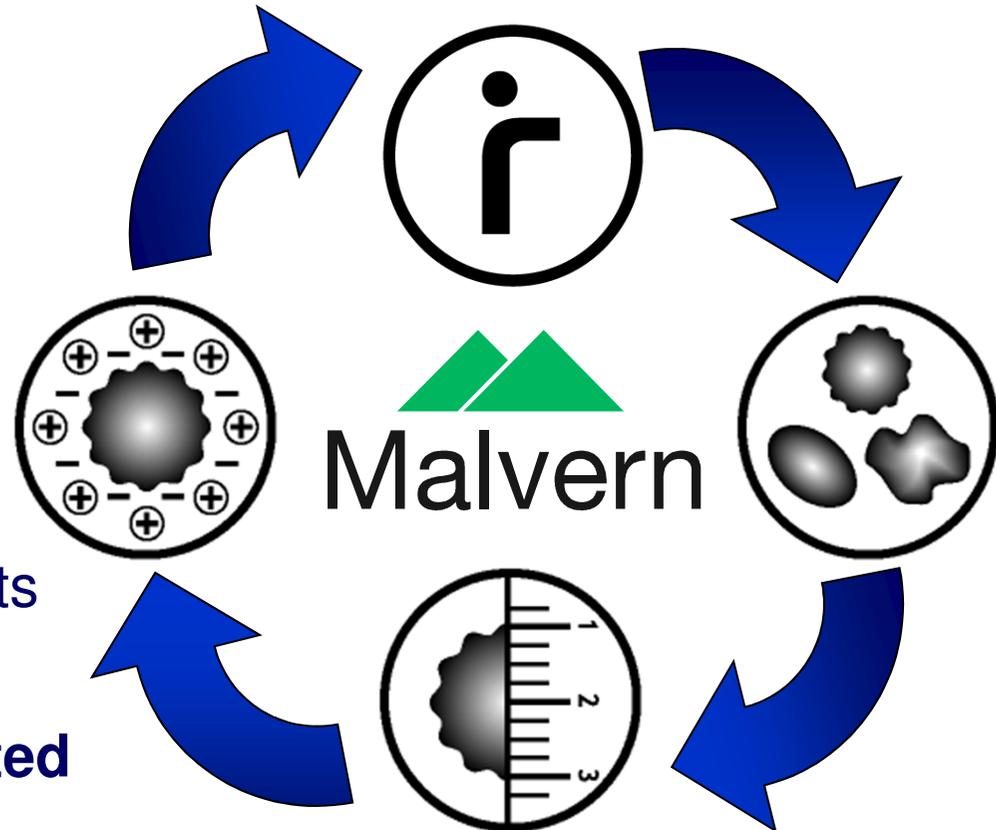


Suspension stability: Why particle size, zeta potential and rheology are important



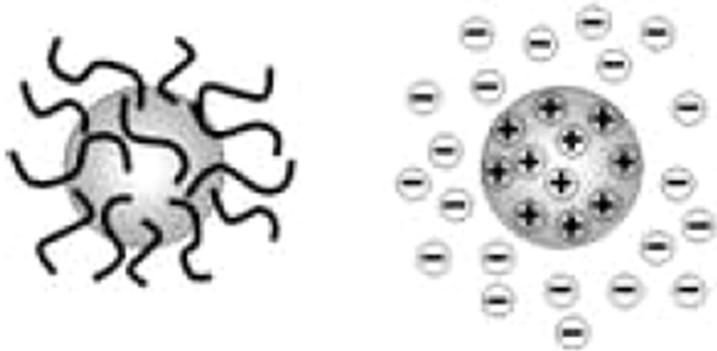
Dr John Duffy/Dr Adrian Hill
Product Technical Specialists
Rheometry Products
Malvern Instruments Limited

Suspension Stability

- ▶ Suspensions/Dispersions are encountered in a wide range of applications
 - *Liquid abrasive cleaners, ceramics, medicines, inks....*
- ▶ In most cases it is necessary to keep the suspension stable for the product lifetime.
- ▶In other cases it may be necessary to destabilise the suspension *i.e. water treatment, de-aeration*

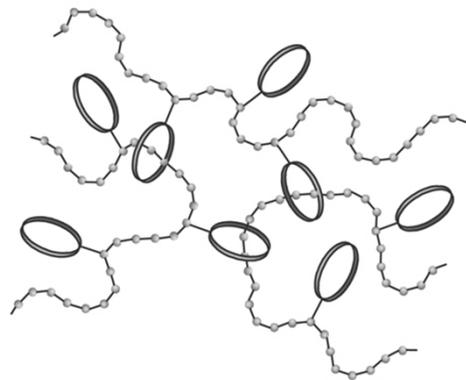
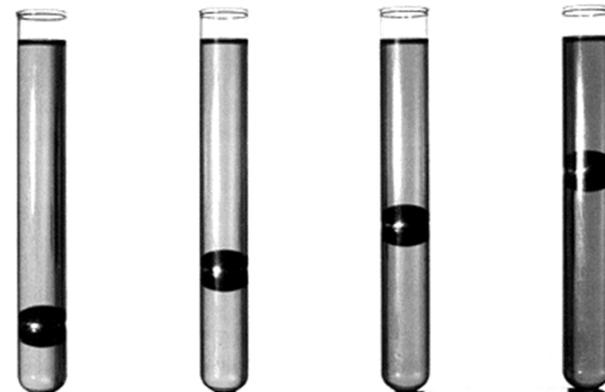


How to achieve this?



Prevent coagulation through inter-particle repulsion

- ▶ Slow down sedimentation by increasing viscosity of continuous phase.



- ▶ Make it Solid by creating a network structure

Which Method?It Depends!!

- ▶ Particle radius (a) will have a large bearing on suspension stability.

$$\frac{a^4 \Delta \rho g}{k_B T}$$

Gravitational Forces

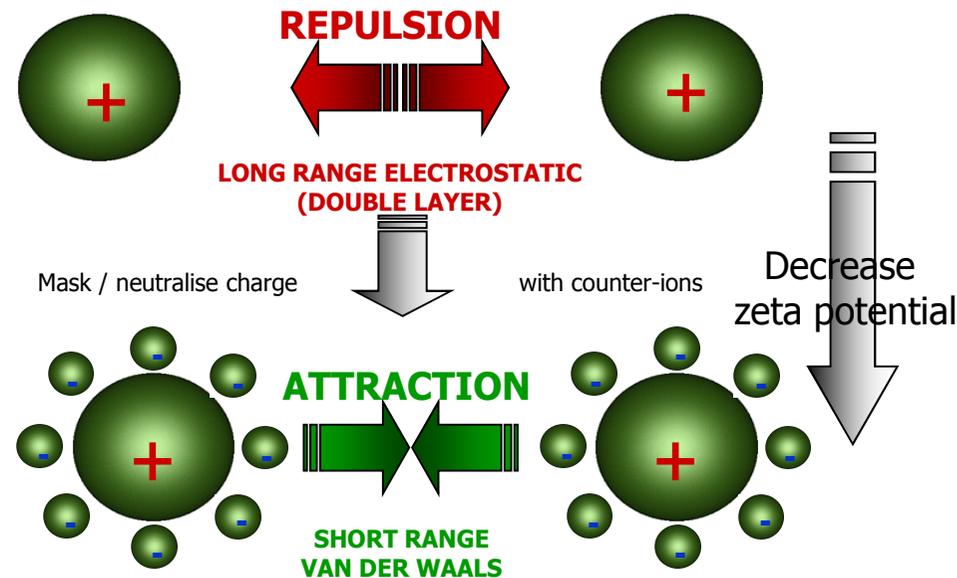
Brownian Forces

- ▶ 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 ($\Delta\rho$).

