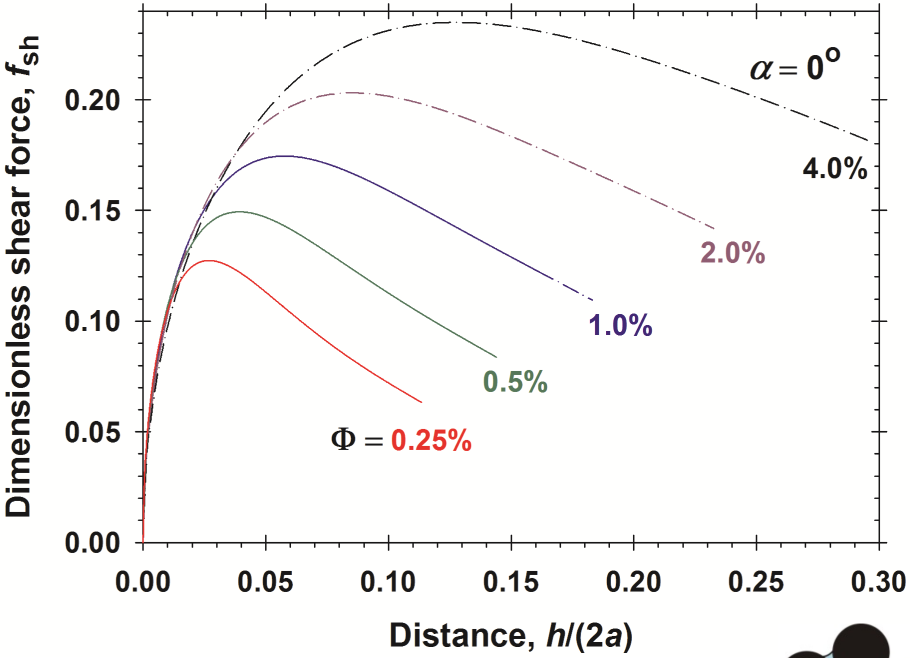
$\alpha = 70^{o}$:

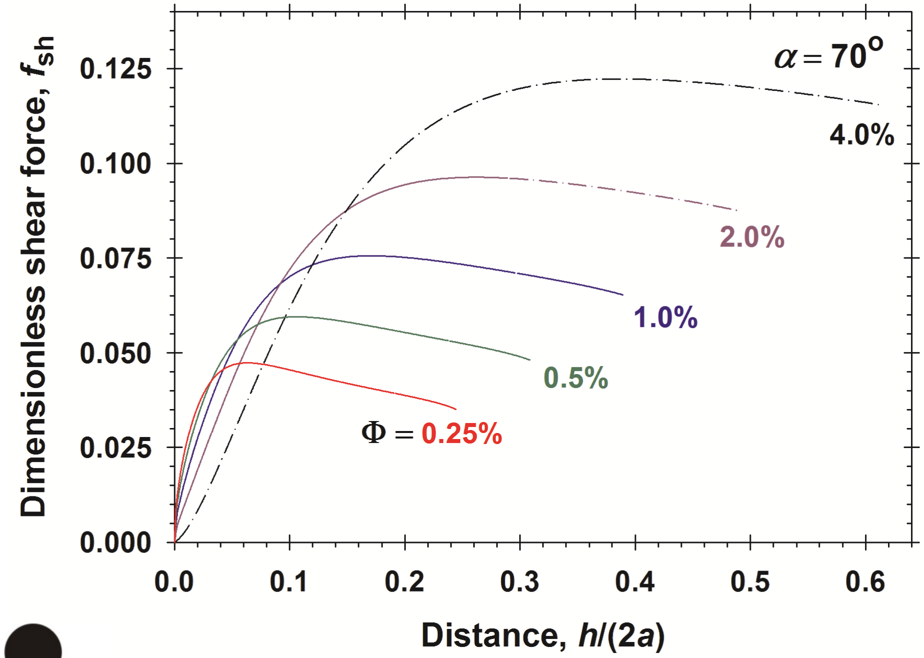
For all bridge volumes Φ, the f_{sh} vs. γ curves have a maximum.

The dashed portions of the lines correspond to unstable bridges with inflection point on the bridge profile (f_{max} is in the zone of stable bridges).

Bridge overlapping and transition from pendular to funicular state

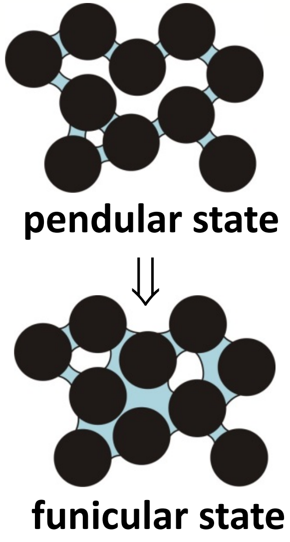
(six bridges per particle assumed)





α = 0:

For Φ = 2% and 4% the maximum appears in the zone of bridge overlap (denoted with dot-dashed line), so that transition to funicular state should be observed.



α = 70°:

Bridge overlap at f_{max} is present only at the greater dl bridge volume, Φ = 4%. These predictions of theory are in agreement with the experiment.

