Complementary Techniques

Particle size, distribution & charge linking rheology

Anamet Seminar, 2019

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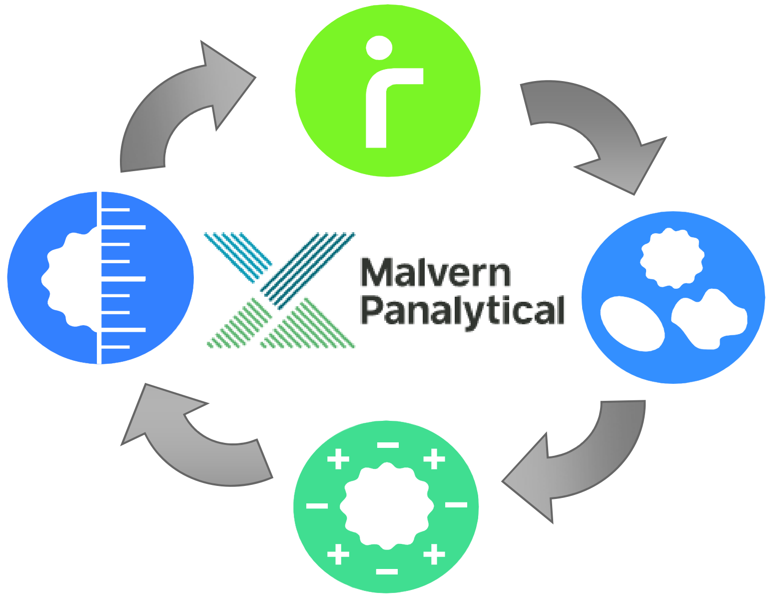
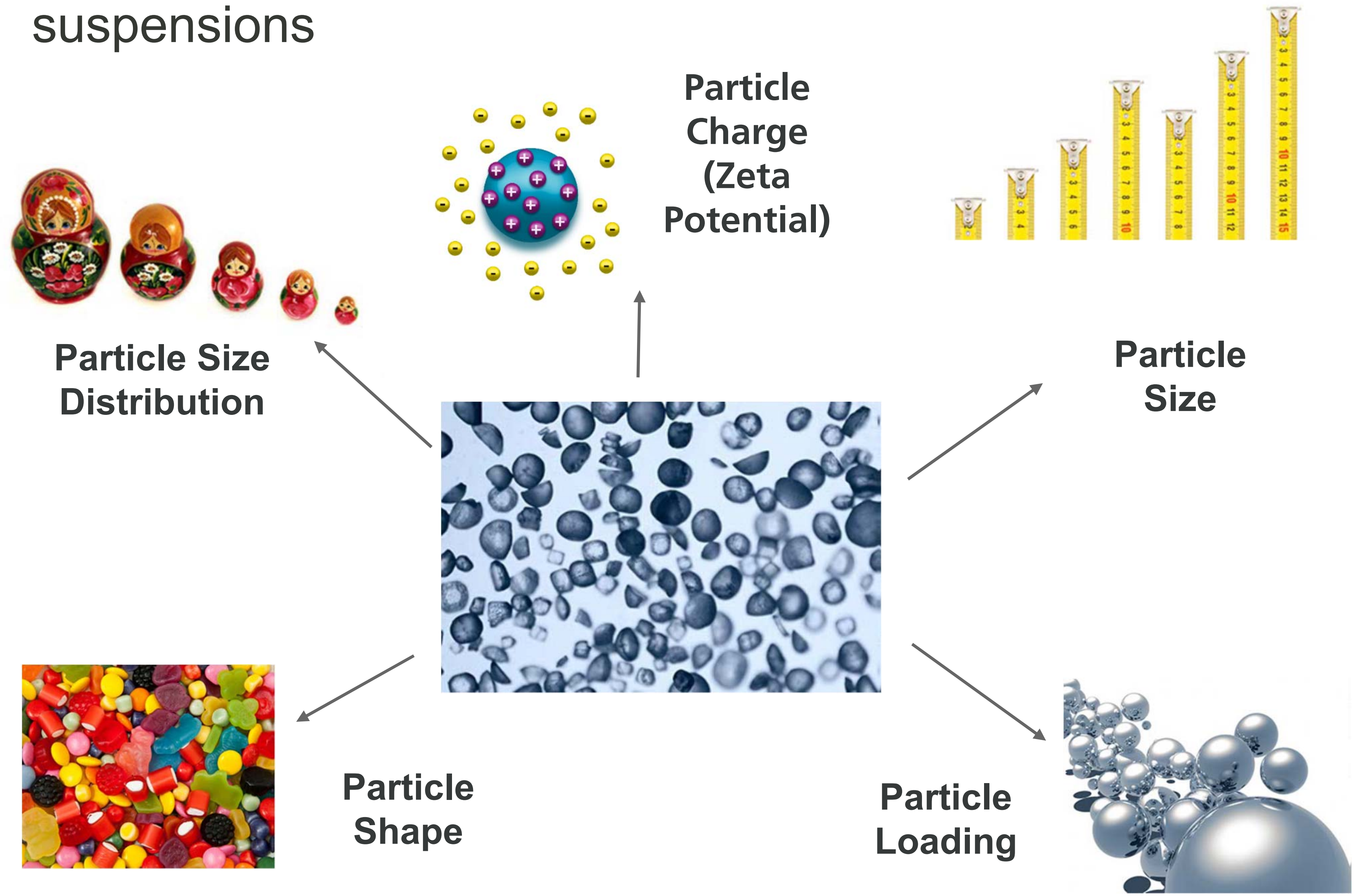
(40 mins)
Brno
May 2019

Overview

- Rheology Overview
- How particle properties link to rheology
- Suspension Stability
  - Particle Size
  - Particle Loading
  - Particle Size Distribution



Rheology-determining factors of suspensions



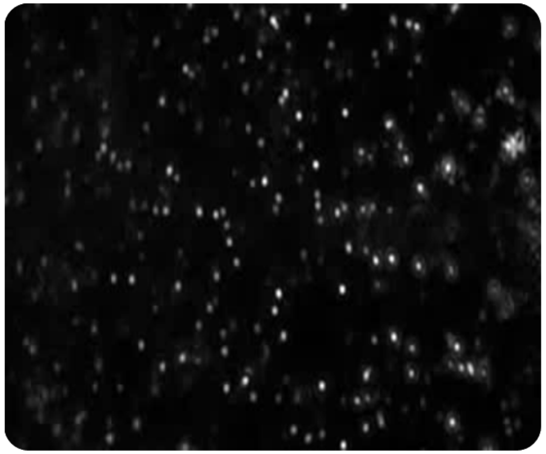
PARTICLE SIZE

Effect of particle size

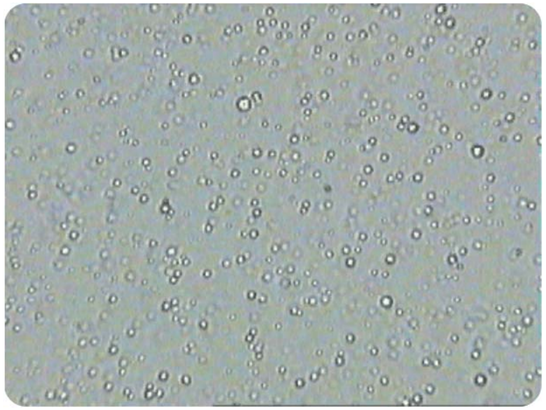
- For **small** (<~1um) particles colloidal effects on rheological properties can be significant:
  - Brownian motion
    - The random movement of particles due to the bombardment by the solvent molecules that surround them
  - Attractive / repulsive colloidal forces

- For **large** (>~1um) particles the direct effect on rheology is much less
  - The affect is more related to the associated change in volume fraction

Nanoparticles **(small)**



Emulsion Droplets **(large)**



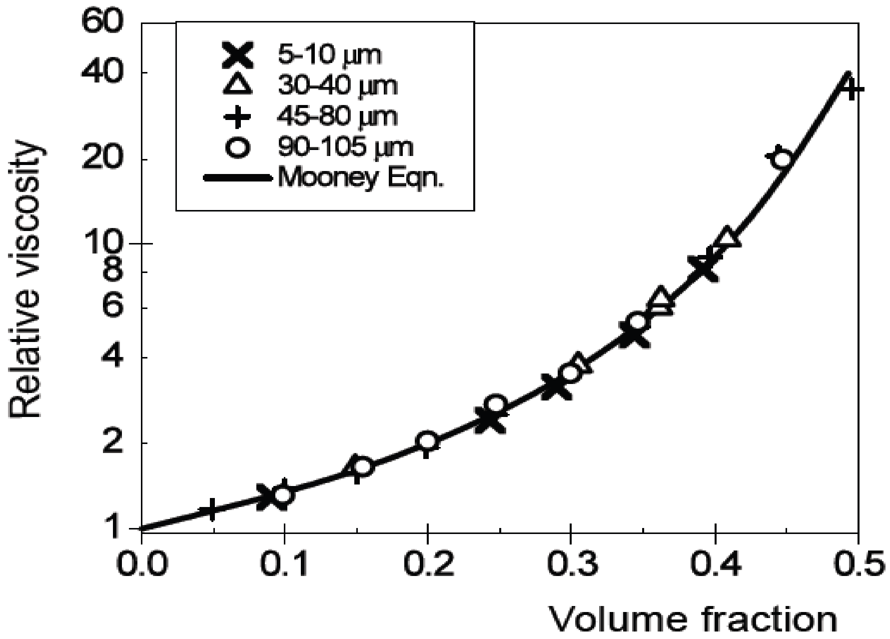
Effect of particle size

- For **large particles** (>~1um) the direct effect of increasing size shows **little viscosity difference** for the **same volume fraction**
- **Increasing volume fraction** for the same particle size, increases viscosity

› For **small particles**,(<~1um) there is a relationship

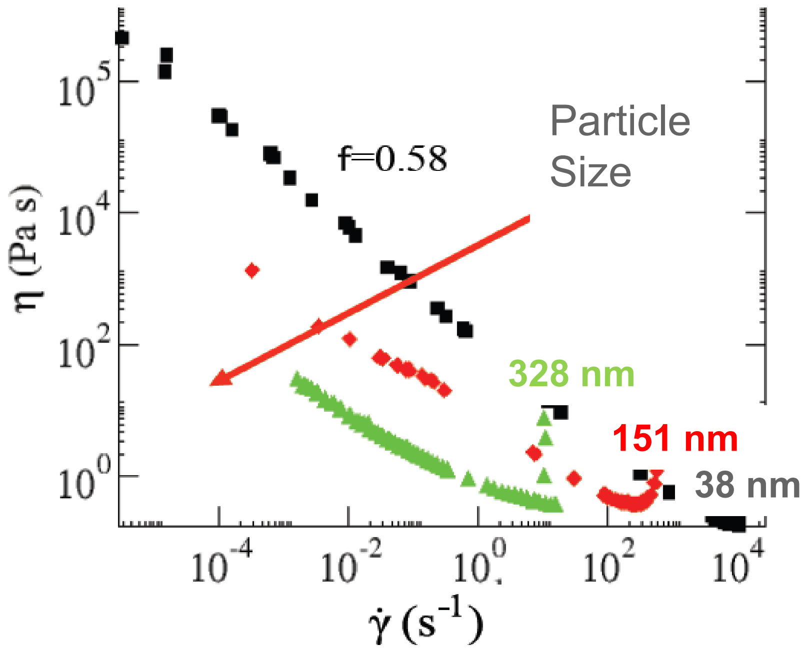
› **Decreasing** particle size gives a **increased** viscosity