The Structure and Rheology of Complex Fluids; R Larson

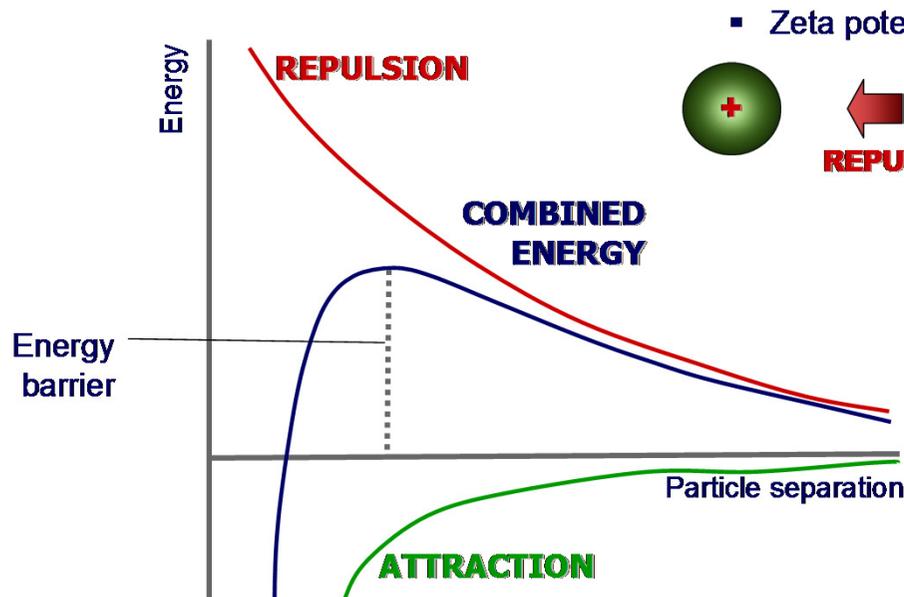
Colloidal Stability

- ▶ 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

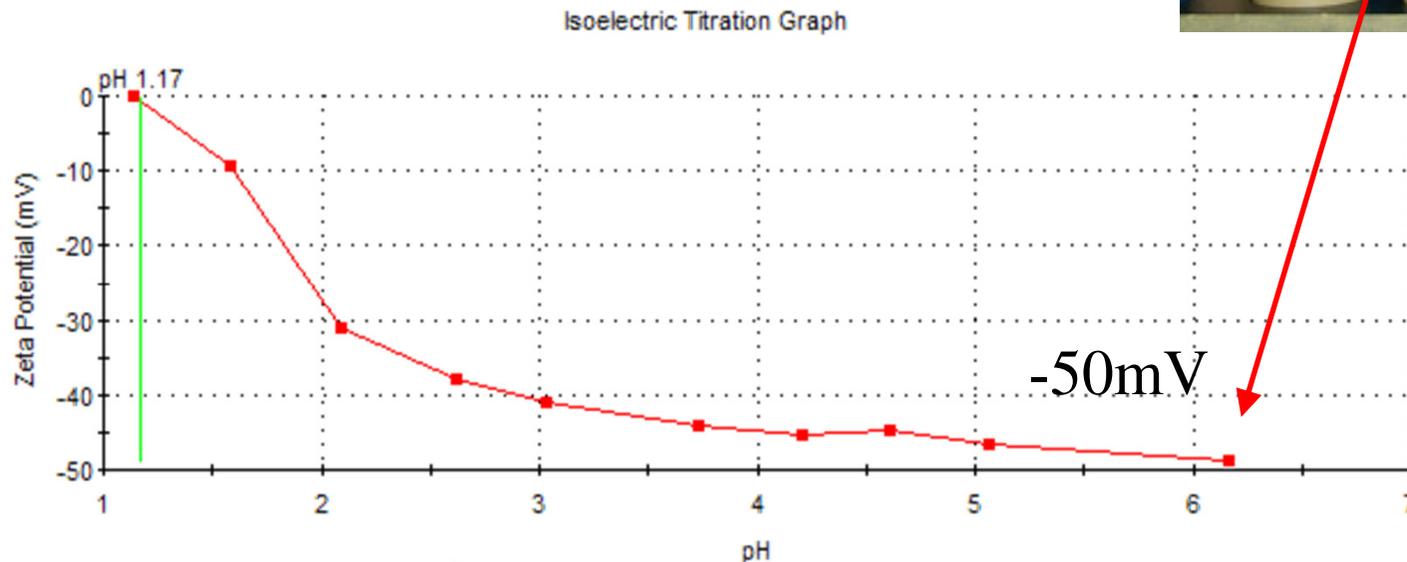
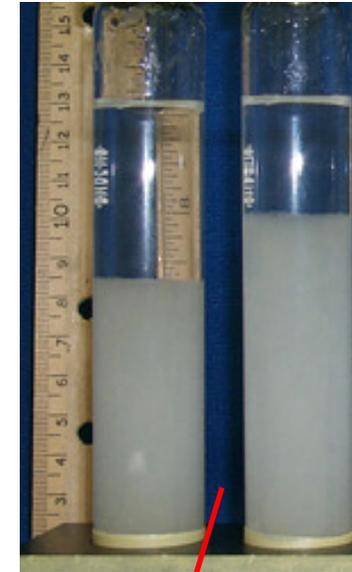
- ▶ So long as particle Kinetic Energy does not exceed this barrier coagulation should not occur.

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 2000 with Hydro S dispersion unit.
- ▶ Rheological properties measured using a Kinexus Pro and a Gemini HR Nano rotational rheometers

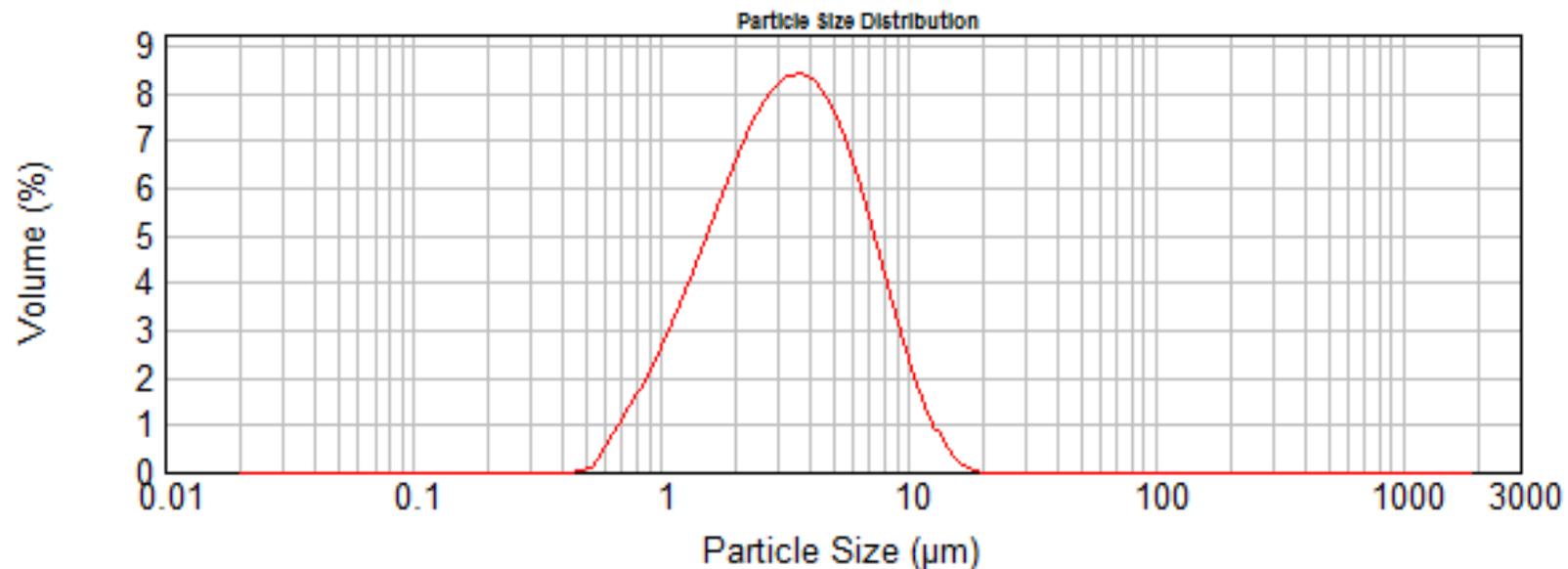
Silica Dispersion Stability

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



Particle Size and Density

- ▶ Sample was characterised on a Mastersizer 2000 and was found to have a median particle size of 3.7 μm .
- ▶ The largest particle was approximately 20 μm



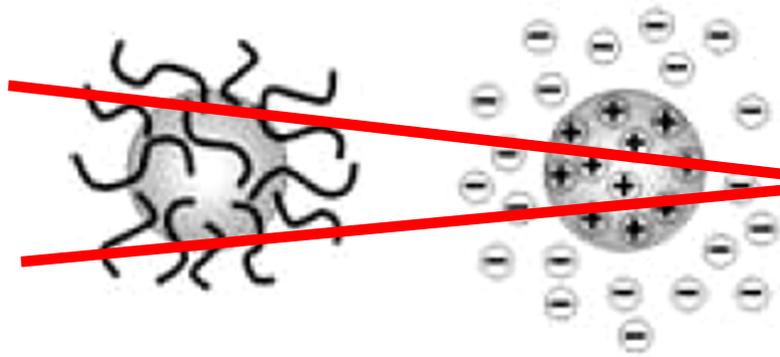
- ▶ Particle density was 2600 kg/m^3

Force Balance on Particle

$$\begin{array}{l} \text{Gravitational Forces} \longrightarrow \\ \text{Brownian Forces} \longrightarrow \end{array} \frac{a^4 \Delta\rho g}{k_B T} \approx 45$$