Comparison of theory and experiment

Expression for the yield stress:

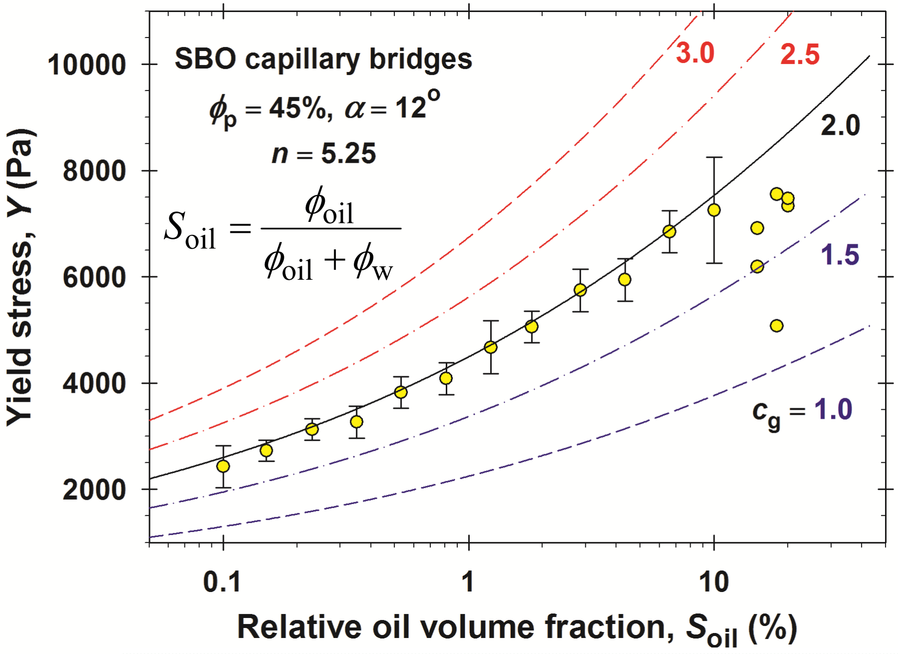
$$Y = \frac{2\sigma}{\underbrace{a}_{(1)}} \underbrace{c_{\mathrm{g}}\phi_{\mathrm{p}}^{2/3}}_{(2)} \underbrace{f_{\max}(\Phi,\alpha)}_{(3)}$$

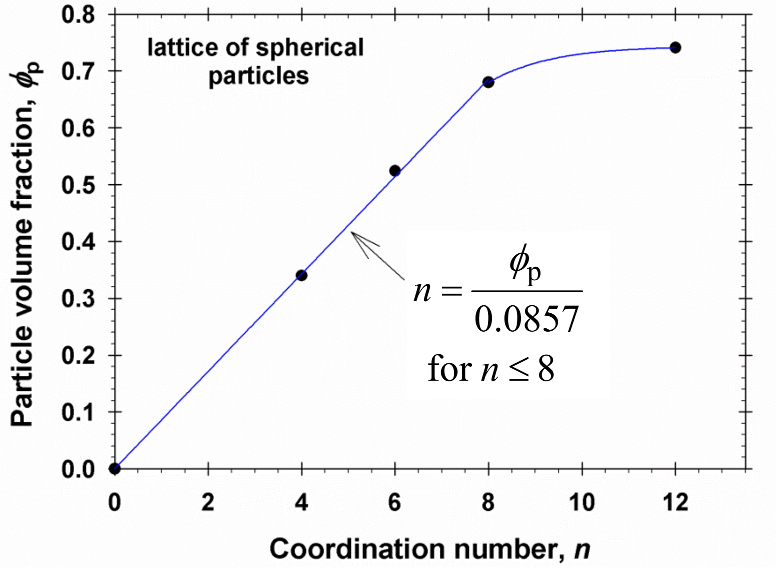
(1) *Y* scales with the capillary pressure $2\sigma/a$; addition of surfactant would decrease σ and *Y*.

(2) Proportional to the number of bridges per unit area of the shear plane; c_{g} is a geometrical coefficient that is to be determined as an adjustable parameter:

(3) $f_{\max}(\Phi,\alpha)$ is a dimensionless universal function that is computed and tabulated.

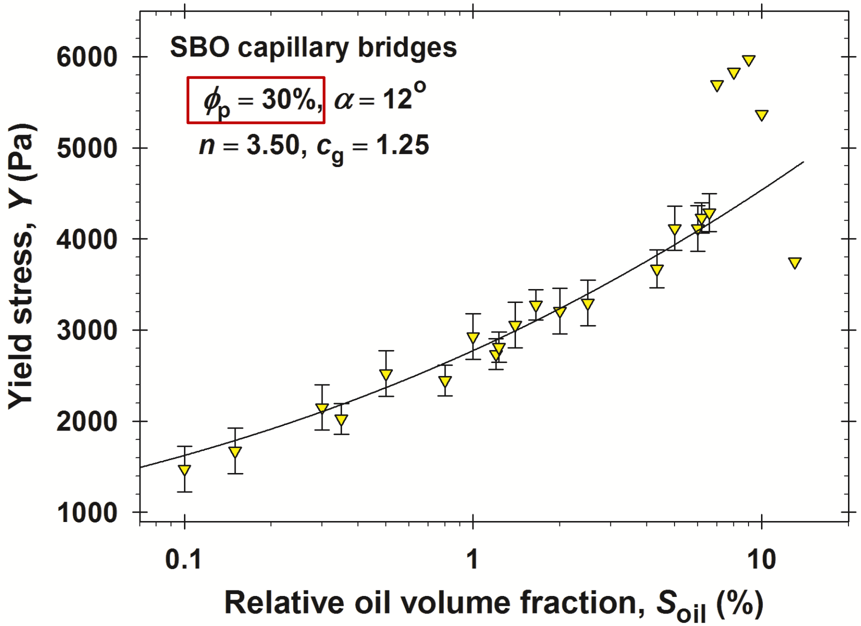
$$\Phi = \frac{1-\phi_{\mathrm{p}}}{n\phi_{\mathrm{p}}} S_i, \quad (i = \mathrm{oil}, \mathrm{w})$$