Large particles



Colloidal Suspension Rheology Jan Mewis, Norman J. Wagner, 2012

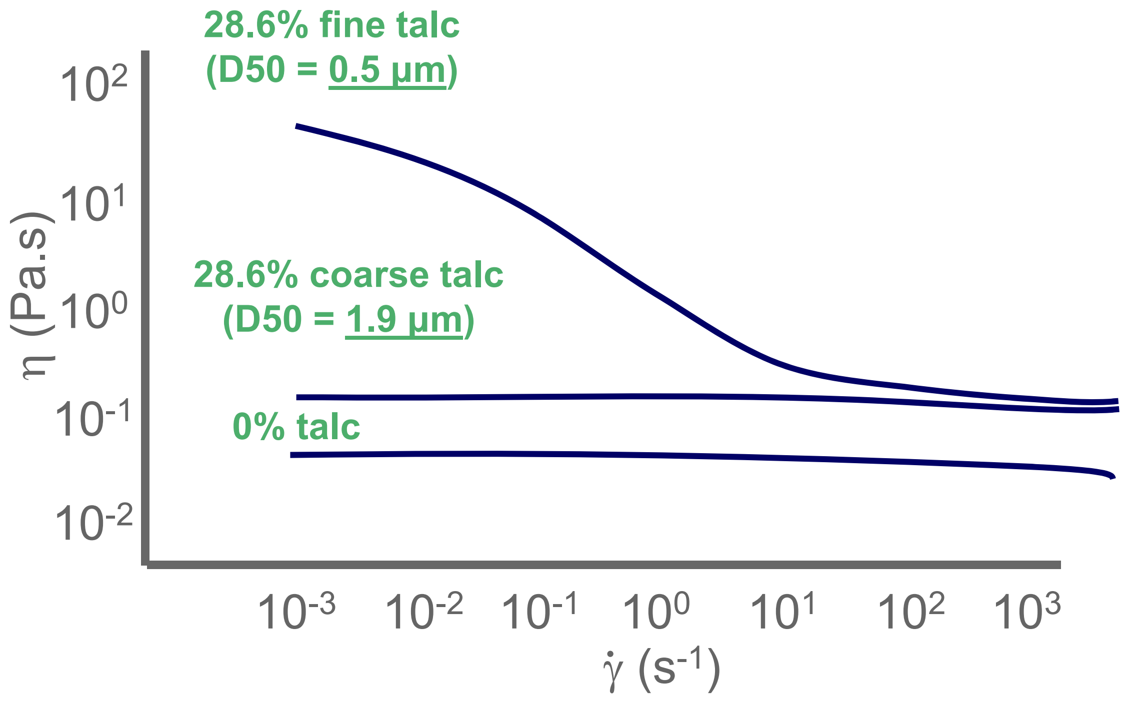
Small particles



Lewis & Nielsen 1968

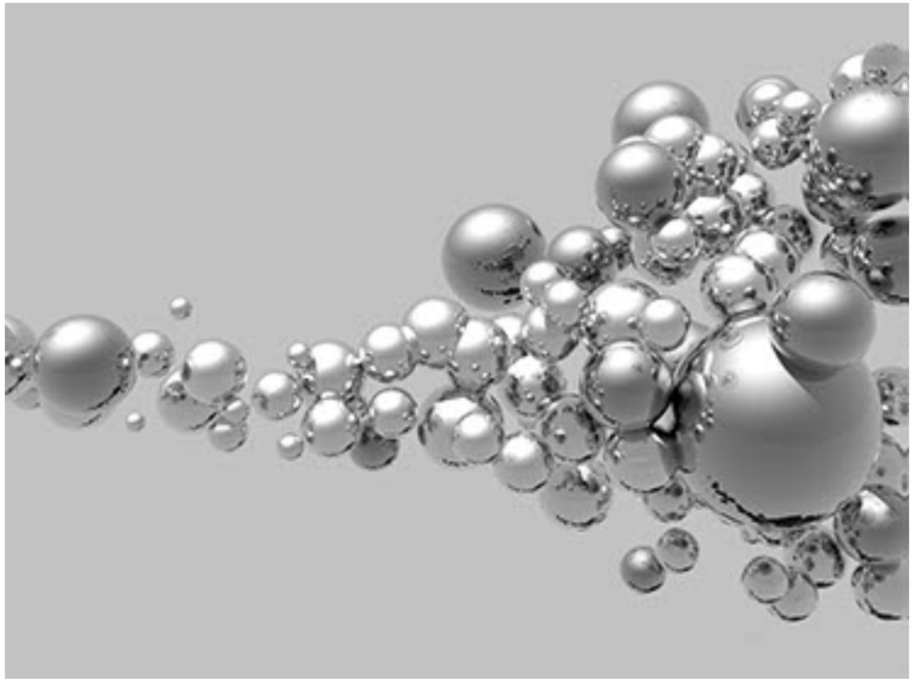
Effect of particle size

- Adding coarse talc to an epoxy
- For constant volume fraction decreasing particle size will increase viscosity
- The increased number of small particles give rise to colloidal repulsion, increasing viscosity at low shear



› This relatively weak force is broken down at higher shear rate leading to the converging of viscosities

PARTICLE LOADING



Effect of particle loading

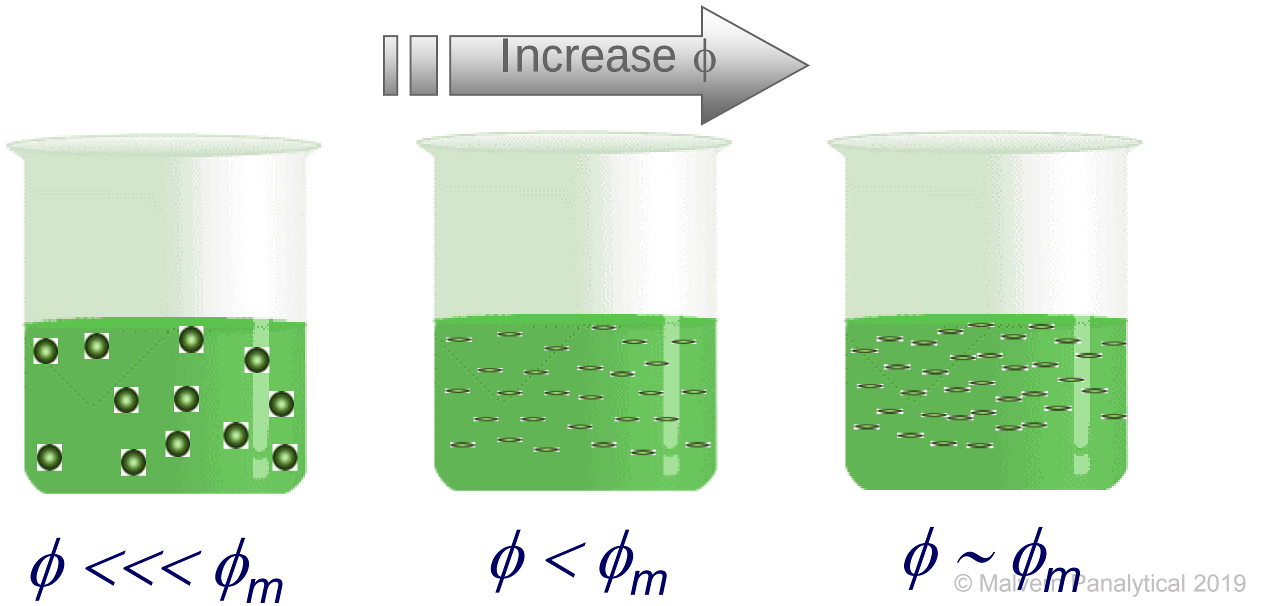
Krieger-Dougherty equation

$$\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

- η – viscosity of the suspension
- η_{medium} – viscosity of the medium
- ϕ – volume fraction of solids in the suspension
- ϕ_m – maximum vol. fraction of solids in the suspension
- $[\eta]$ – intrinsic viscosity of the medium (2.5 for spheres)

Volume fraction, ϕ

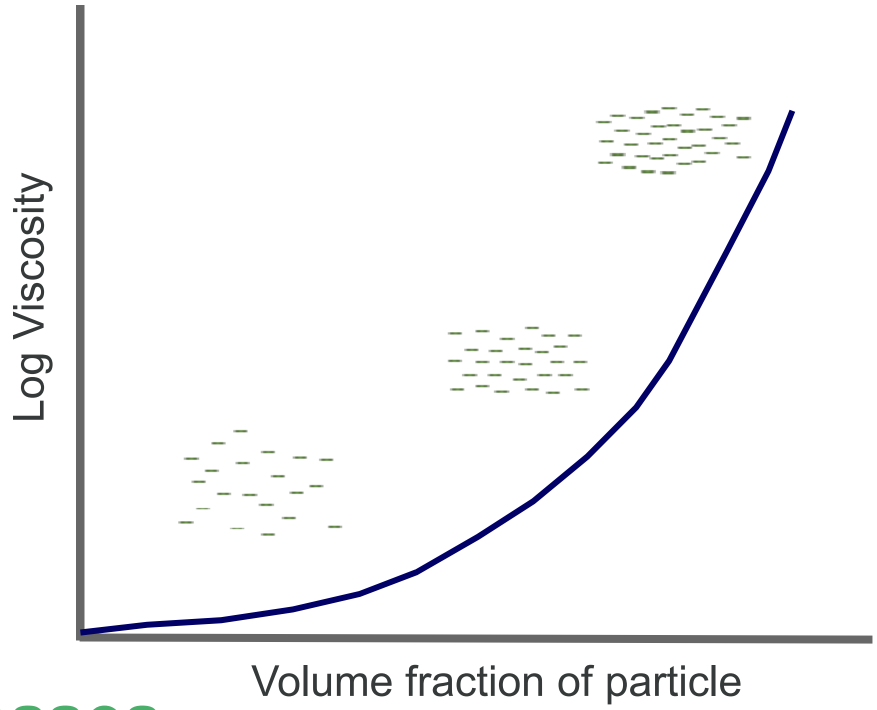
- Describes the **amount of particles** in a material
- ϕ – volume fraction of solids in a suspension
- ϕ_m – maximum volume fraction of solids in the suspension (i.e. the maximum amount of particles that can be added to the suspension)



Effect of particle loading

As volume fraction (ϕ) increases…

$$\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$



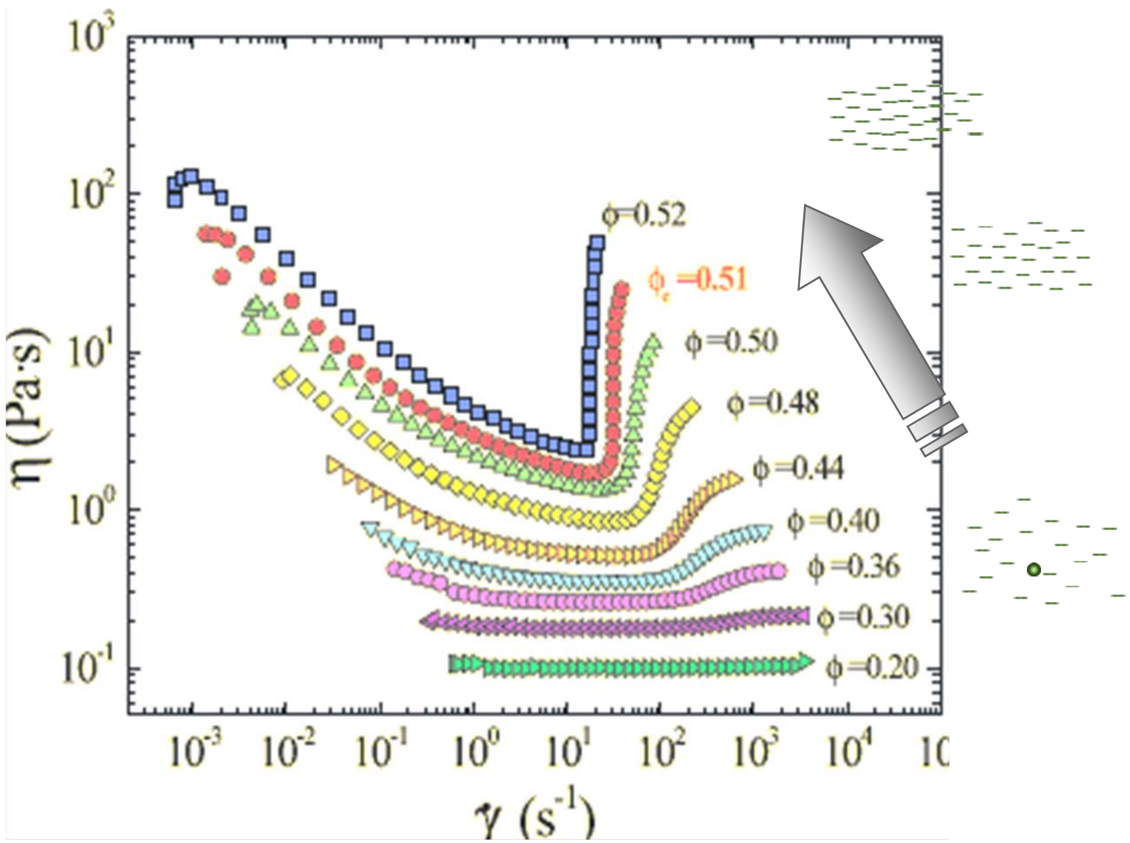
- Then **viscosity (η) increases**.
- Packing more molecules makes flow more difficult.