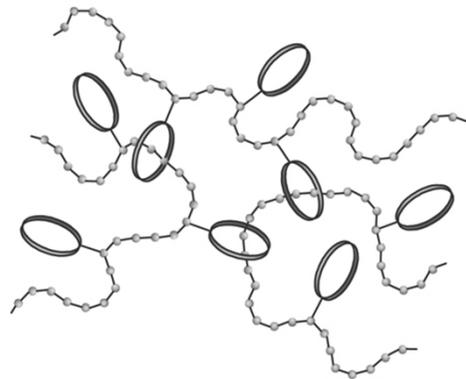
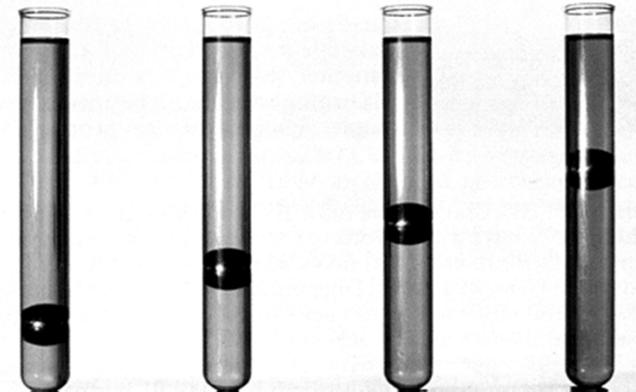
- ▶ Inputting these values into above equation for the median particle size gives a value of 45 and for the largest particle a much higher value of 4×10^4 .
- ▶ This means that gravitational forces are dominant for this sample.
- ▶ This would explain why sedimentation occurs and indicates that another approach is required to induce stability

How to achieve this?



~~Prevent coagulation through antiparticle repulsion~~

- ▶ Slow down sedimentation by increasing viscosity of continuous phase.



- ▶ Make it into a solid by creating a network structure

Effect of Viscosity (Dilute Systems)

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

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

Effect of Viscosity (Concentrated Systems)

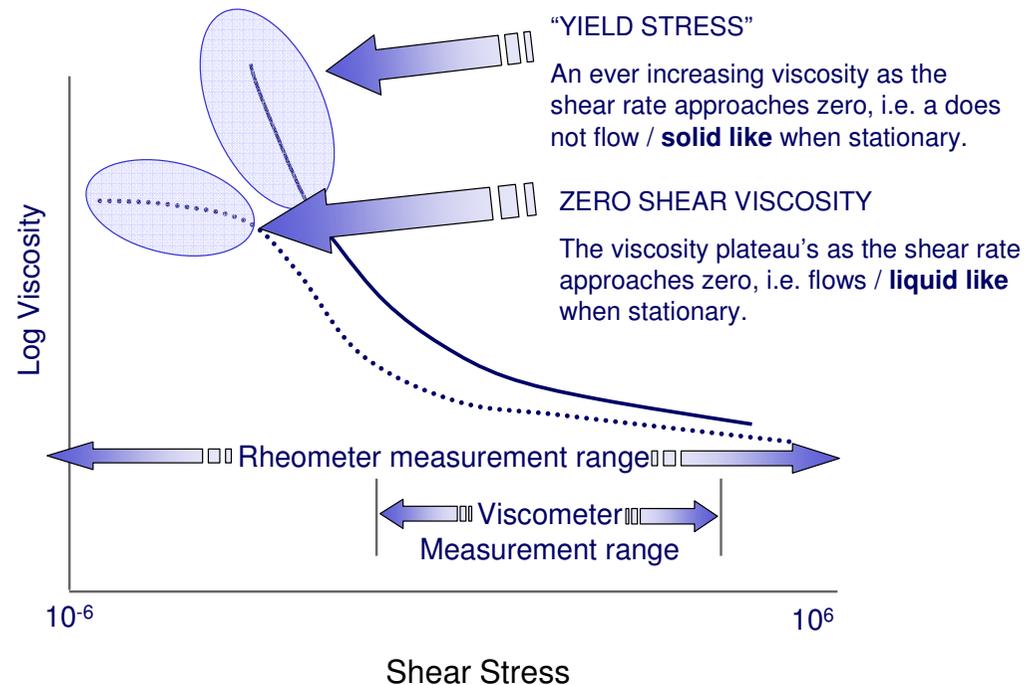
$$V = \frac{2\Delta\rho g a^2}{9\eta} (1 - \phi)^{5 \pm 0.25}$$

- ▶ For concentrated systems a crowding factor must be introduced which incorporates the phase volume ϕ .
- ▶ Increasing phase volume decreases sedimentation rate due to the viscosity increase resulting from crowding.
- ▶ If 5mm sedimentation per year was acceptable we would need a viscosity in the region of 11 Pas for this Silica dispersion.

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

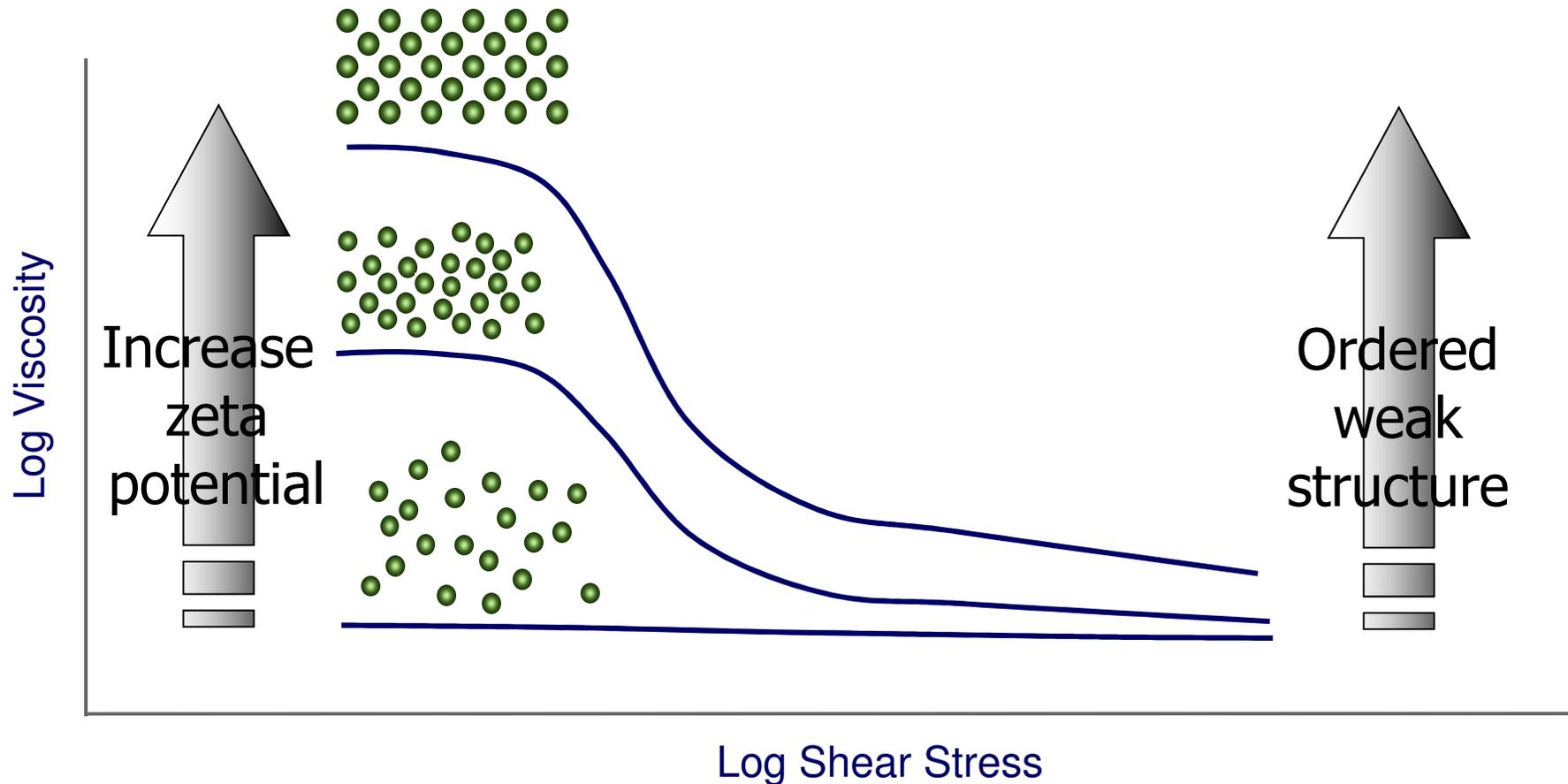
Additives for Increasing low shear Viscosity