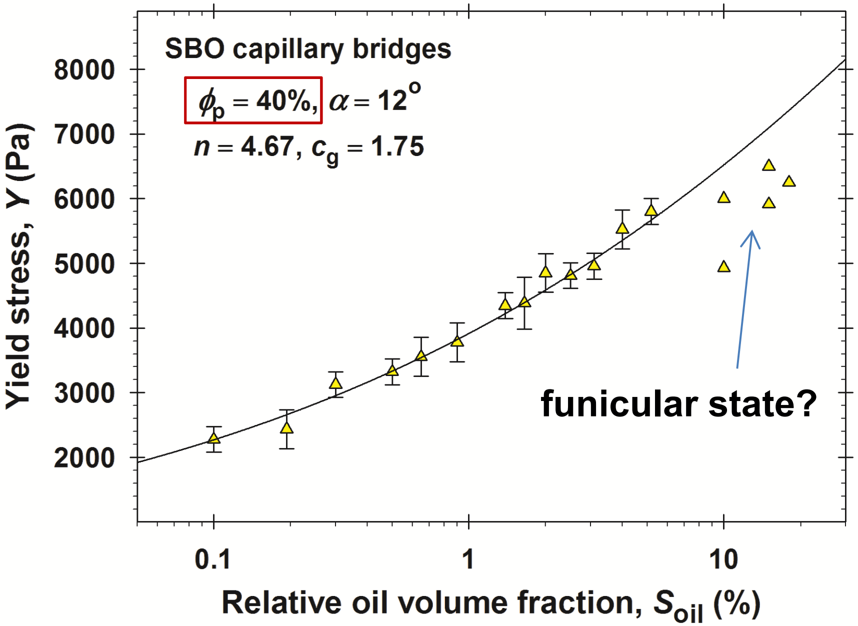


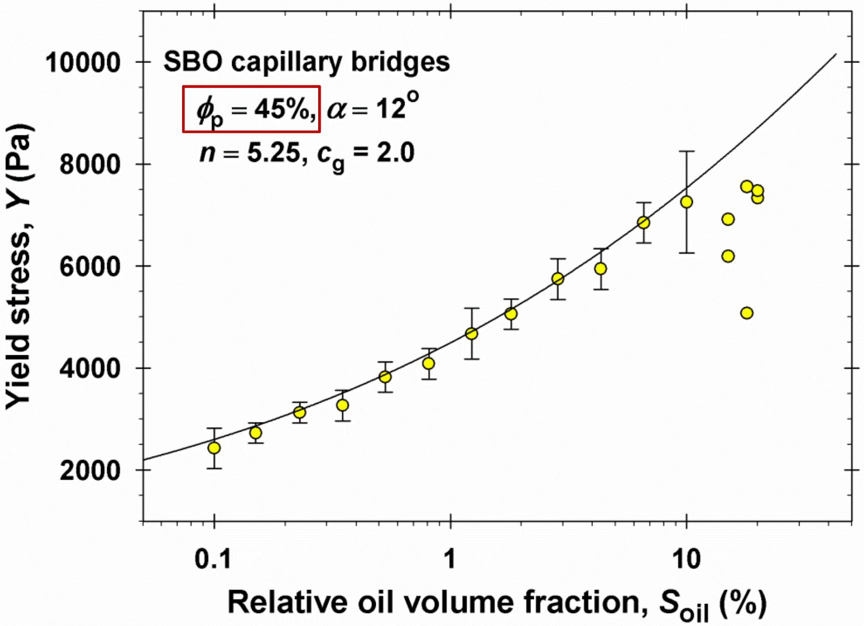


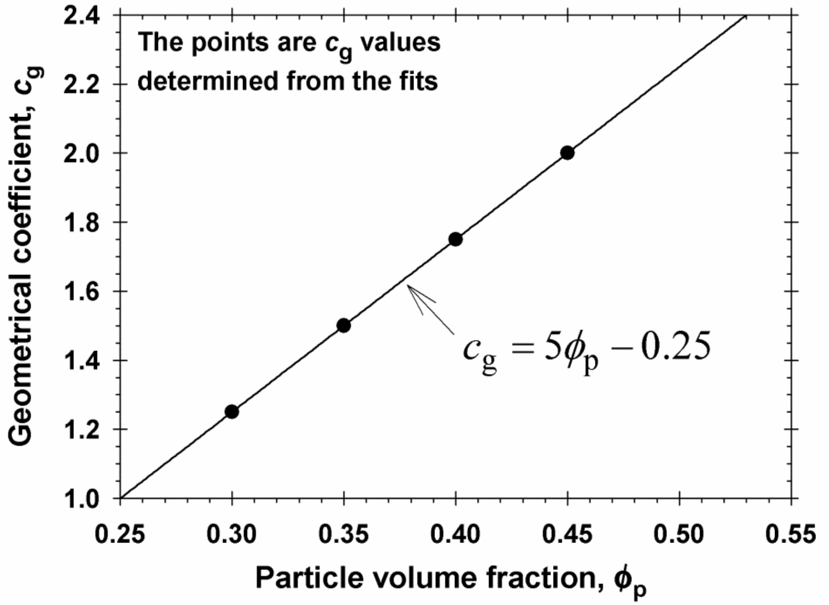
Comparison of theory and experiment (continued)