Volume fraction

- Viscosity **(η)** is increasing with an increased volume fraction as suggested by **Krieger-Dougherty**

$$\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

› Packing more molecules makes flow more difficult



Kinetic Sand

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Kinetic Sand vs. Play Putty

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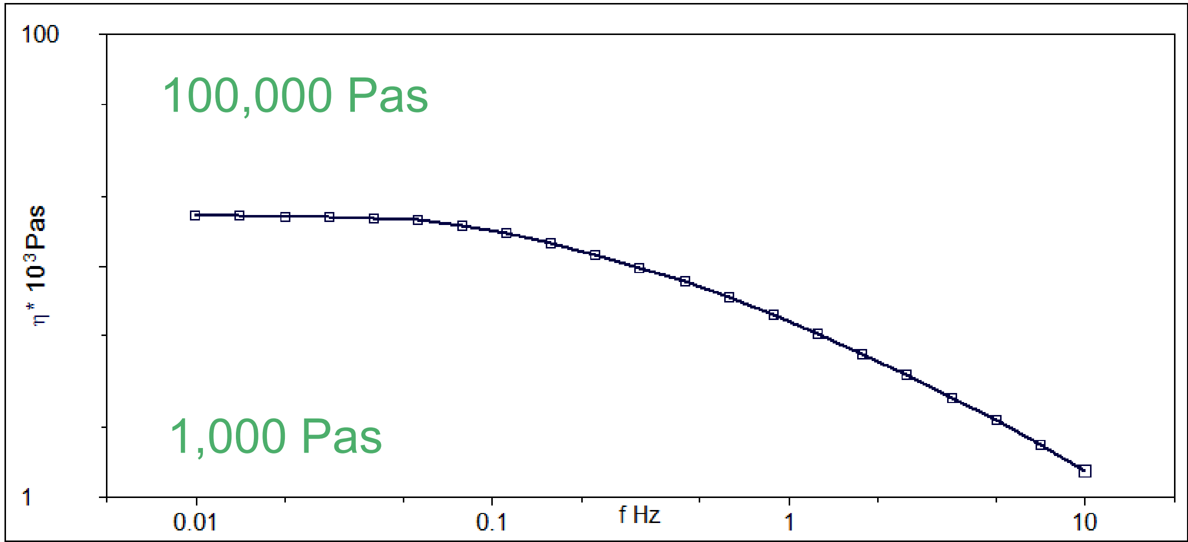
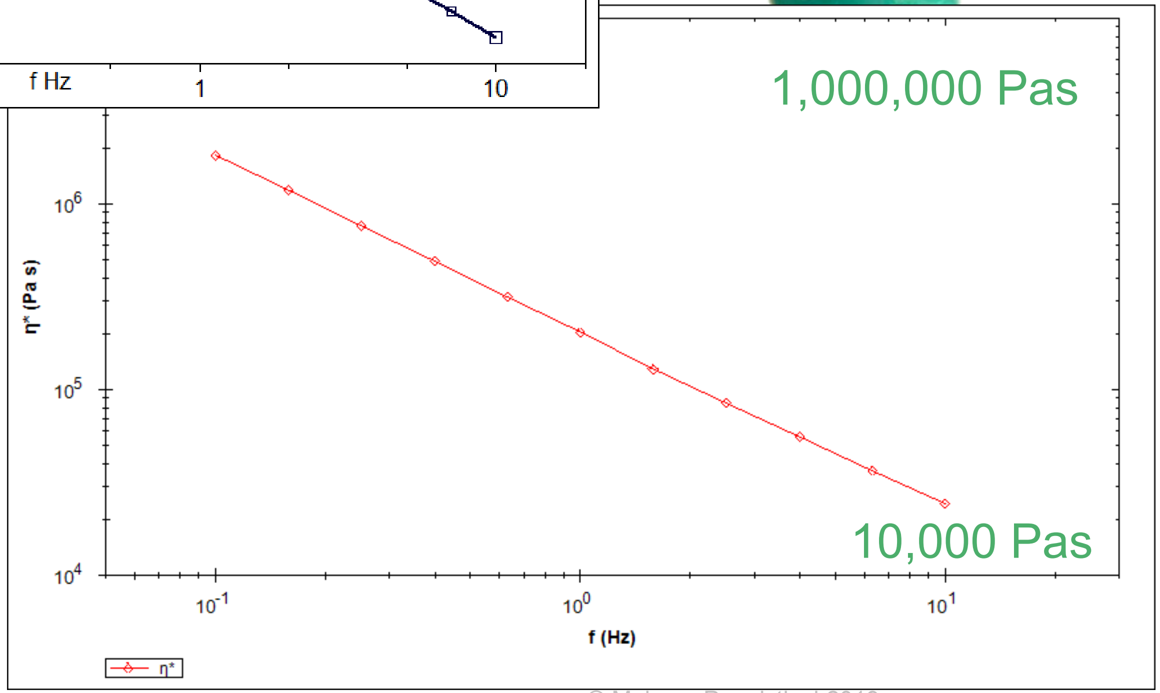
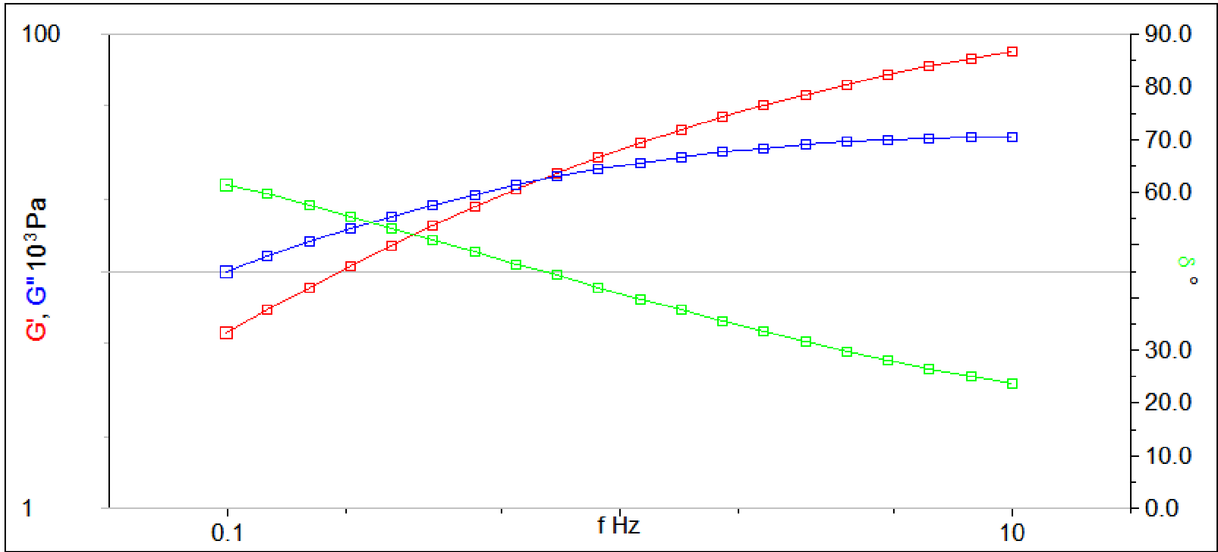


Play Putty



Kinetic Sand

Kinetic Sand vs Play Putty

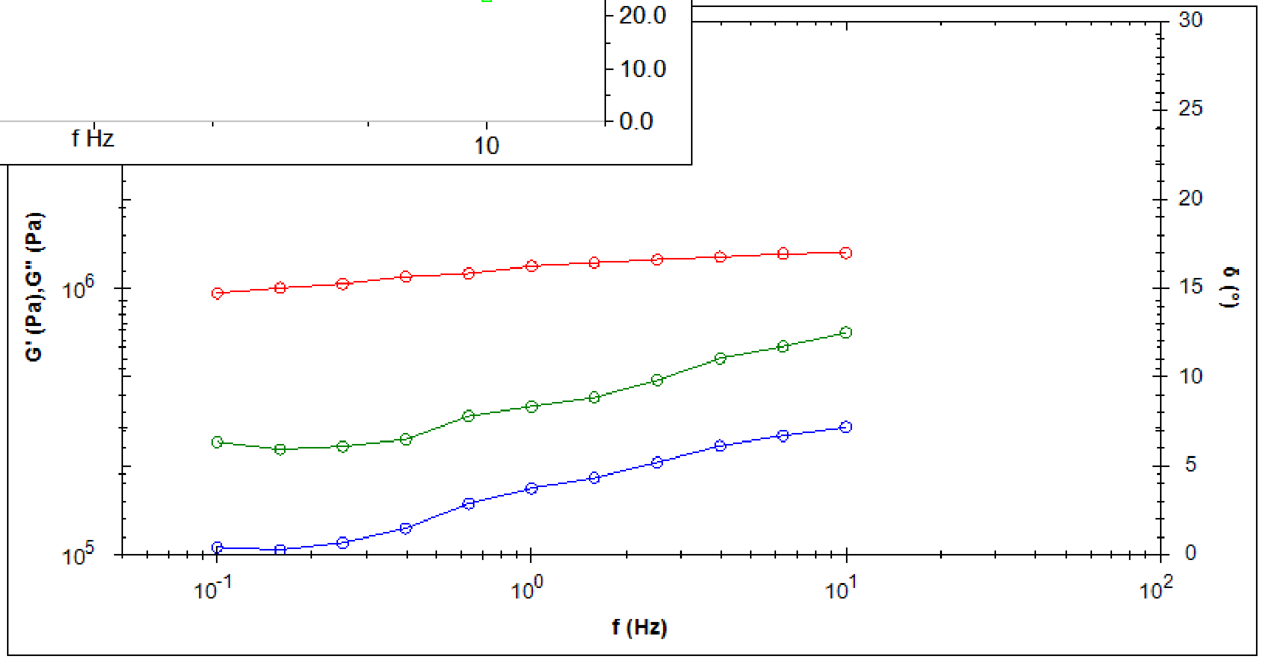


Play Putty

Viscoelastic LIQUID

Phase angle approaches

90˚ towards 0Hz



Viscoelastic SOLID

Phase angle approaches

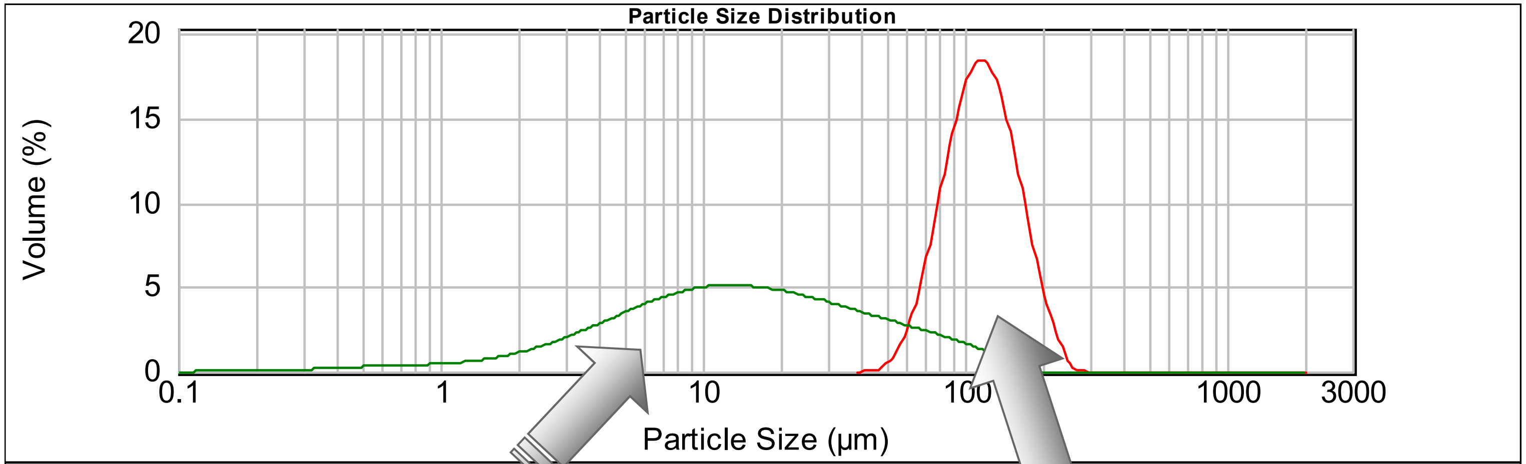
0˚ towards 0Hz

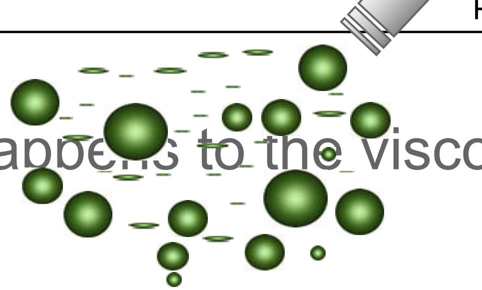
Kinetic Sand

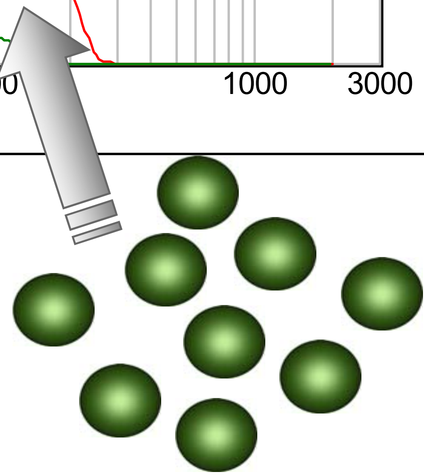
PARTICLE SIZE DISTRIBUTION

Effect of particle size distributions

- We can keep the volume fraction (ϕ) the same.
- Now, change the particle size distribution…



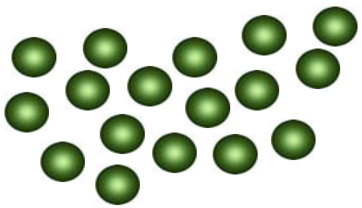
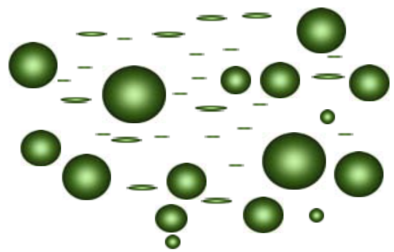




- What happens to the viscosity?