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



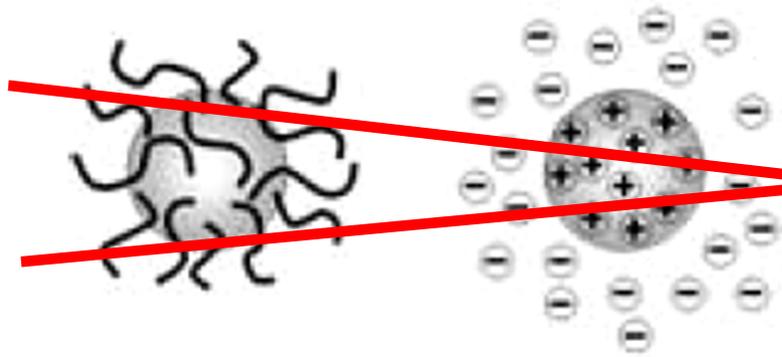
- Choice of thickener will depend on system compatibility and required flow properties – some may induce a yield stress

Effect of zeta potential on low shear viscosity



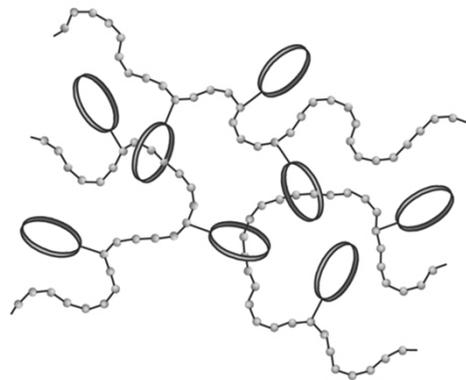
- ▶ Low shear viscosity increases with increasing zeta potential due to a larger effective phase volume
- ▶ Thus high charge will help slow down sedimentation

How to achieve this?



Prevent coagulation through antiparticle repulsion

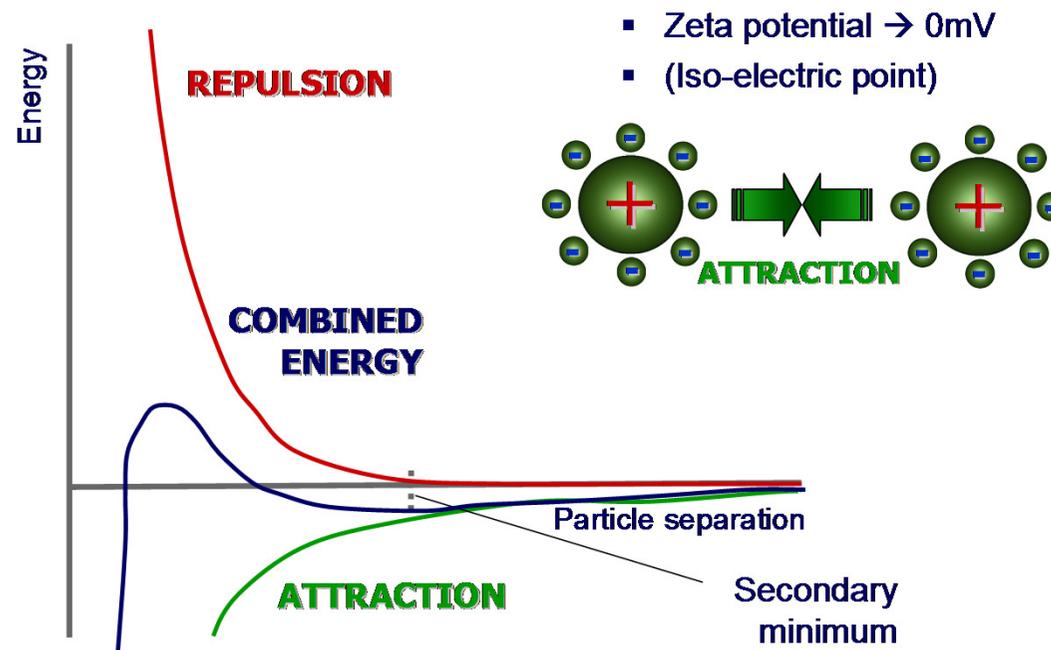
- ▶ Slow down sedimentation by increasing viscosity of continuous phase.