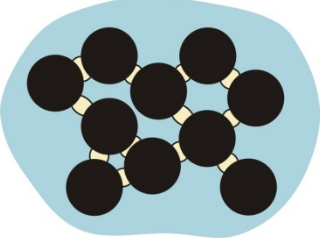
(oily capillary bridges; SBO = soybean oil, vegetable oil; $\alpha = 12^o$)



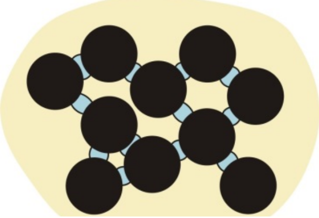


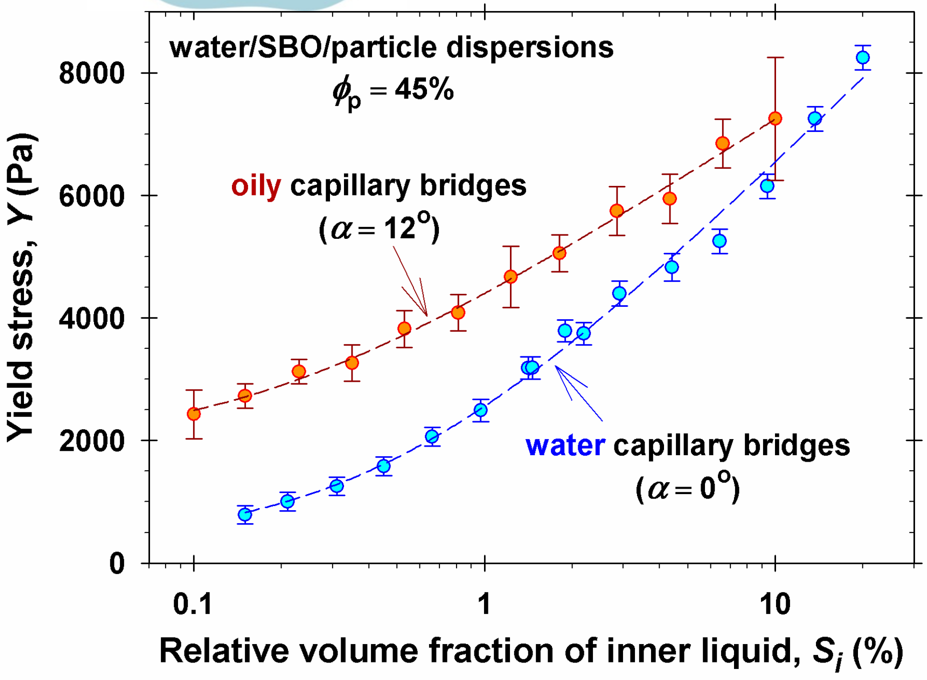


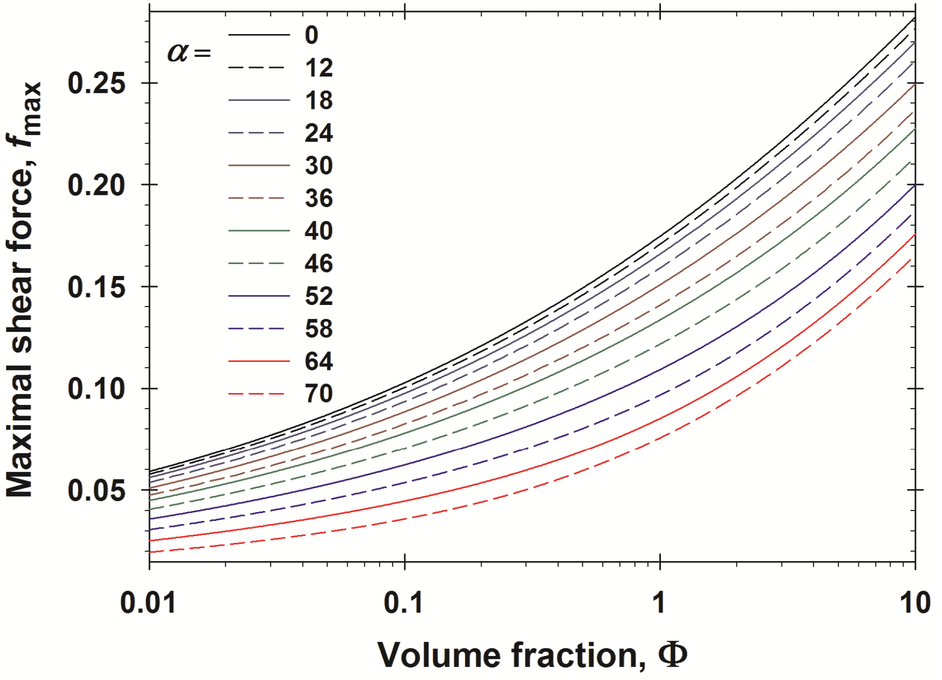




Oily vs. Water Capillary Bridges







$$Y = \frac{2\sigma}{a} c_g \phi_p^{2/3} f_{\max}(\Phi, \alpha)$$

All parameters are the same for the oily and water capillary bridges.