Effect of Distribution on Maximum Packing Fraction

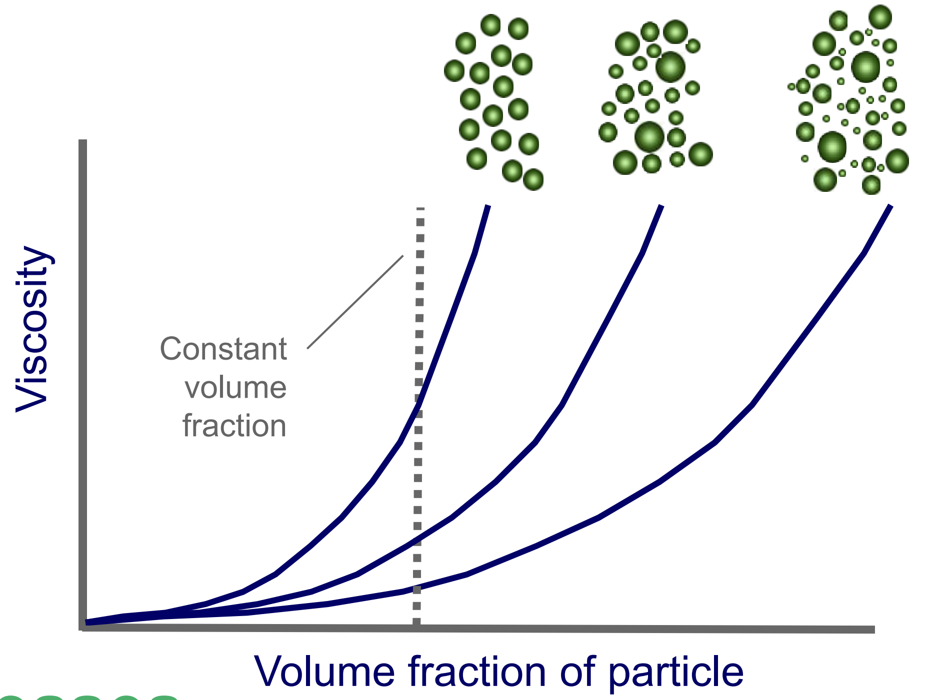
- As the particle size distribution increases, this allows a greater packing fraction.

Random monodispersed close packing	Random polydisperse close packing
	
$\phi_m \approx 0.62$	$\phi_m \geq 0.74$

Effect of Maximum Packing Fraction

- As **maximum packing fraction increases…**

$$\frac{\eta}{\eta_{medium}} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$

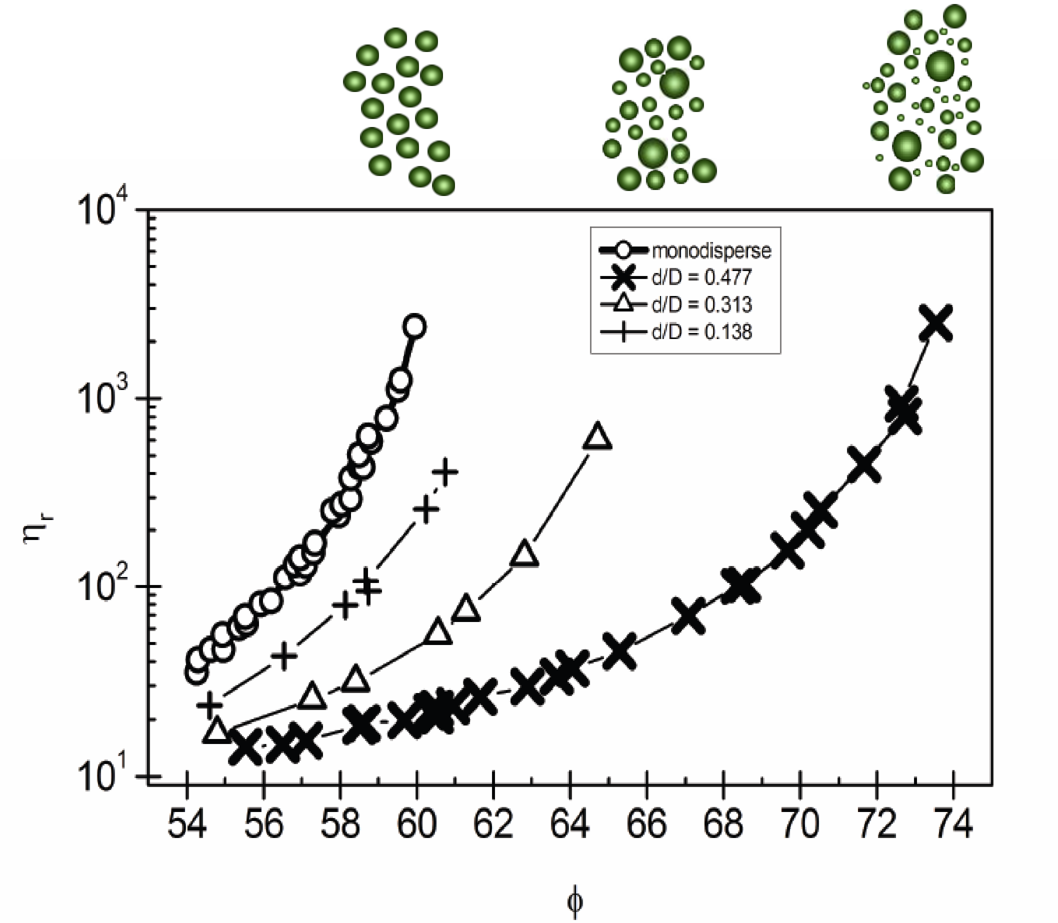


› Then **viscosity (η) decreases.**

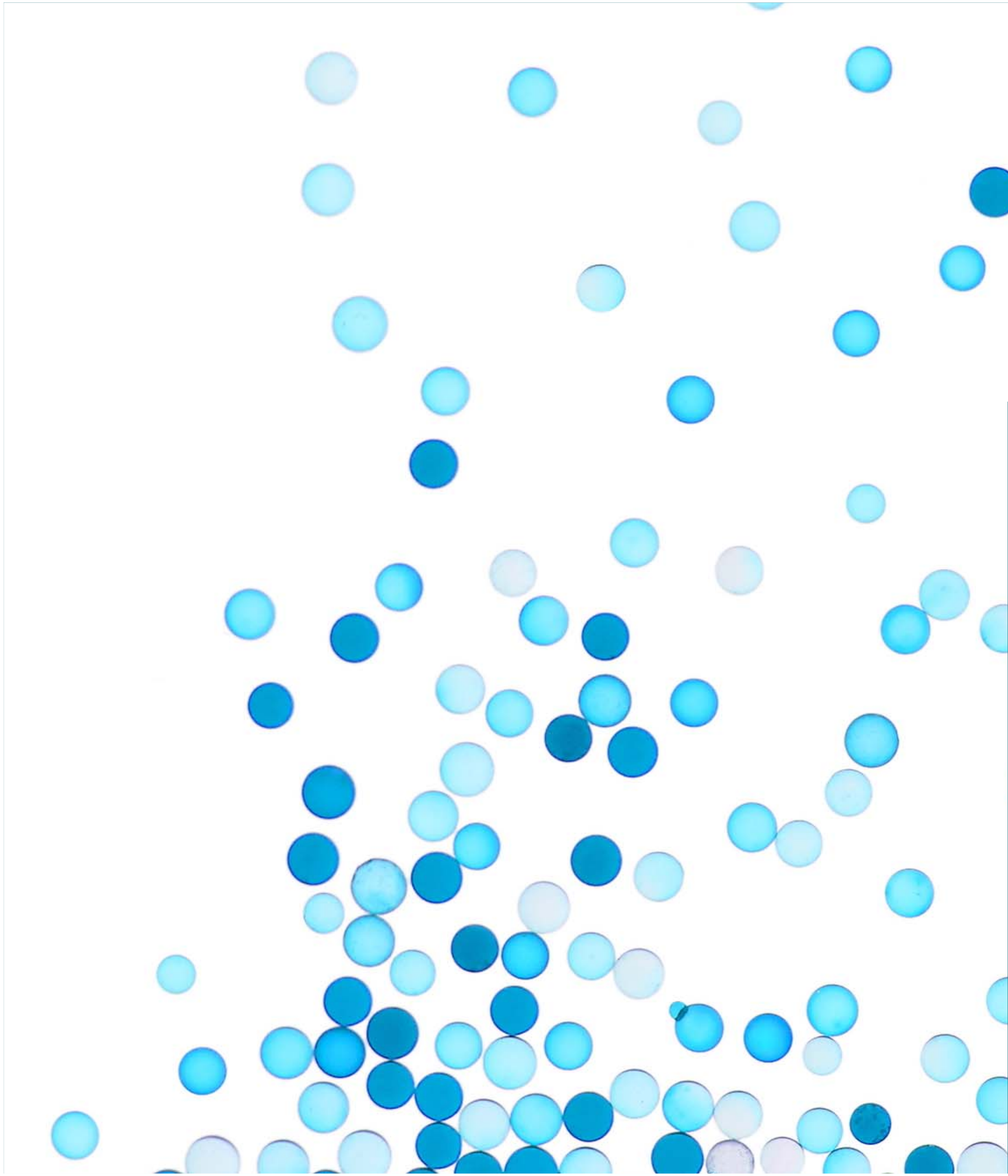
› Allows more free flowing particles (self lubricating)

Effect of particle size distribution

- For the same volume fraction and particle size, a **narrow particle size distribution** has a **higher viscosity** compared to a broad particle size distribution.
- As size **distribution increases**, Φ_m increases in the Krieger Dougherty equation, resulting in a **reduced viscosity**.



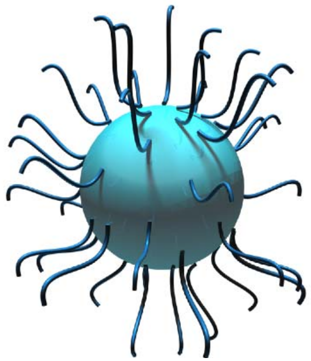
Chong et al. 1971

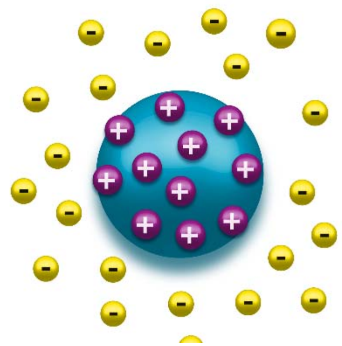


Stability

How to Achieve Stability?

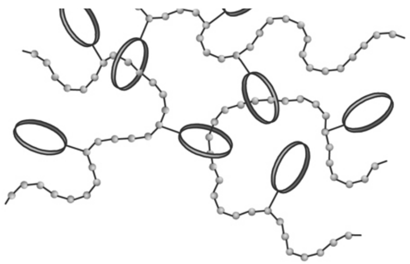
- Prevent coagulation through **inter-particle repulsion**





- Slow down sedimentation by **increasing viscosity** of continuous phase

- Make it ‘solid’ by creating a **network structure**



Stability: Which Method?

…. It Depends

- **Particle radius** (a) will have a large bearing on suspension stability
- For **sub micron** particles **Brownian motion** is usually significant to overcome effect of gravity
- For **larger particles gravity dominates** if there is a significant density difference (*Δρ*)

Gravitational Forces $a^4 \Delta\rho g$ $k_B T$ Brownian Forces

The Structure and Rheology of Complex Fluids; R Larson

al 2019

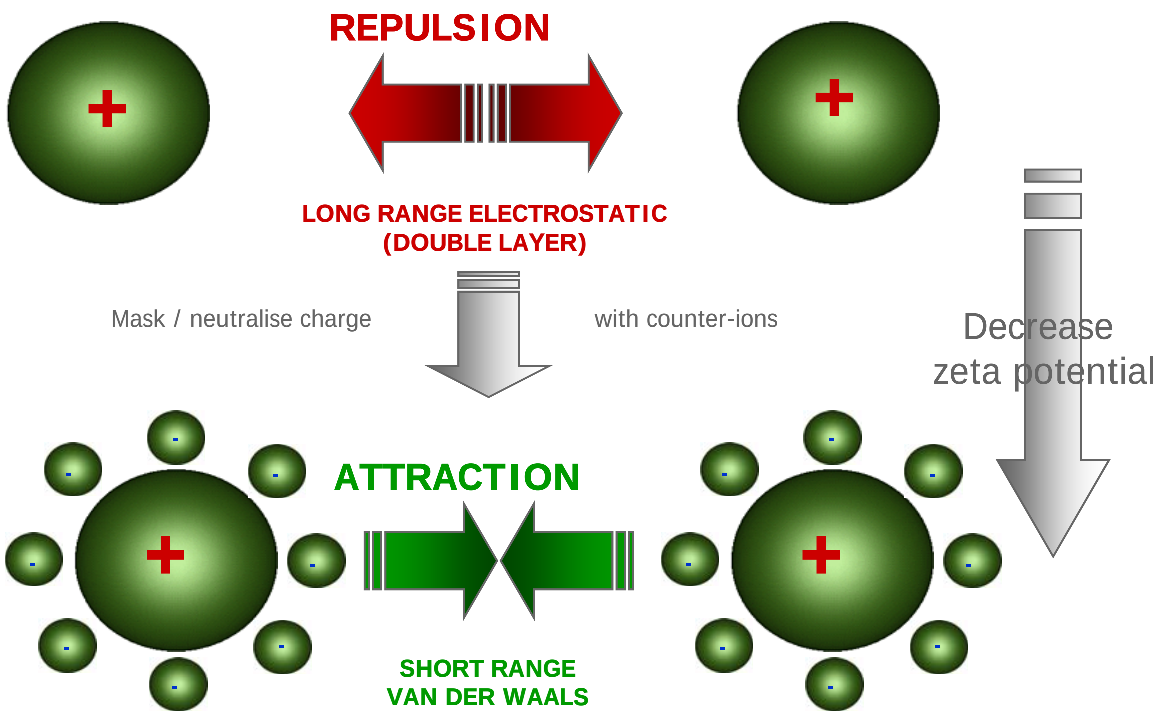
EXPERIMENTAL EXAMPLE

Experimental

- 75% w/w Silica dispersion made up in deionised water
- Zeta potential evaluated using a Malvern **Zetasizer Nano** ZS with autotitrator
- Particle size evaluated using a Malvern **Mastersizer**
- Rheological properties measured using a **Kinexus** rheometer