- ▶ Make it into a solid by creating a network structure

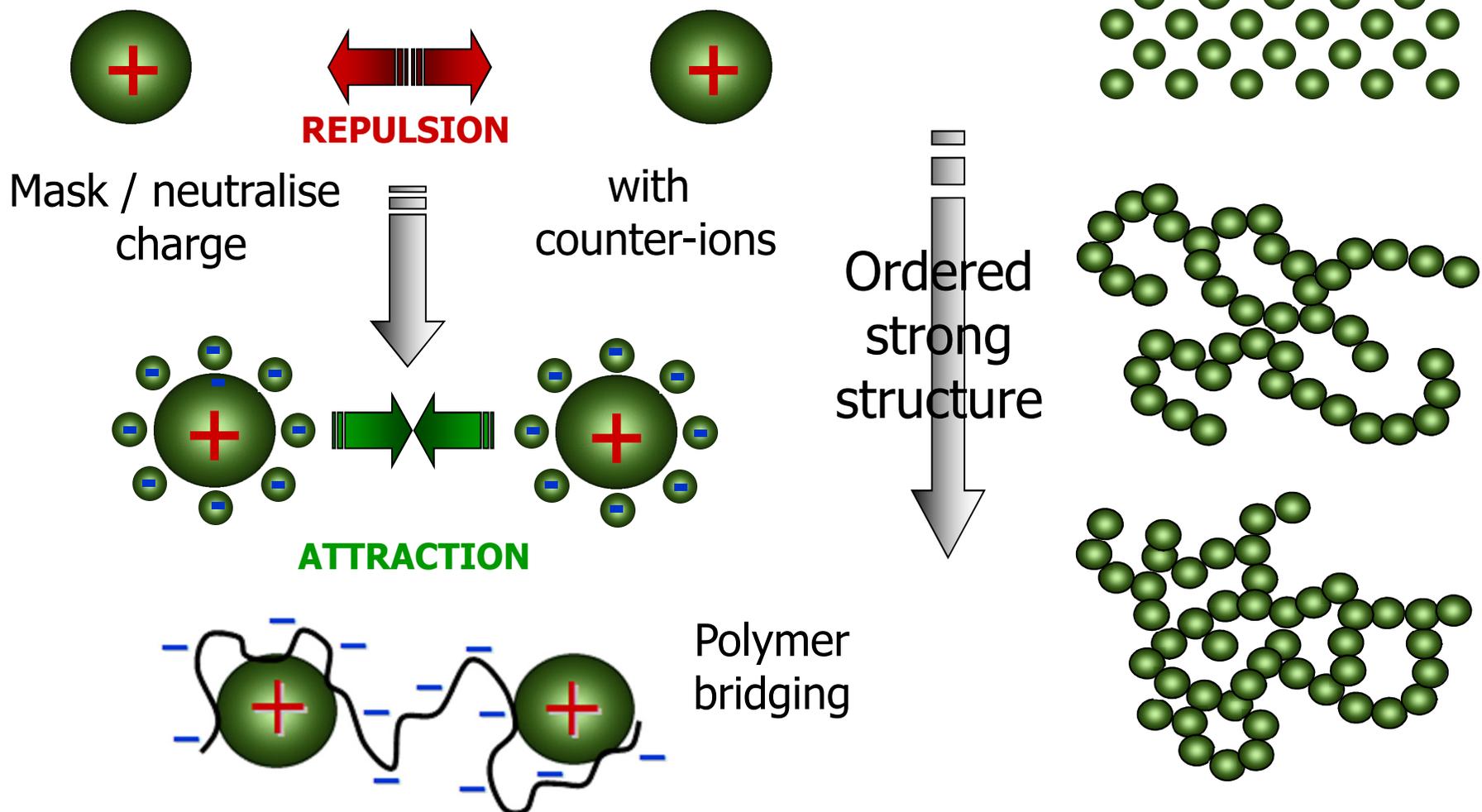
Colloidal Stability and DLVO Theory

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



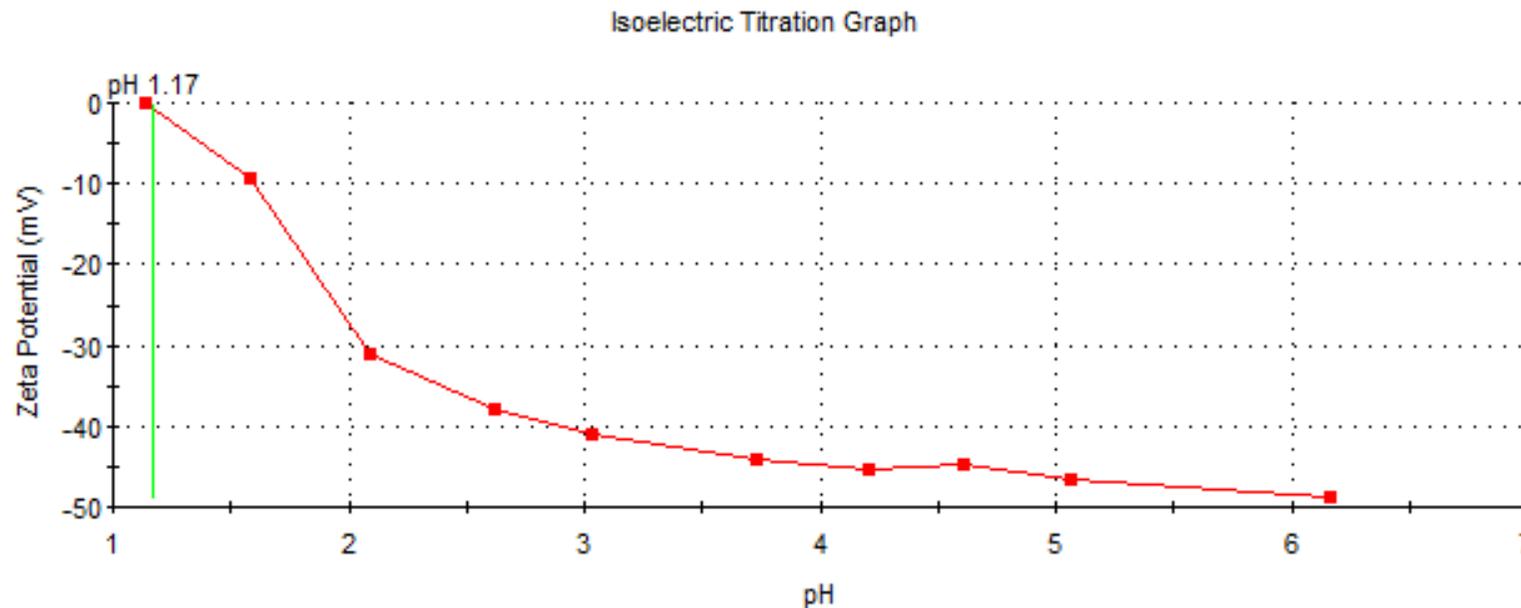
- ▶ If secondary minimum is deep enough can form a strong reversible flocculated network.

Forces in a Stable Dispersion (DLVO Theory)



Zeta Potential

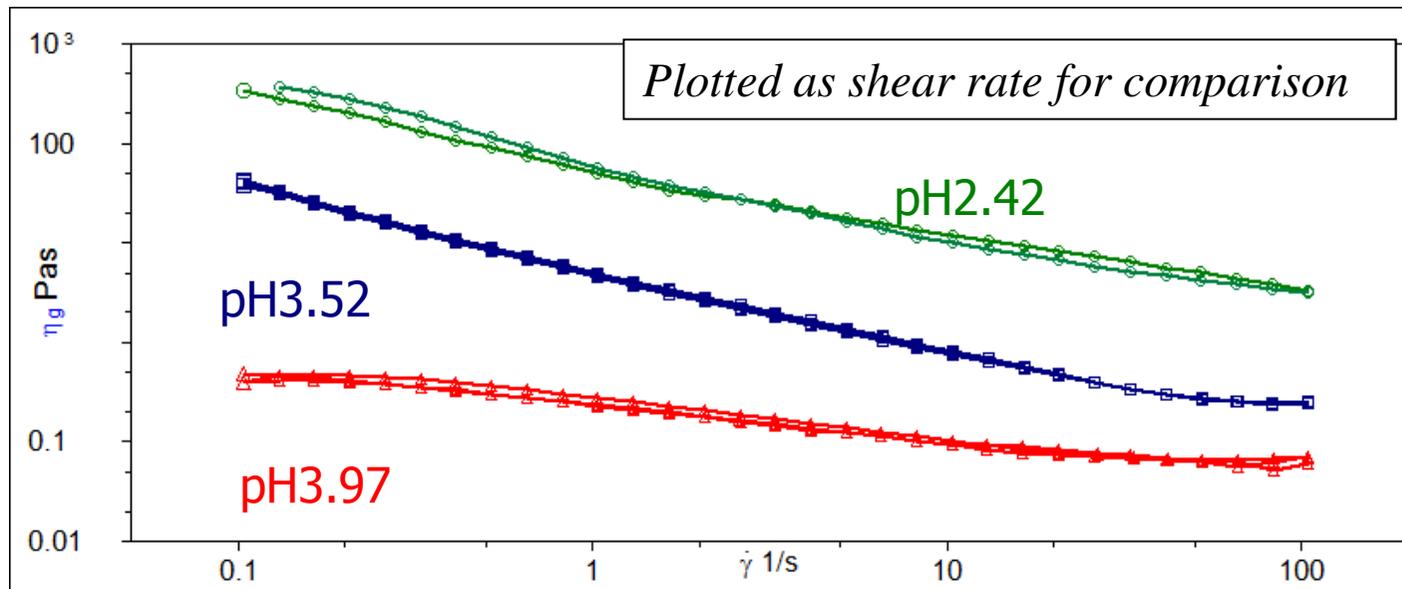
- ▶ Titrating the silica sample with HCl on a Zetasizer Nano with MPT-2 autotitrator.



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

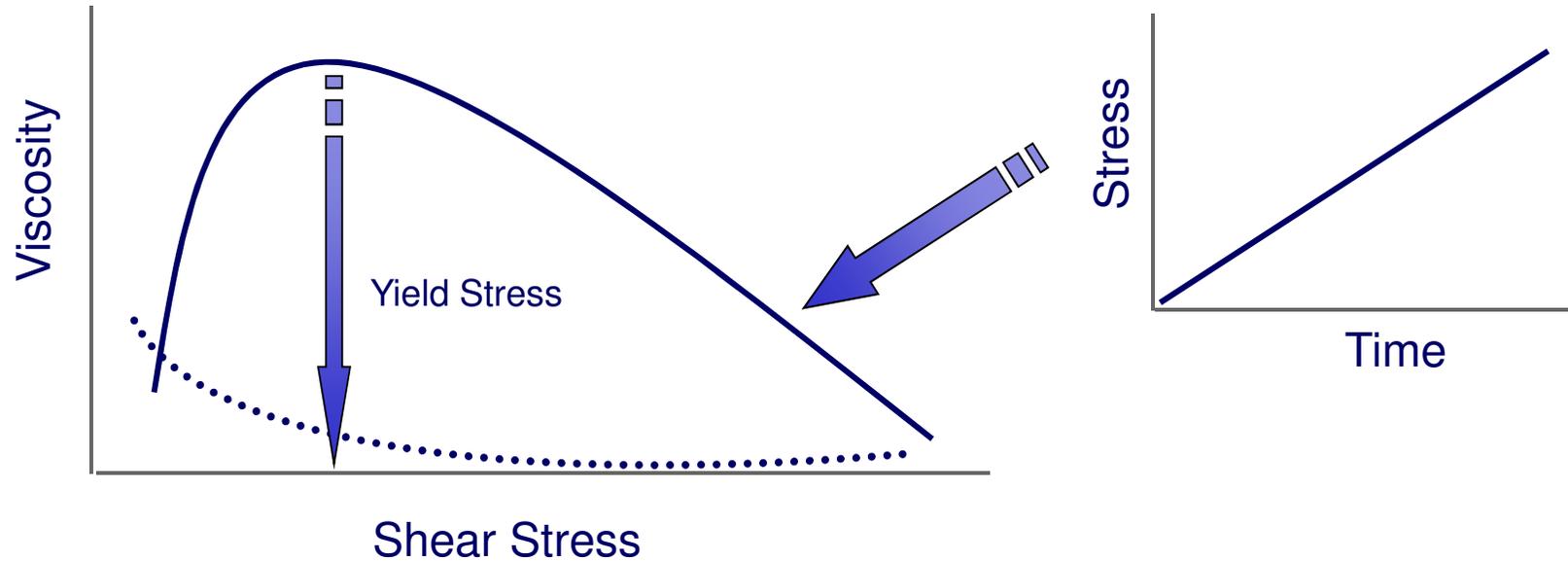
Rheology of dispersions at different pH

- ▶ At lower pH's particles associate more causing an increase in viscosity. This is favourable for stability