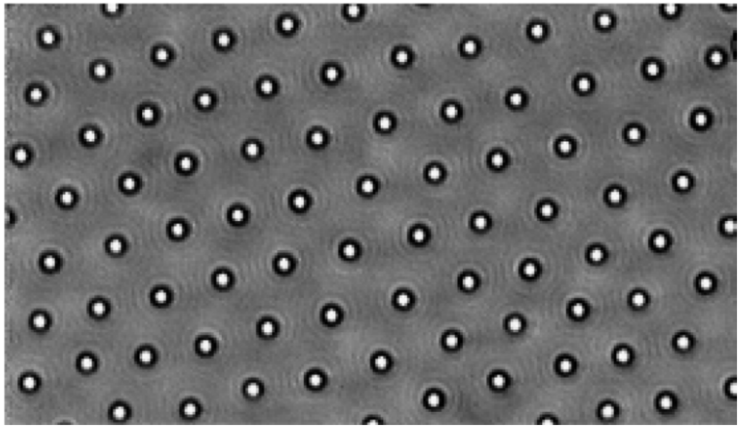
Why the yield stress *Y* is significantly lower for the water capillary bridges in oil?

The difference between the f_{max} vs. Φ curves for $\alpha = 0^o$ and 12^o is insignificant!

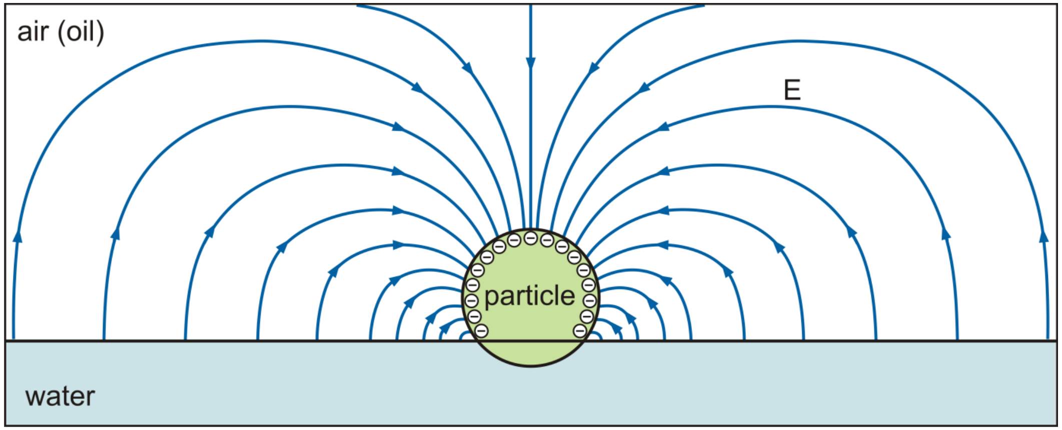
In both systems, the water phase contains 0.5 M NaCl (suppressed electrostatic interactions in the water phase).

However, the electrostatic repulsion across the oil phase is not screened!

Charged particles at an oil/water interface repel each other



R. Aveyard et al. *Langmuir* 2000, *16*, 1969; latex particles at octane/water interface

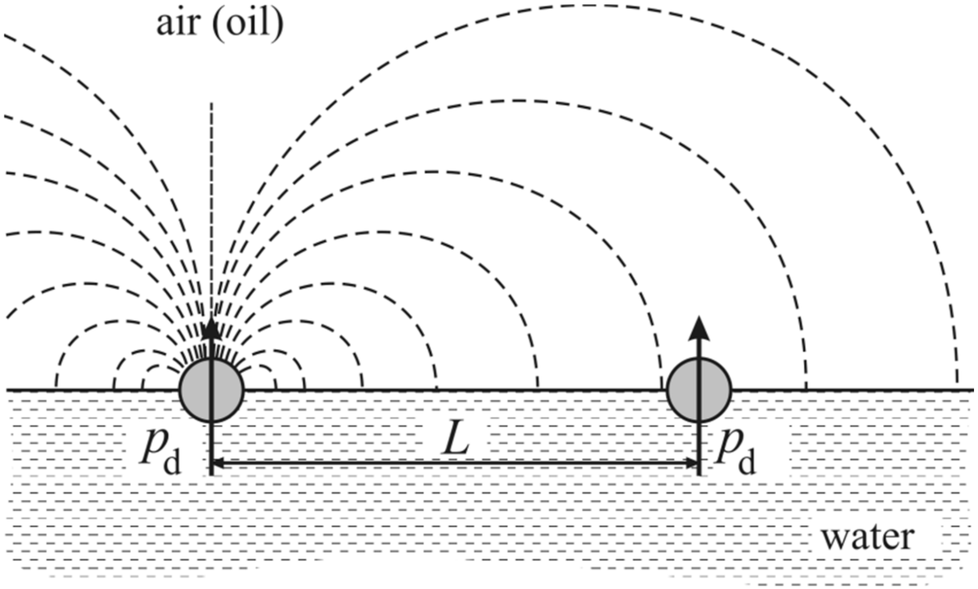


The interparticle repulsion is due to charges at the particle/oil interface.

Each two particles repel each other as two effective parallel dipoles:

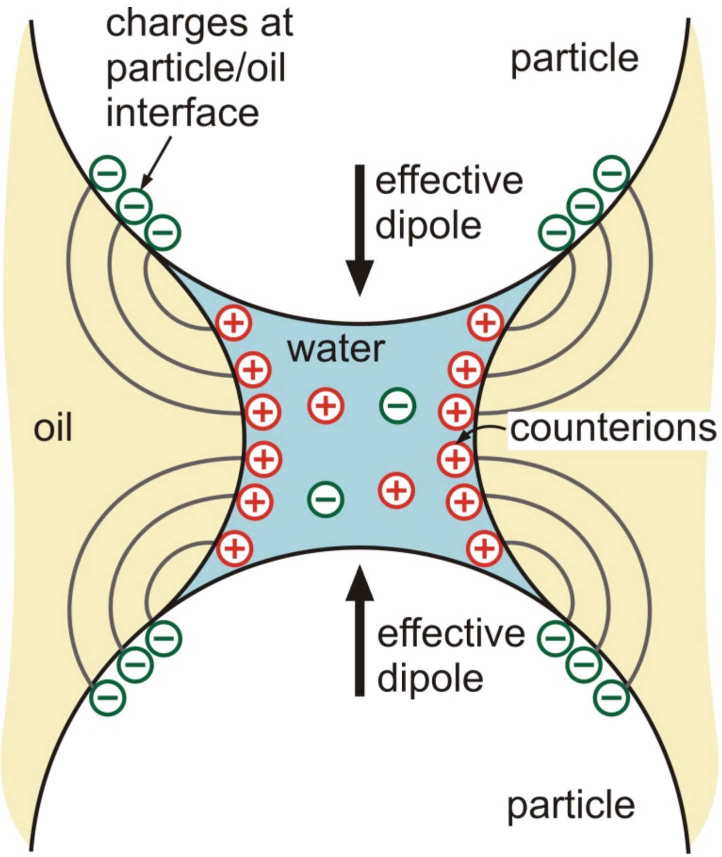
$$F = \frac{3p_\mathrm{d}^2}{8\pi\varepsilon_0\varepsilon_\mathrm{n}L^4}$$

Similar effect could be present for two particles connected by an aqueous capillary bridge in oil.



Danov et al. *J Colloid Interf Sci* 298 (2006) 213; Petkov et al. *J Colloid Interf Sci* 462 (2016) 223.

Charged particles at an oil/water interface repel each other



(the size of the capillary bridge is **exaggerated**)

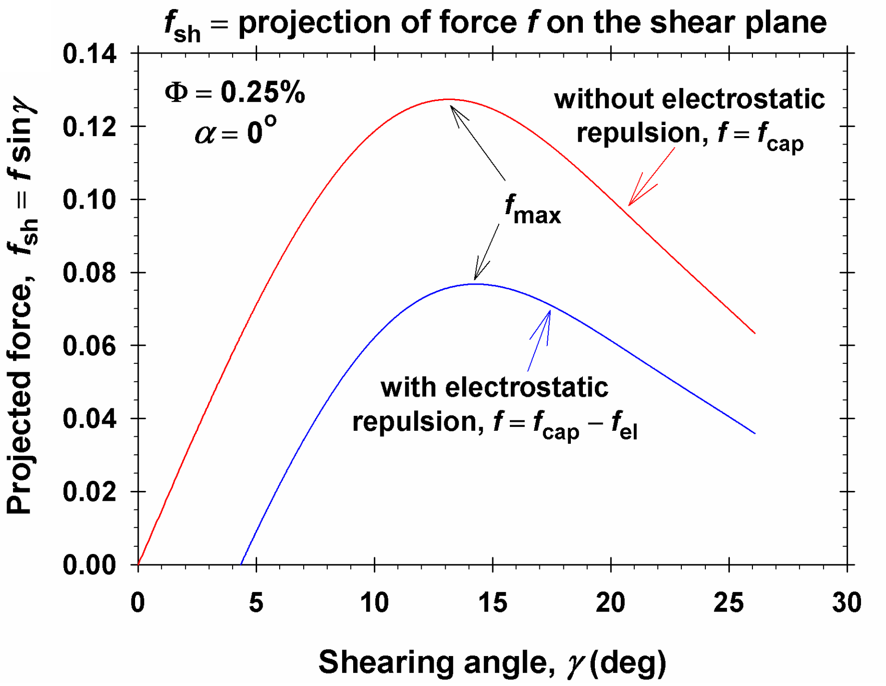
Force of electric repulsion between two oppositely directed dipoles:

$$F_{\mathrm{el}} = \frac{3 p_{\mathrm{d}}^2}{2\pi\varepsilon_0\varepsilon_{\mathrm{oil}}L^4}$$

The shear response force, F_{sh}, of due to the capillary bridge decreases because of the electric force:

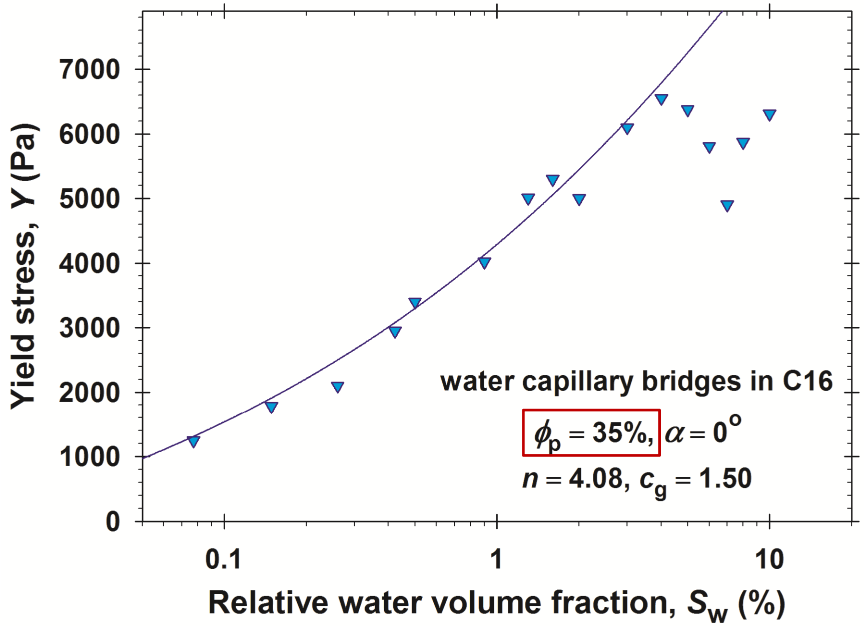
$$F_{\mathrm{sh}} = (F_{\mathrm{cap}} - F_{\mathrm{el}})\sin\gamma$$