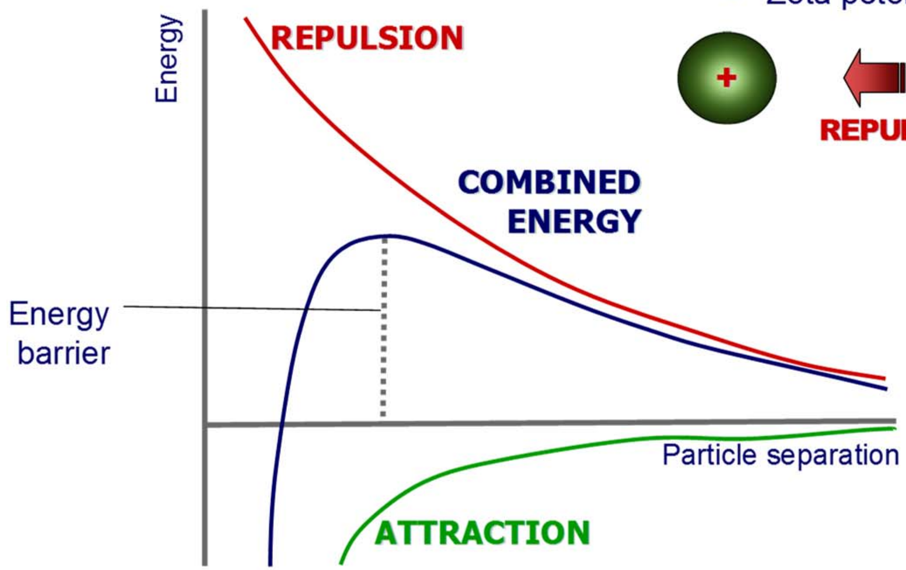
Colloidal Stability

- To maintain stability through Brownian motion we need to prevent particles sticking when they collide
- This can be achieved by increasing the charge associated with the particle i.e. **zeta potential**.



Colloidal stability and DLVO Theory

- An energy barrier resulting from combination of the attractive and repulsive forces prevents particles approaching each other closely.

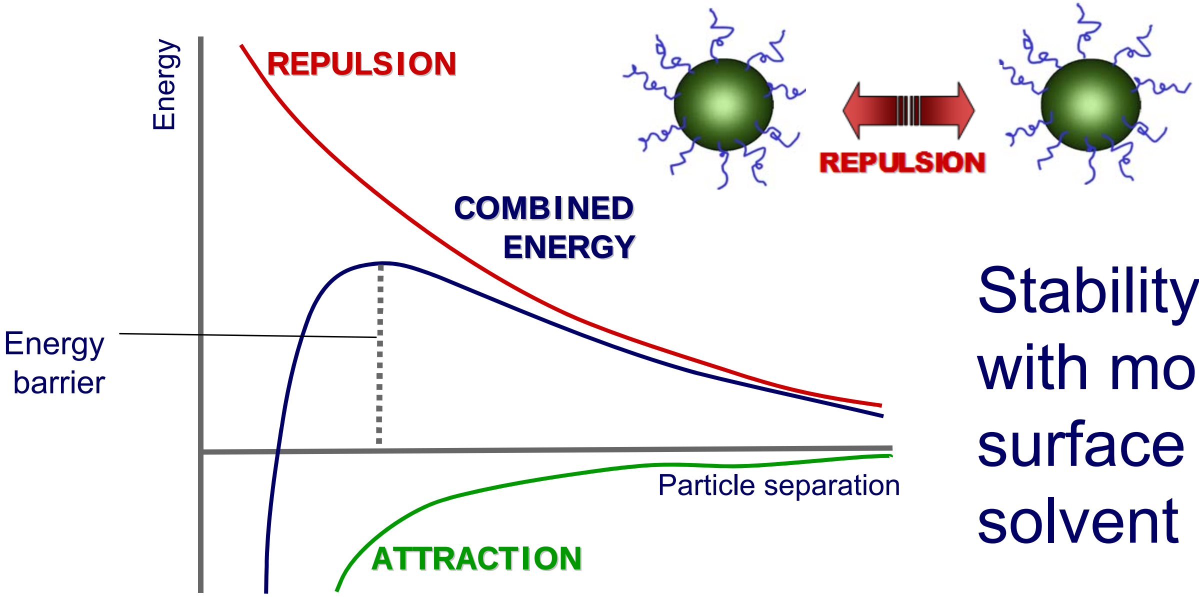


+/- 30mV considered suitable threshold value for stability

- So long as particle Kinetic Energy does not exceed this barrier coagulation should not occur.

Colloidal stability by steric means

- An energy barrier can also result by adsorbing of amphiphilic polymers onto the particle surface preventing close approach

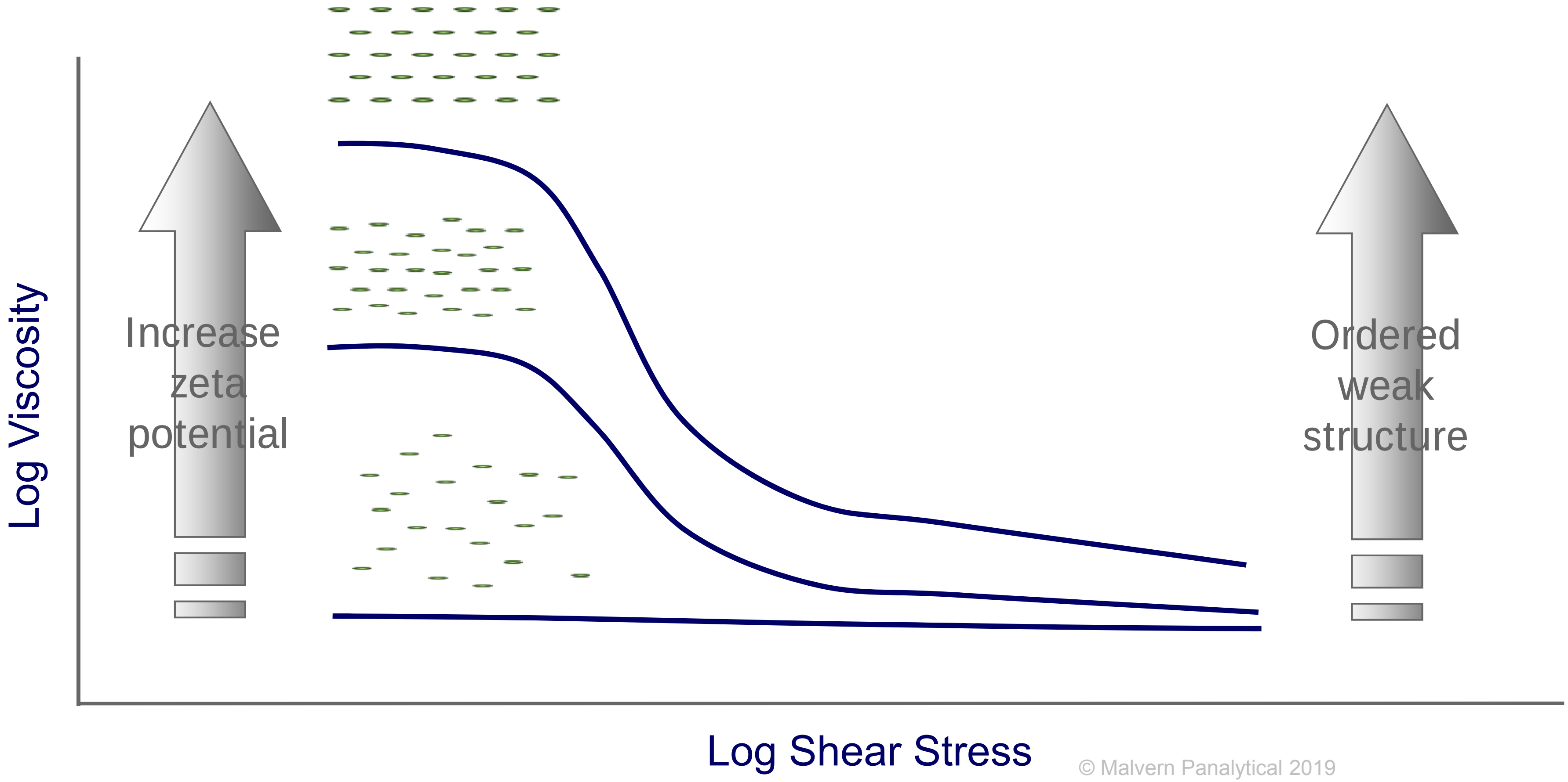


Stability tends to increase with molecular weight, surface coverage and solvent affinity

- A steric mechanism is likely to be much more efficient in non-aqueous solvents and high electrolyte systems

Effect of zeta potential on low shear viscosity

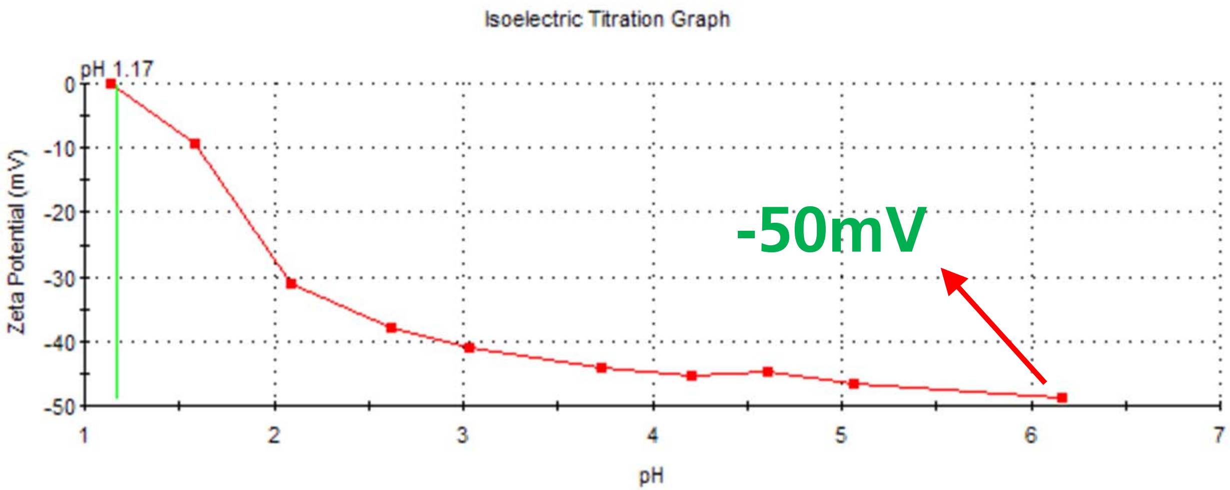
- Low shear viscosity increases with increasing zeta potential thus high charge will help slow down sedimentation



Silica Dispersion Stability

Why is it not stable?

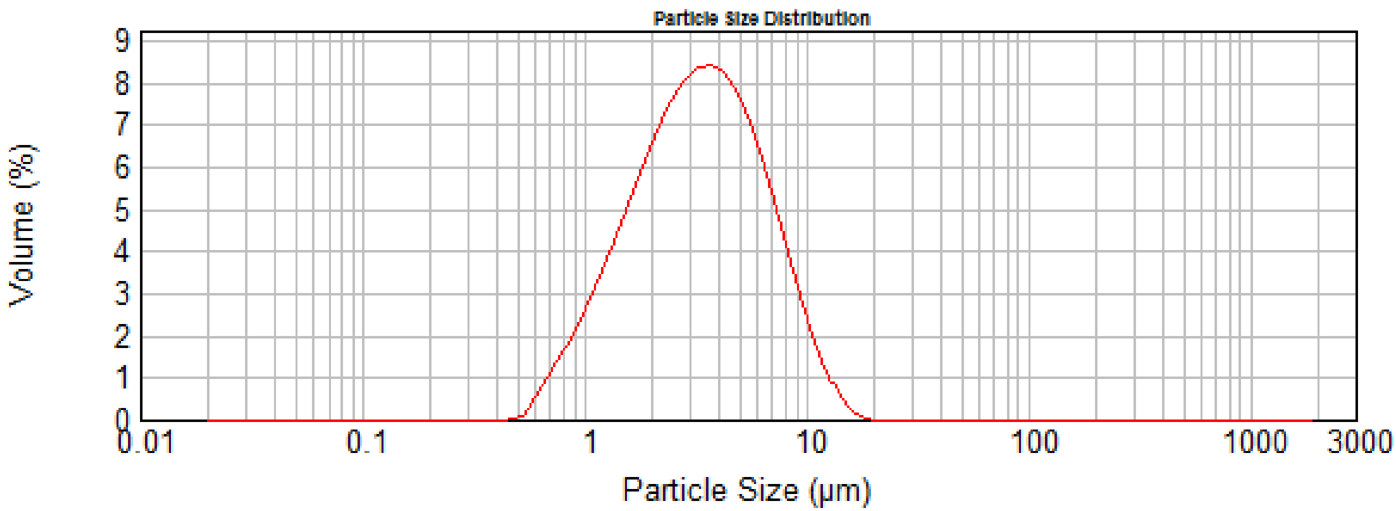
- Initial sample evaluation made using at natural pH of dispersion 6.2.
- Despite having a zeta potential of – 50 mV the suspension was found to be unstable.