- ▶ Low pH samples show no viscosity plateau suggesting solid like behaviour at rest
- ▶ Measurements repeatable on loaded sample suggesting reversible flocculation due to secondary minimum

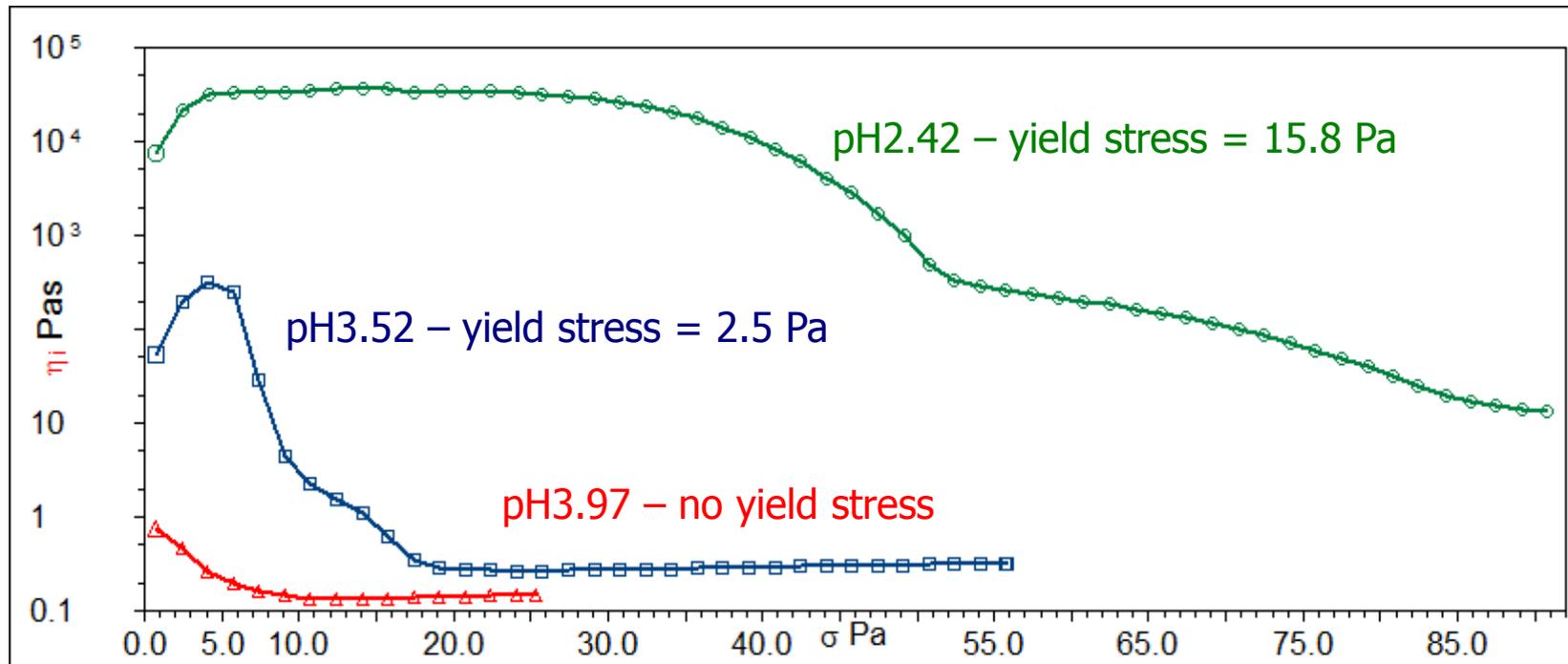
Yield Stress Ramp Test



- ▶ A material with a yield stress will stretch out like an elastic material, until the yield point and will then begin to flow.
- ▶ Peak in viscosity indicates stress required to snap structure
- ▶ No peak, no elastic structure and hence no yield stress
- ▶ Important to choose the right yield stress test and parameters (see later slides)

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.



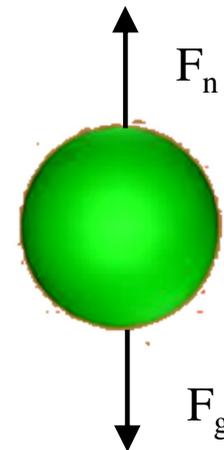
What Yield Stress is sufficient?

- ▶ For a particle to stay suspended the yield stress must be 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 which has been shown to have a range of values based on various studies

| Y | Method of Determination |
|------|---|
| 0.1 | Solving flow patterns for yielded/unyielded systems |
| 0.11 | Stokes law assuming shear rate = $V/2r$ |
| 0.12 | Observing settling behaviour in a carbopol gel |
| 0.18 | Suspending objects in a carbopol gel using a thread and balance |
| 0.33 | Stokes law assuming a shear rate = $3V/2r$ |
| 0.42 | Integrating stress components around a sphere <small>(stress over area of sphere)</small> |
| 1.33 | Using area of sphere intersection normal to the force |



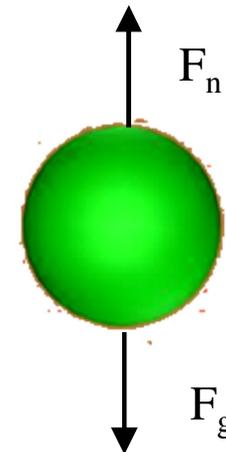
P. B. Laxton and J. C. Berg. Gel trapping of dense colloids. *J. Colloid Interface Sci.* **285**:152–157 (2005).

What Yield Stress is sufficient?

- ▶ For a particle to stay suspended the yield stress must exceed the gravitational force acting on the particle.
- ▶ If we take Y to be 0.33 then the following equation can be used

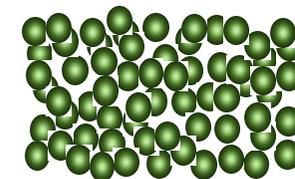
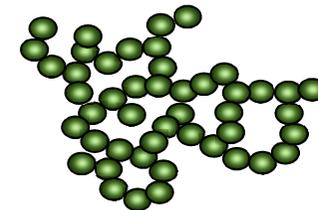
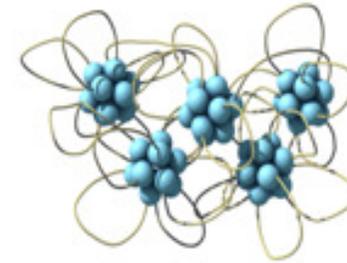
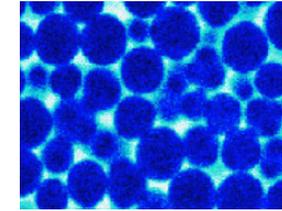
$$\sigma_y = \frac{(\rho_D - \rho_C)rg}{3}$$

- ▶ For the silica dispersion $\sigma \approx 0.05$ Pa for the largest particle ($\sim 20 \mu\text{m}$).
- ▶ Low pH systems can generate yield stresses of 15.8 Pa. These systems have been shown to be stable over long times
- ▶ Important to take into account external stresses which can be much greater than particle stresses i.e. *transportation*

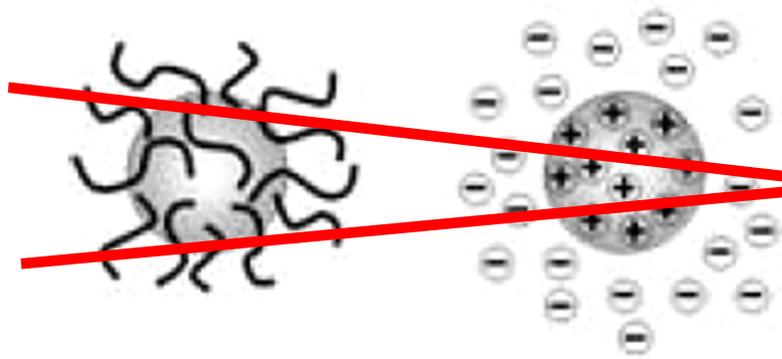


Yield stresses occur in.....

- ▶ 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 this?



~~Prevent coagulation through antiparticle repulsion~~

- ▶ Slow down sedimentation by increasing viscosity of continuous phase.