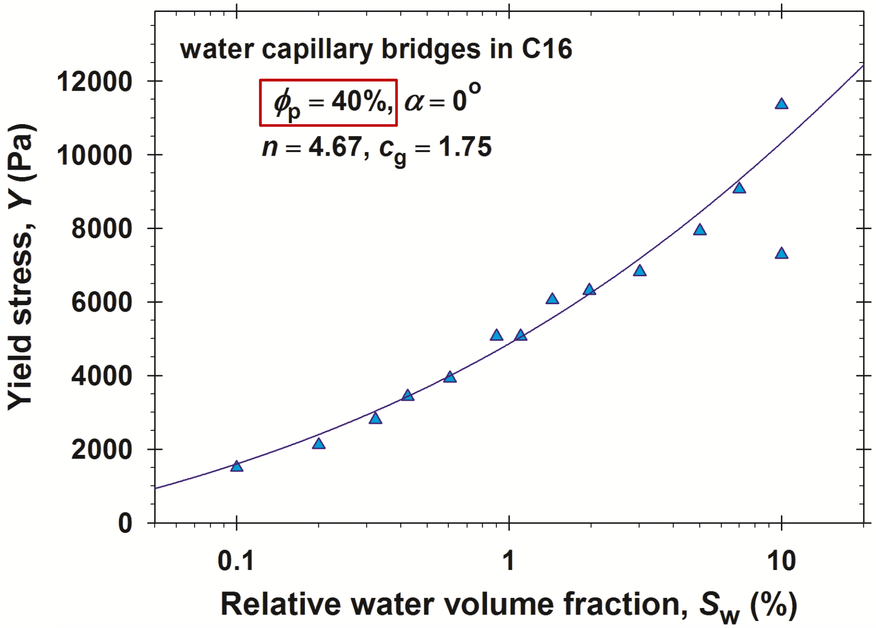
$Y \sim f_{\max}$ decreases because of the electrostatic repulsion:

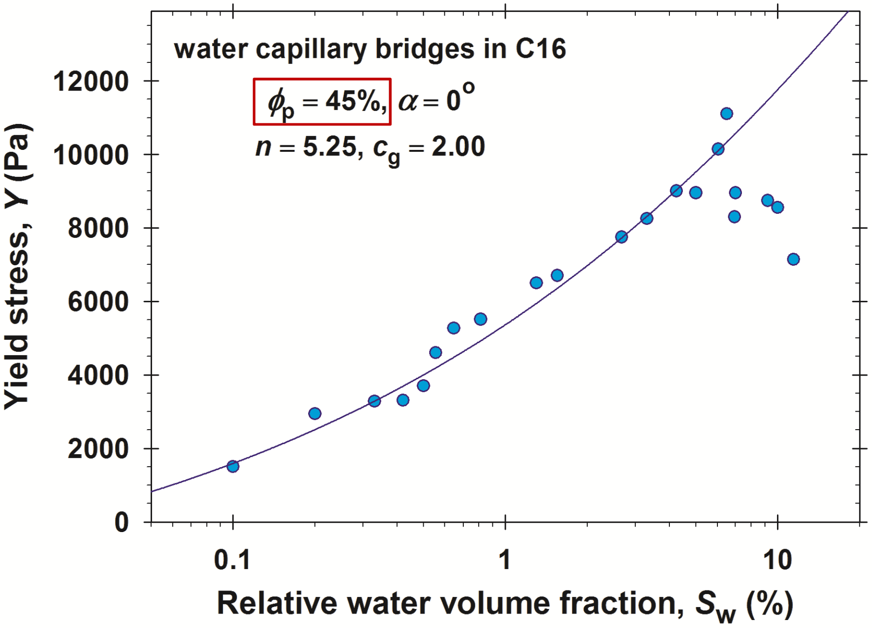


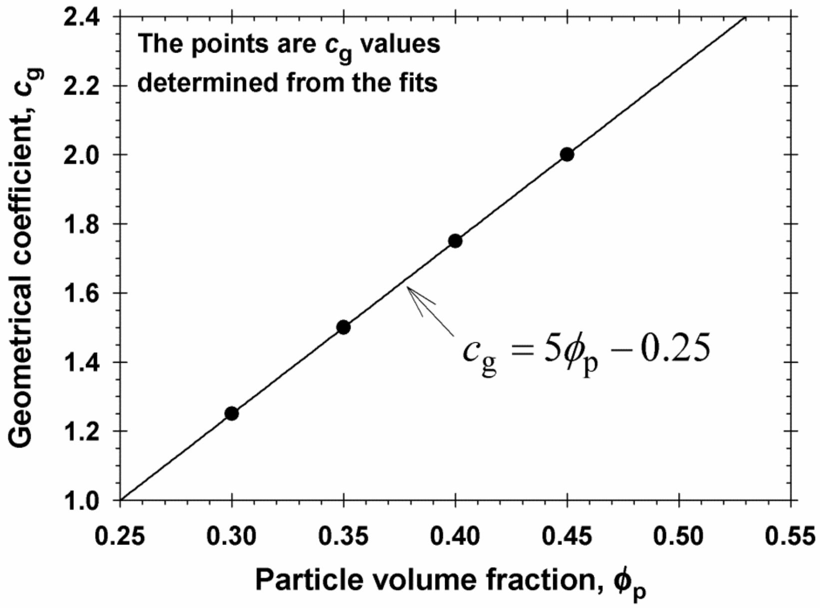
Comparison of theory and experiment

(water capillary bridges; C16 = hexadecane; $\alpha = 0°$)