- Lets check particle size…

Particle Size and Density

- Sample was characterised on a Mastersizer and was found to have a **median particle size of 3.7 µm.**
- The **largest** particle was approximately **20 µm.**



- Particle density was 2600 kg/m^3

Force Balance on Particle

- The above relationship for the median particle size (3.7 µm) gives a value of **45** and for the largest particle (20 µm) a much higher value of **38,000**!!
- This means that **gravitational forces are dominant** for this sample
- This would explain why **sedimentation occurs** and indicates that another approach is required to induce stability

How to Achieve Stability?

No one method

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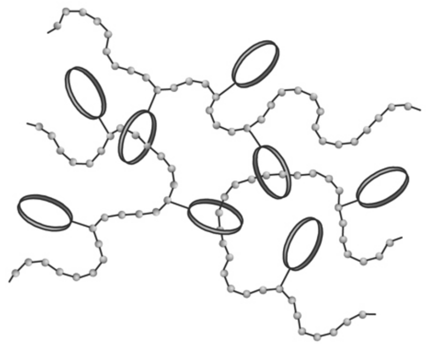
- Prevent coagulation through inter-particle repulsion

Only for particles less than 1 micron

- Slow down sedimentation by increasing viscosity of continuous phase

- Make it Solid by creating a network structure



VISCOSITY / KINETIC STABILITY

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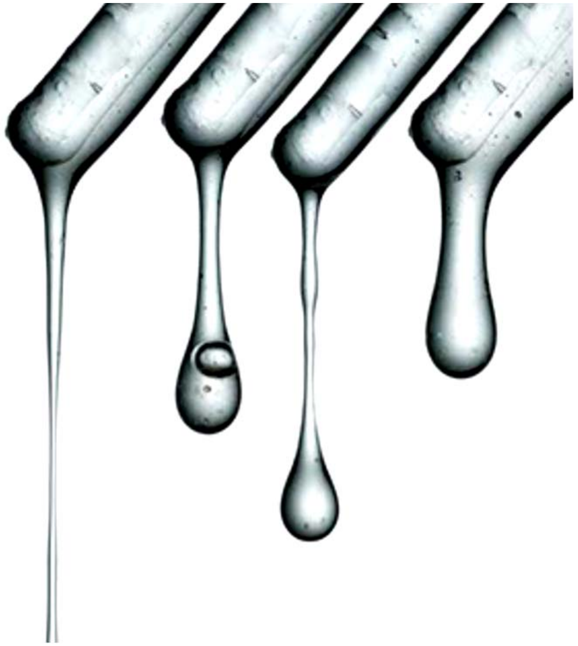
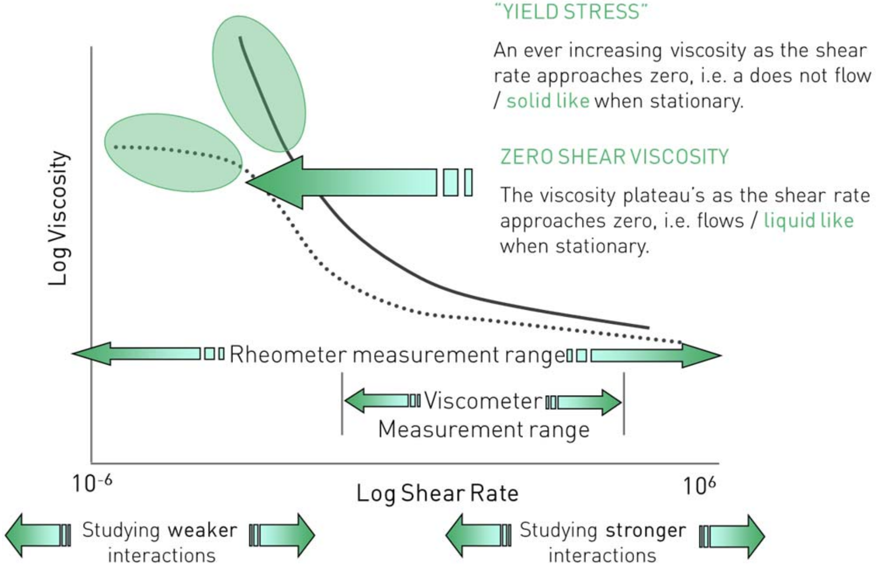
Effect of Viscosity (Dilute Systems)



- Stokes equation can be used to predict settling velocity (V) of a dilute suspension within a continuous phase; viscosity (η)

$$V = \frac{2\Delta\rho g a^2}{9\eta}$$

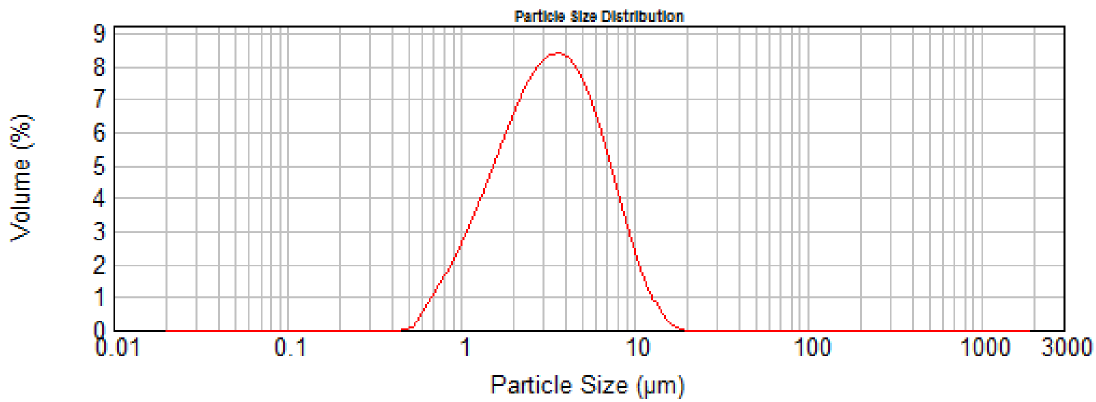
- Velocity increases with **the square of particle size** making this the most critical parameter
- To slow down sedimentation rate:
  - Increase low shear viscosity
  - Decrease particle size
  - Match density of dispersed and continuous phases



Silica dispersion, what viscosity?

Using our example in the equation

- **If 5mm sedimentation per year** was acceptable we would need a viscosity in the region of **11 Pas** for this Silica dispersion
  - This is ~11,000 times the viscosity of water! But at low shear…
  - Details of a concentrated system modification in the reference below

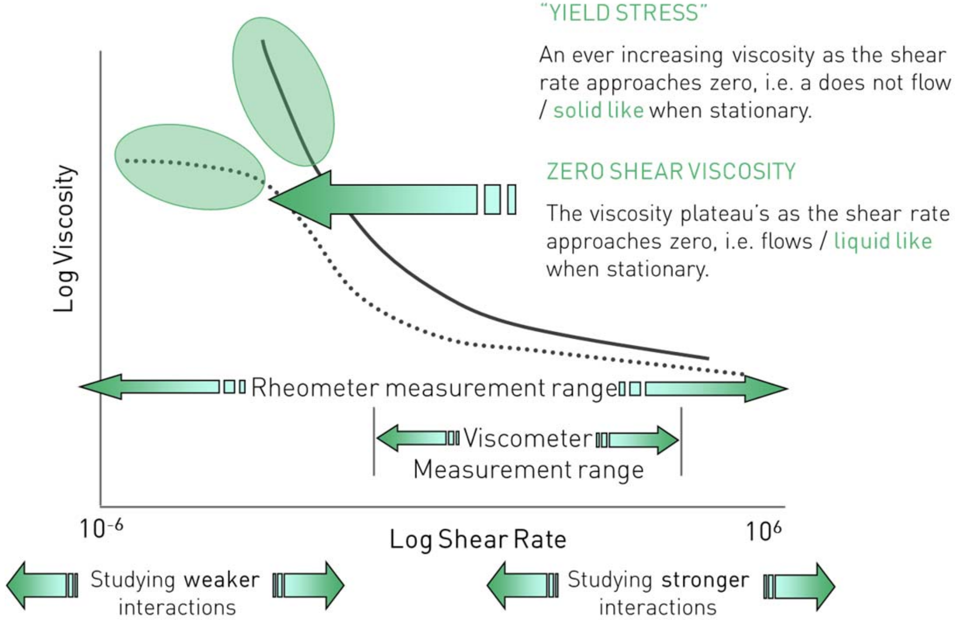


$$V = \frac{2\Delta\rho g a^2}{9\eta}$$

Barnes, H A (1992), *Recent advances in rheology and processing of colloidal systems,* The 1992 IChemE Research Event, pp. 24-29, IChemE, Rugby

Additives for Increasing Low Shear Viscosity

- Alginates
- Methylcellulose
- Acacia gum
- Gellan gum
- Hydroxyethylcellulose
- Bentonite clay
- Laponite clay
- Tragacanth
- Xanthan gum
- Associative Polymers
- Surfactant Lamellar

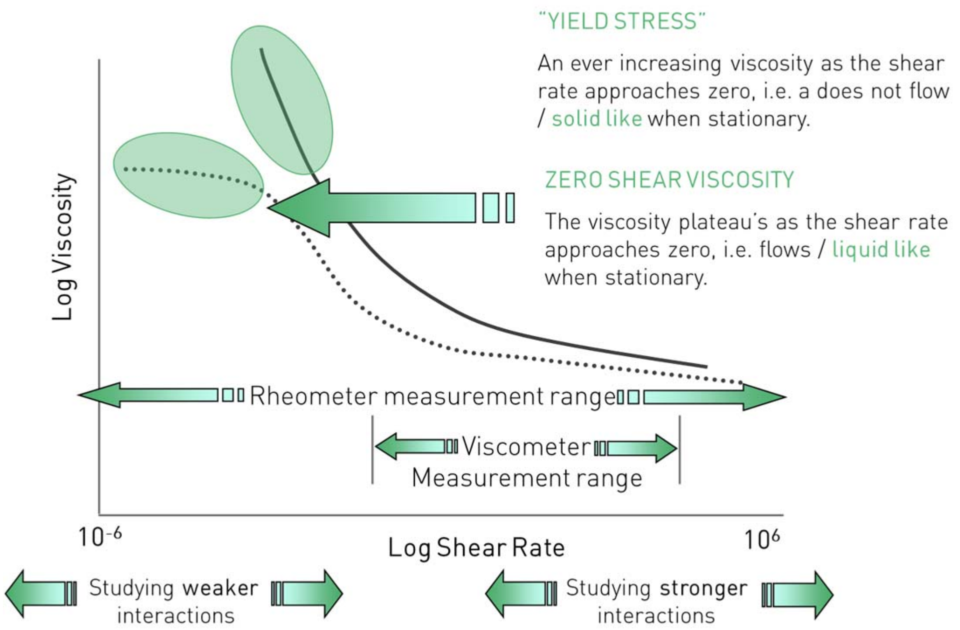


› Choice of thickener will depend on system compatibility and required flow properties – some may induce a yield stress

Non-colloidal gold!

Approx. "Particle Size"		
Length	2	mm
Width	2	mm
Thickness	0.1	um
Approx. radius equivalent (a)	**45.7**	**um**

Additives for Increasing Low Shear Viscosity



- Alginates
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Maintaining performance and functionality

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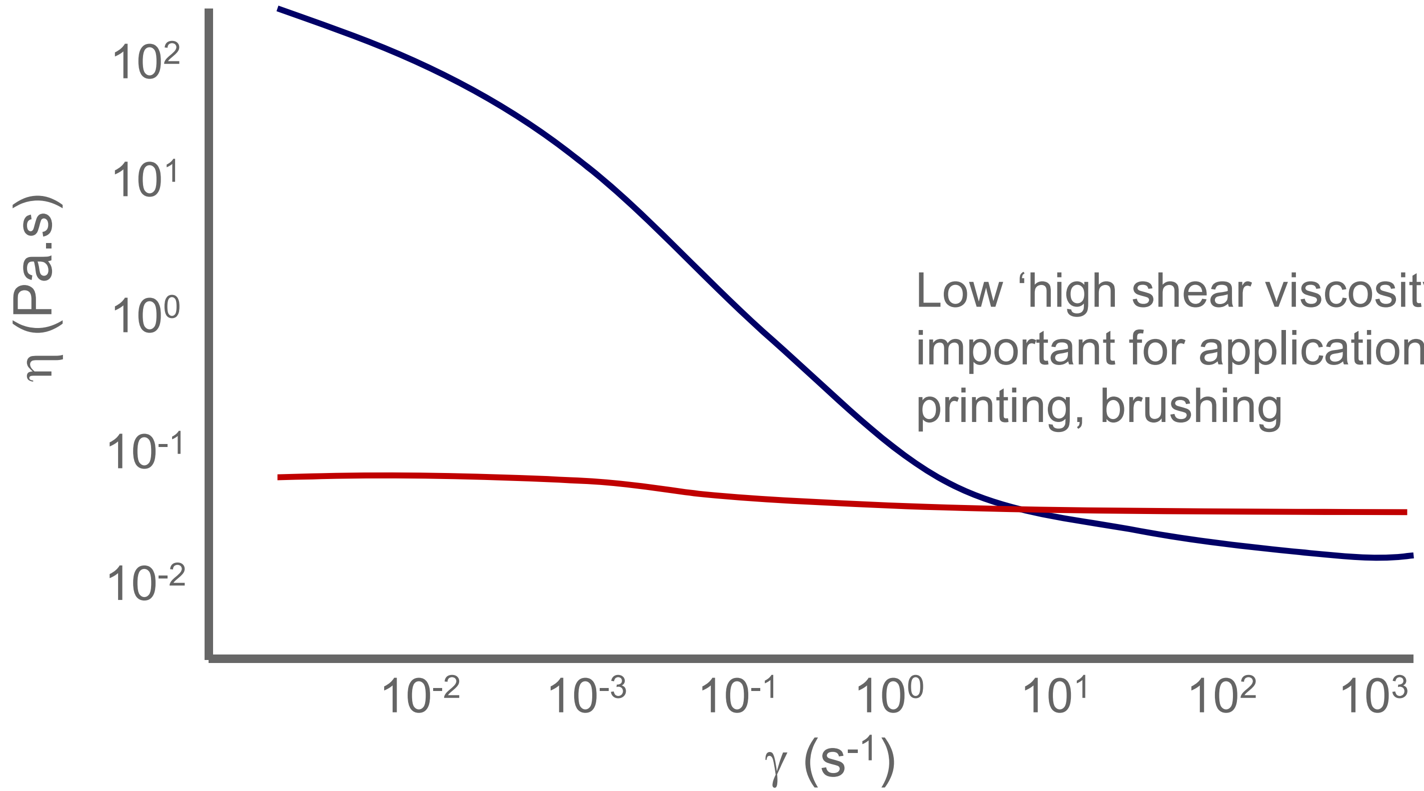
High 'low shear viscosity' helps to slow down sedimentation



Low 'high shear viscosity' important for application e.g. printing, brushing

How to Achieve Stability?