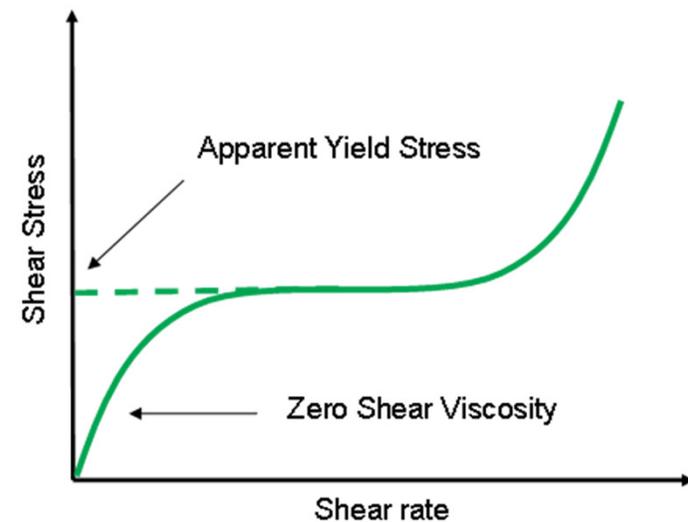
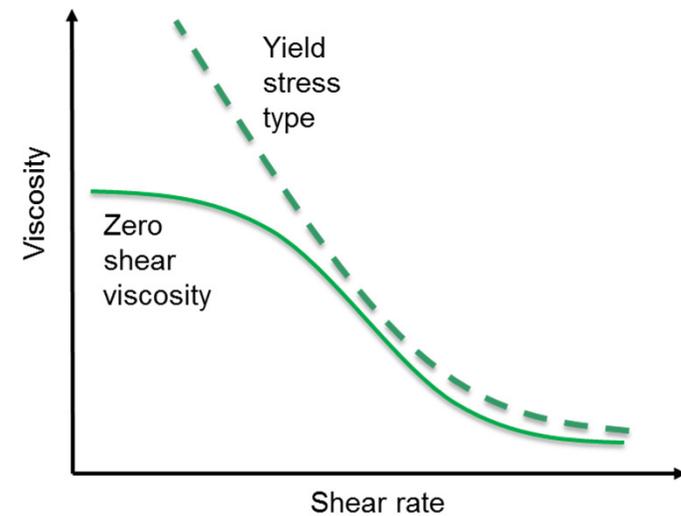
Kinetic Stability



Thermodynamic Stability

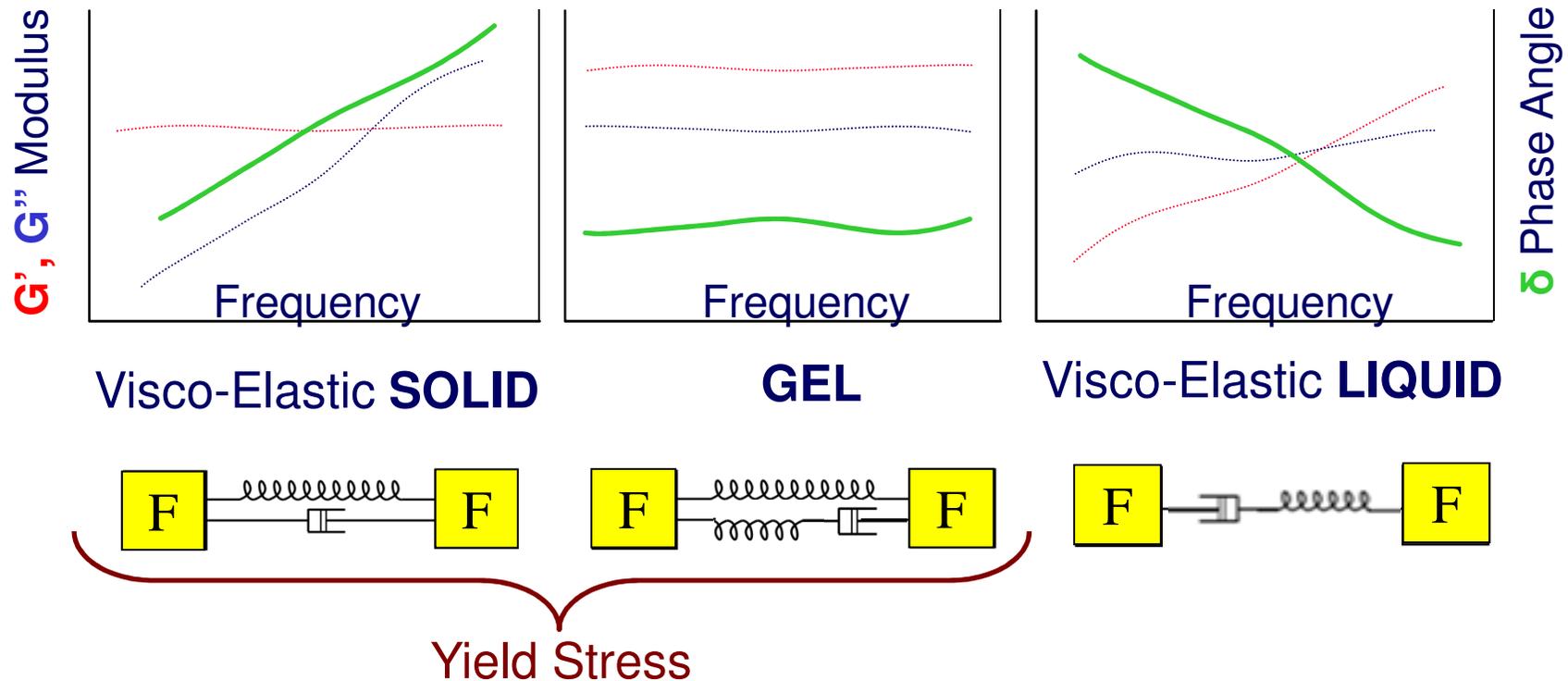
Does my sample have a yield stress?

- ▶ Materials with a true yield stress will have an infinite viscosity at shear rates approaching zero
- ▶ Non yield stress materials will have a finite viscosity value or zero shear viscosity
- ▶ Sometimes it is incorrectly inferred that a material has a true yield stress if not measured to low enough shear rates
- ▶ In this case the term apparent yield stress is more suitable

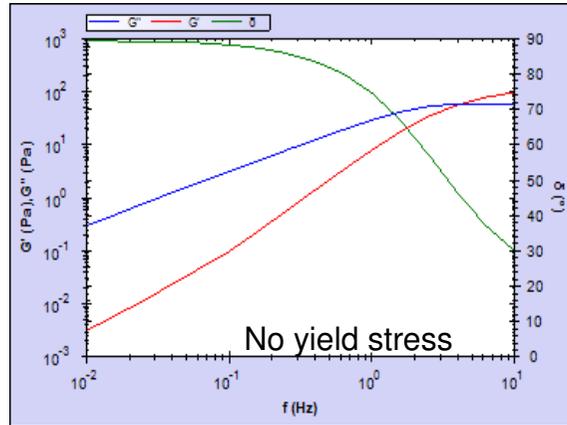


Does my sample have a yield stress?

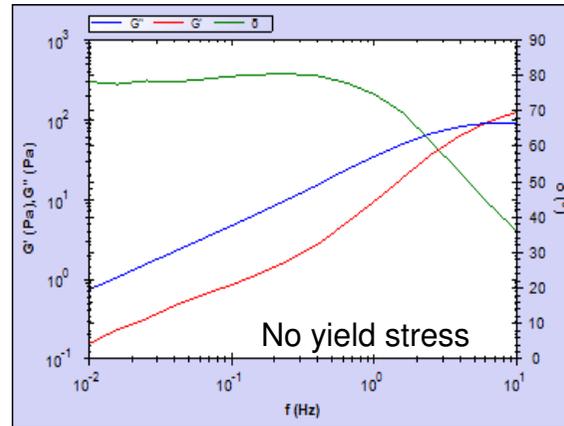
- ▶ If G' exceeds G'' towards low frequencies this indicates a network structure and hence a **Yield Stress**
- ▶ Yield stress can be determine from an amplitude sweep at appropriate frequency i.e. *drop in G' , peak in σ*



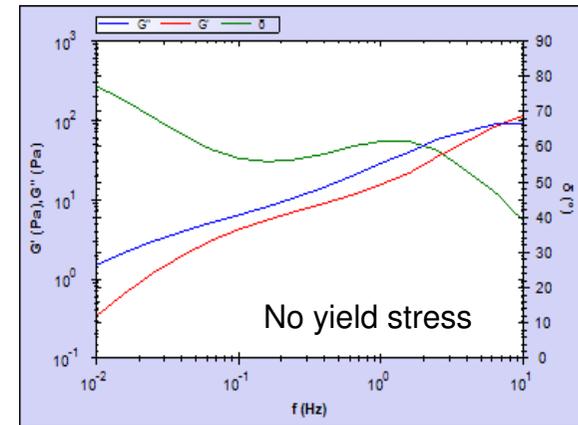
Stabilising bubbles in a shower gel with HASE polymer