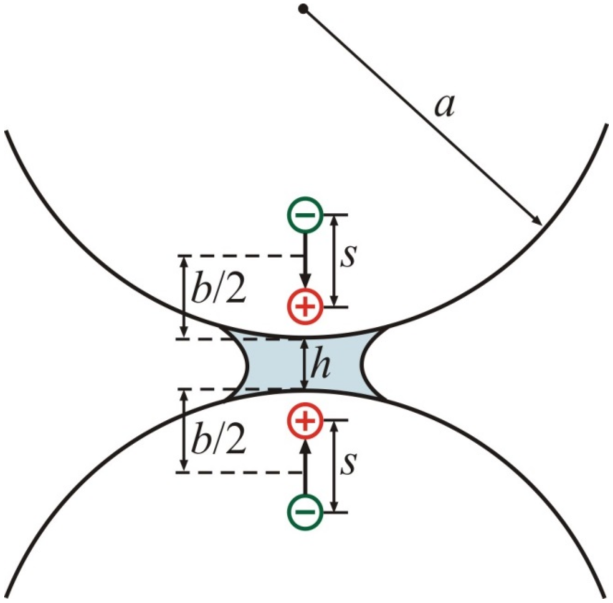


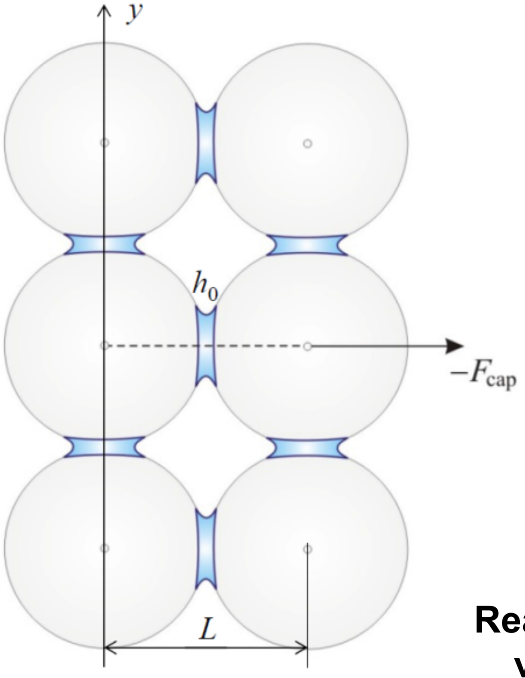






Parameters determined from the fits





Initial state

$$f_{\mathrm{el}} = \frac{F_{\mathrm{el}}}{2\pi a\sigma} = \frac{3p_{\mathrm{d}}^2}{4\pi^2 a\sigma\varepsilon_0\varepsilon_{\mathrm{oil}}L^4}$$

$$p_{\mathrm{d}} = qs = \frac{4\pi a^2}{n}\rho_{\mathrm{el}}s$$

$$L = b + h$$

$$s = \frac{s_1}{n}, \qquad b = \frac{b_1}{n}, \qquad (s_1, b_1 = \mathrm{const.})$$

(for greater *n*, the surface area that contributes to the dipole is smaller)

$$f_{\mathrm{el}} = \frac{12a^3(\boxed{\rho_{\mathrm{el}}s_1})^2}{\varepsilon_0\varepsilon b_1^4\sigma}\left(1 + n\frac{h}{\boxed{b_1}}\right)^{-4}$$

All 4 experimental curves are simultaneously fitted by varying only 2 adjustable parameters: $(\rho_{\mathrm{el}}s_1)$ and b_1

Reasonable parameter values are obtained: $\rho_{\mathrm{el}} \approx 0.30\,\mu\mathrm{C/cm}^2$ and $b/2 \approx a/2$

Conclusions

(1) The hardness (yield stress, Y) of three-phase particles/oil/water dispersions was investigated for particle volume fractions 35% $\le \phi_p \le$ 55%.

(2) Quantitative theoretical model was developed, which relates Y with the maximum of the resultant of capillary bridge force as a function of shearing angle; the model agrees very well with the experimental data.

(3) The yield stress Y increases with the rise of interfacial tension, σ, and with the volume fractions of particles, ϕ_p, and capillary bridges, Φ, and decreases with the rise of particle radius, a, and contact angle α.

(4) For water-in-oil bridges, Y is systematically lower than for the respective oil-in-water bridges because of electrostatic repulsion between the particles across the oil phase, which opposes the capillary-bridge attraction.

(5) Deviations between theory and experiment (due to dynamic reasons) were observed at greater contact angles of the bridge phase and higher viscosities of the continuous phase.

For more details, see the papers:

K.D. Danov, M.T. Georgiev, P.A. Kralchevsky, G.M. Radulova, T.D. Gurkov, S.D. Stoyanov, E.G. Pelan, ***"Hardening of Particle/Oil/Water Suspensions Due to Capillary Bridges: Experimental Yield Stress and Theoretical Interpretation."*** *Adv. Colloid Interface Sci*. **251** (2018) 80–96.

M.T. Georgiev, K.D. Danov, P.A. Kralchevsky, TD. Gurkov, D.P. Krusteva, L.N. Arnaudov, S.D. Stoyanov, E.G. Pelan. ***"Rheology of Particle/Water/Oil Three-Phase Dispersions: Electrostatic vs. Capillary Bridge Forces"***. *J. Colloid Interface Sci*. **513** (2018) 515–526.