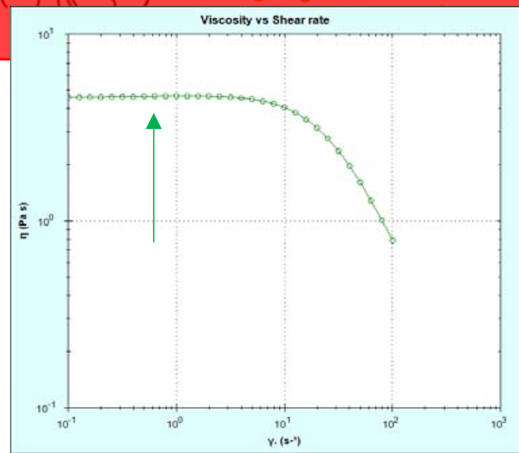
No one method

- Prevent coagulation through inter-particle repulsion

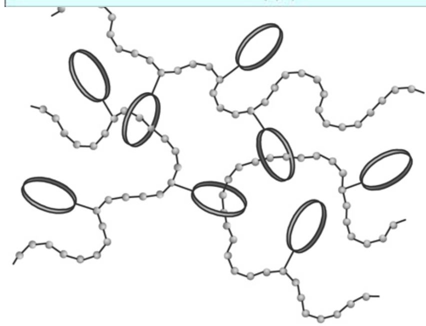
Only for particles less than 1 micron

- Slow down sedimentation by increasing viscosity of continuous phase

KINETIC STABILITY



- Make it Solid by creating a network structure



YIELD STRESS / THERMODYNAMIC STABILITY

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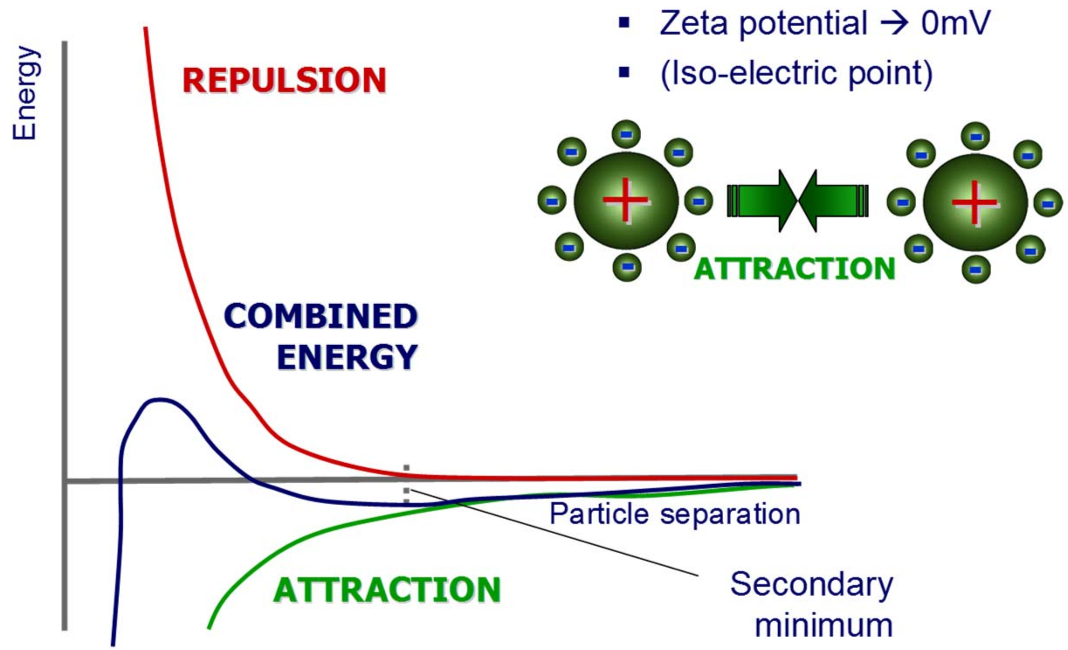
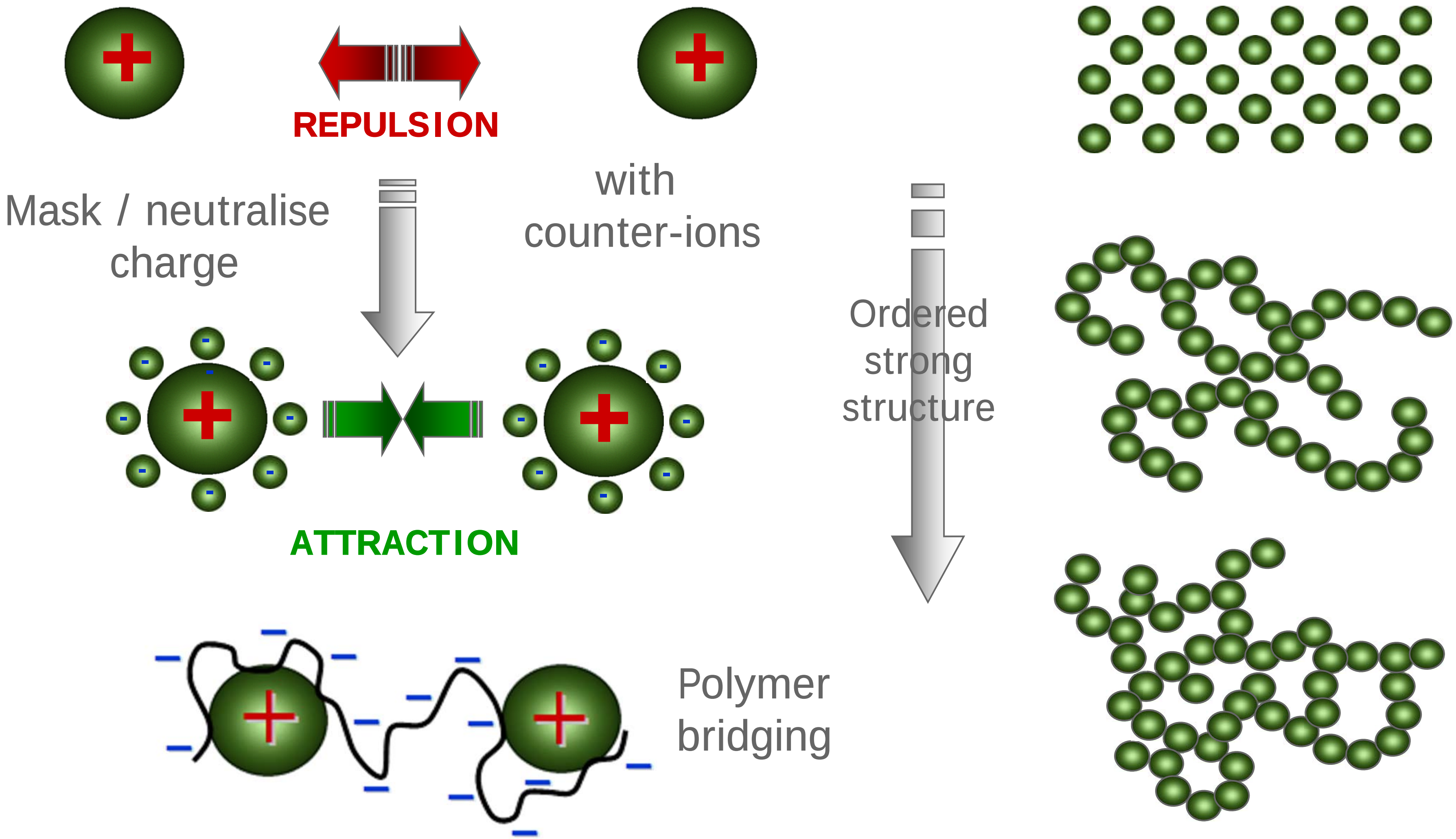
Colloidal stability and DLVO theory

- When electrostatic forces can be minimized it is possible to produce a secondary minimum.



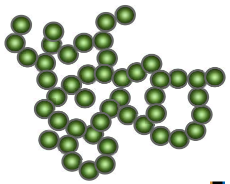
- If secondary minimum is deep enough a strong reversible flocculated network can be formed

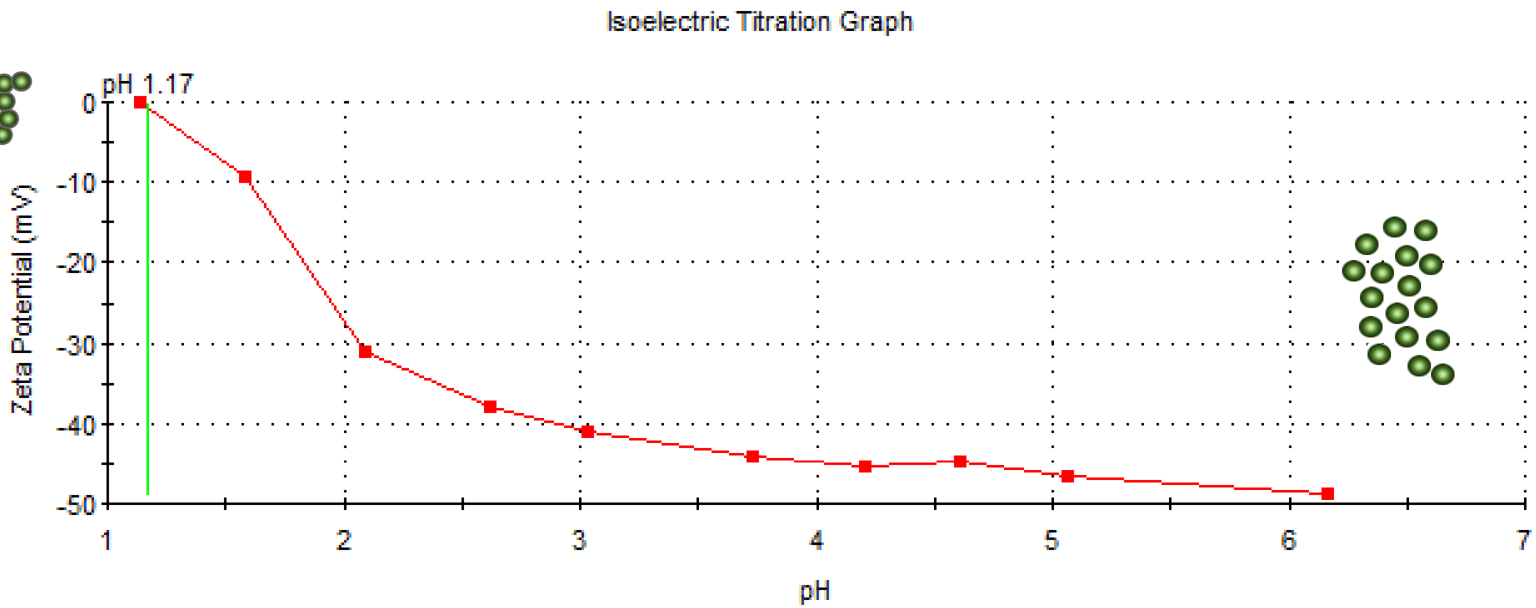
Forces in a stable dispersion



Zeta Potential

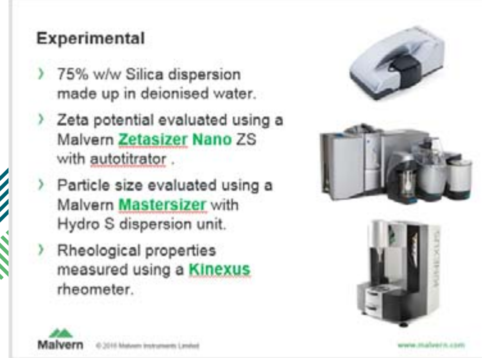
- Titrating the silica sample with HCl on a Zetasizer Nano with MPT-2 autotitrator.



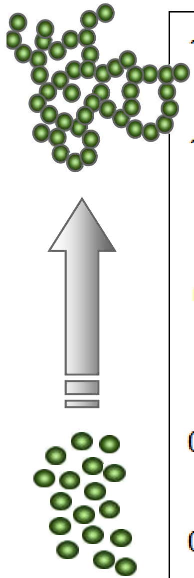


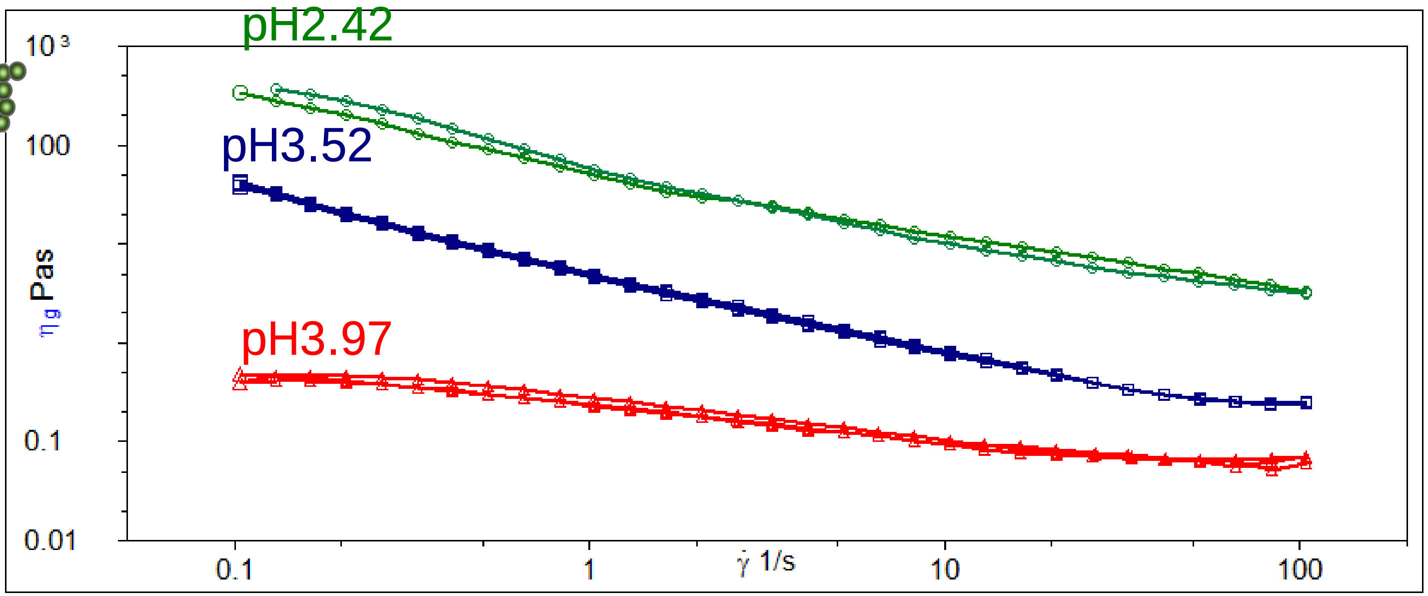
- The isoelectric point (where the zeta potential is zero) is in the very acidic (pH 1) region.

Rheology of dispersions at different pH



- At lower pH's particles **associate** more causing an **increase in viscosity** as approaching isoelectricpoint
- This is favourable for stability



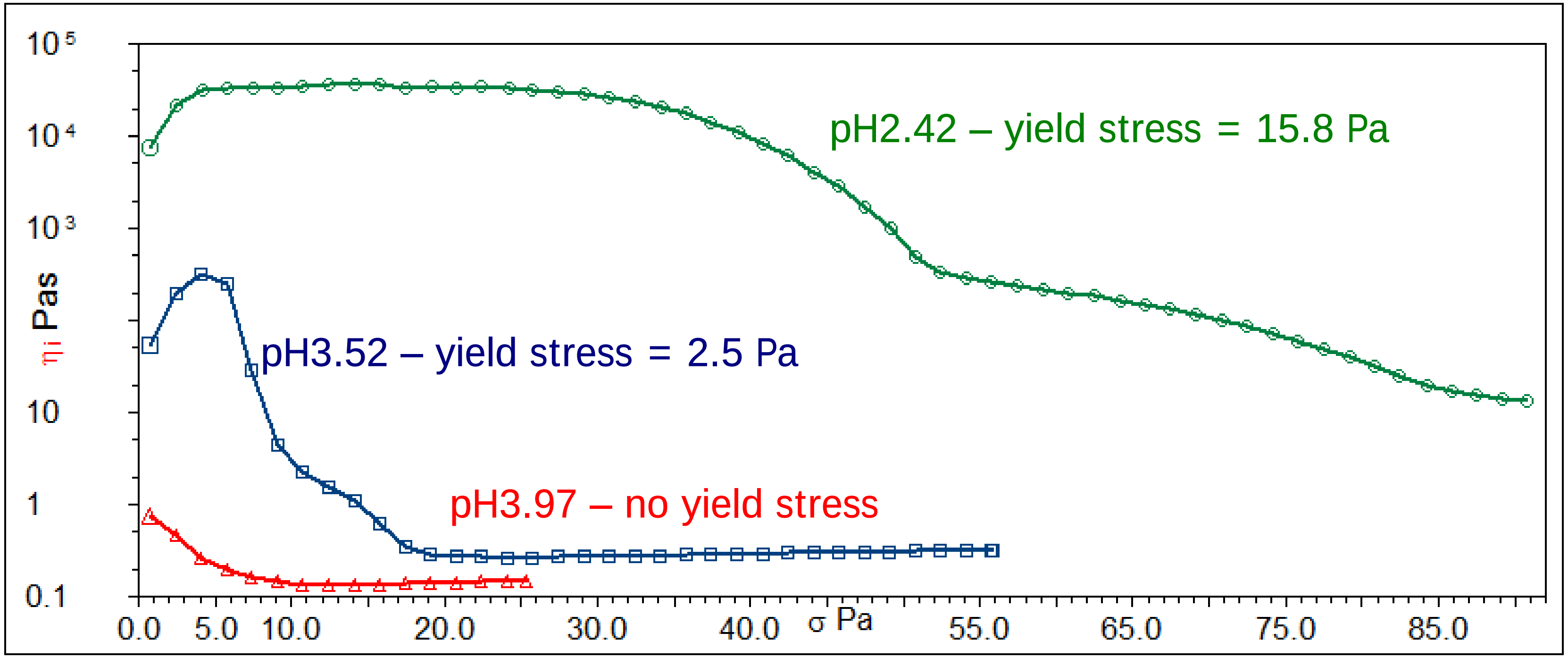


No Yield Stress

- Low pH samples show no viscosity plateau suggesting solid like behaviour at rest
- Measurements repeated on the same loaded sample indicate reversible flocculation due to a secondary minimum

Yield Stress

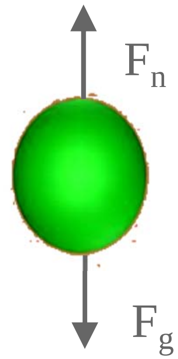
- At high pH there is no elastic network hence no yield stress observed.
- As pH is lowered stronger interactions occur leading to larger yield stress.



What Yield Stress is sufficient?

- For a particle to stay suspended the **yield stress must exceed the gravitational force** acting on the particle
- This can be estimated from the following equation:

$$\sigma_y = Y(\rho_D - \rho_C)rg$$

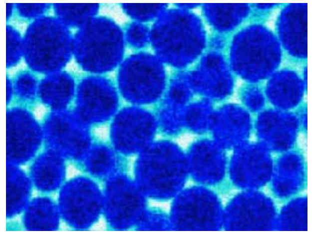


- Y is the **critical yield parameter** (0.33 for Stokes law) which has been shown to have a range of values based on various studies
- For the **silica** sample, a **σ_y of just 0.1 Pa** will do!

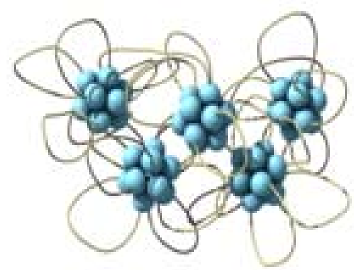
P. B. Laxton and J. C. Berg. Gel trapping of dense colloids. J. Colloid Interface Sci. ***285****:152–157 (2005)*

Yield Stresses Occur In…..

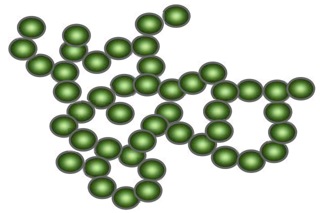
- **Emulsions, foams and dispersions** where components are tightly **packed** together



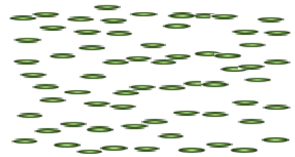
- **Associative polymers** that interact strongly enough to form an **extended network** through the dispersion medium



- **Flocculated dispersions** which form a strong **extended network**



- **Glassy materials** which are essentially **frozen in** a solid state



How to Achieve Stability?

No one method

- Prevent coagulation through inter-particle repulsion

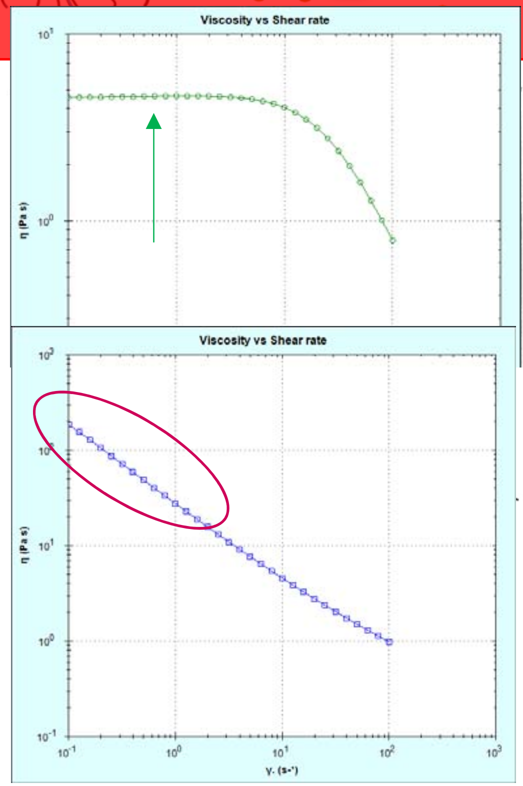
Only for particles less than 1 micron

- Slow down sedimentation by increasing viscosity of continuous phase

KINETIC STABILITY

- Make it Solid by creating a network structure

THERMODYNAMIC STABILITY

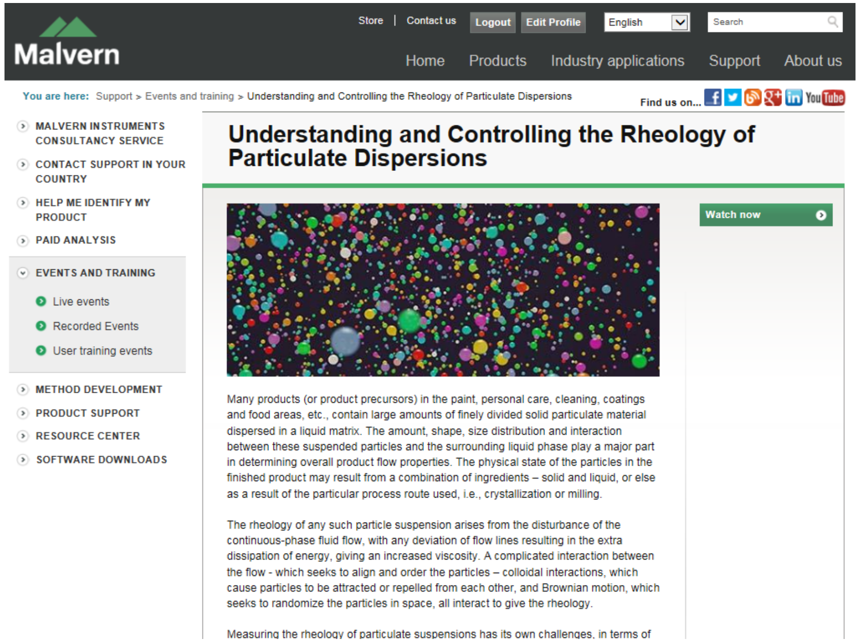


Summary - Stable suspensions

- Particle sizes < 1 µm
  - Create a large charge on the particle, ±30 mV
  - Optimise for long range electrostatic repulsion
  - More stable with higher LOW shear viscosity
- Particle sizes > 1 µm (depending on density)
  - Now particles are large enough that gravity has an effect
  - Rheology is now needed to make a stable dispersion
  - Induce a yield stress through network forming polymers or clays
  - Slow down sedimentation by increasing low shear viscosity through use of appropriate additives

Useful Links

- http://accessintelligence.imirus.com/Mpowered/book/vchei15/i1/p1
  - Search: “chemengonline paint a clear picture”
- http://www.malvern.com/en/support/events-and-training/webinars/W160922RheologyParticulateDispersions.aspx
  - Search: “malvern understanding controlling rheology particulate”



Thank you for your attention

Any Questions?

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