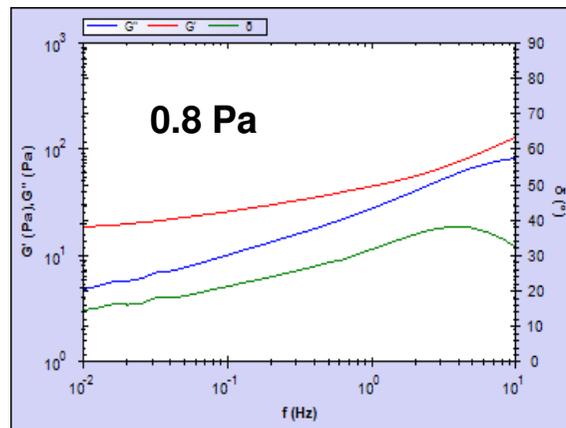
0% HASE



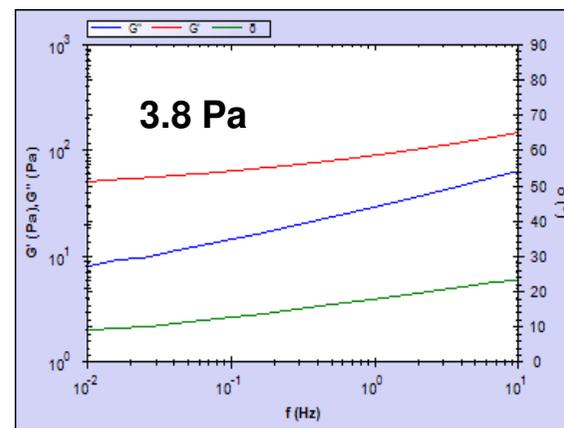
1.5% HASE



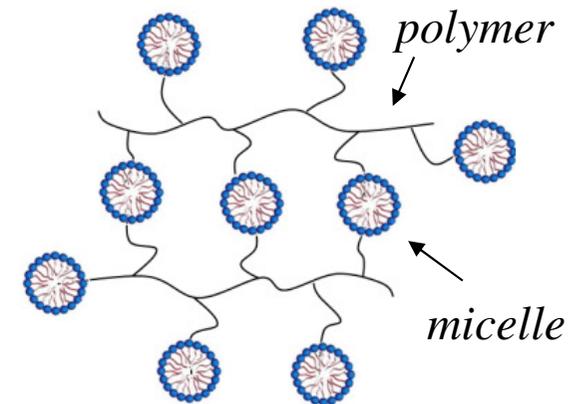
3.0 % HASE



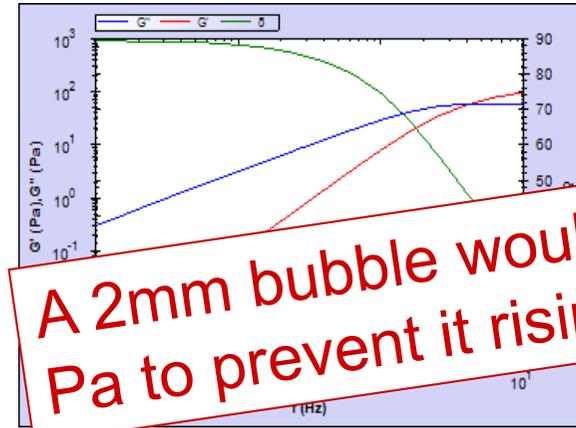
4.5 % HASE



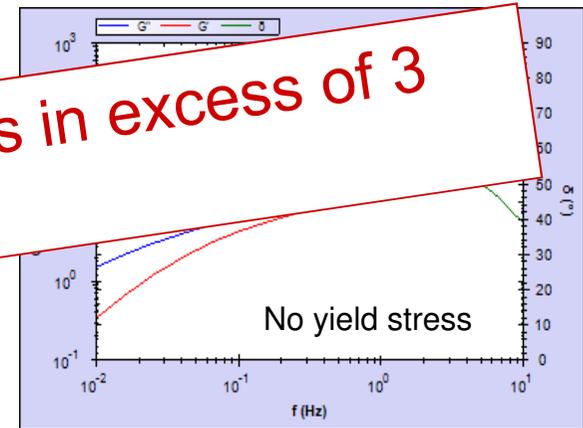
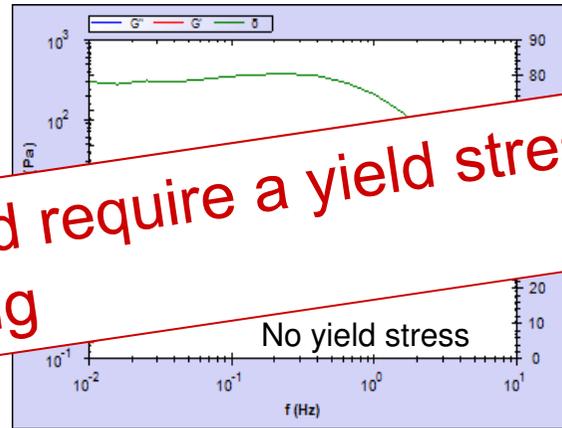
6 % HASE



Stabilising bubbles in a shower gel with HASE polymer



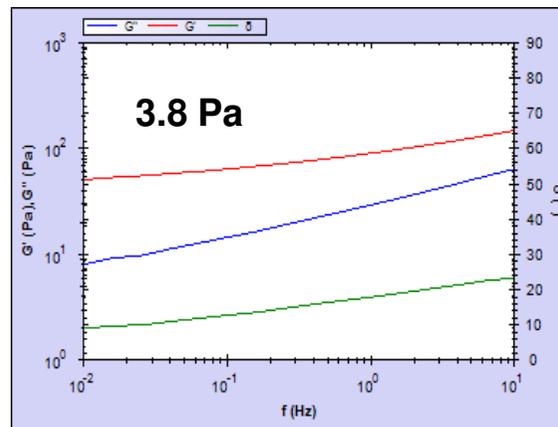
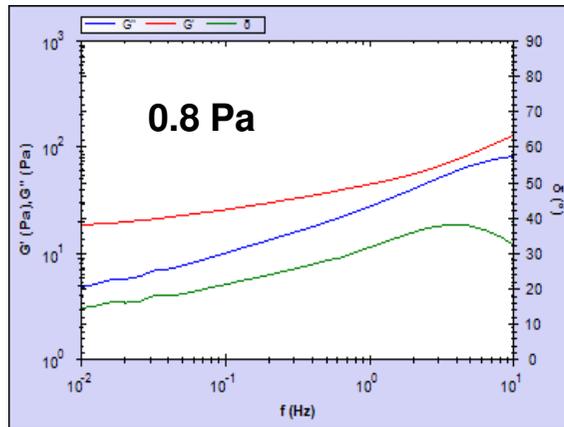
A 2mm bubble would require a yield stress in excess of 3 Pa to prevent it rising



0% HASE

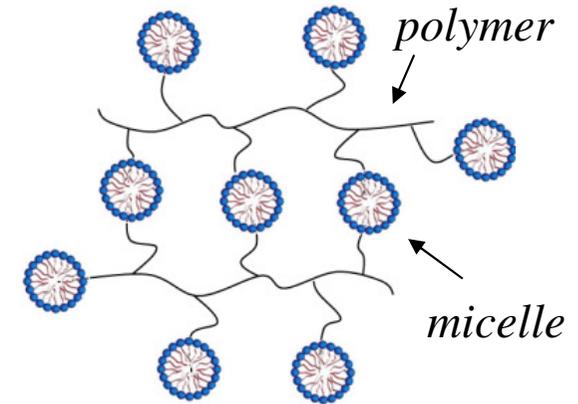
1.5% HASE

3.0% HASE



4.5% HASE

6% HASE



Yield stress values for a Carbopol based hair gel

| | Model Fit | | |
|-------------------------|---------------|------------------|--------|
| | Bingham | Herschel Bulkley | Casson |
| Yield stress | 81.6 | 59.3 | 68.5 |
| Corr coefficient | 0.9291 | 0.9997 | 0.9861 |
| | Stress growth | | |
| Shear rate (s^{-1}) | 0.01 | 0.1 | 1 |
| Yield stress | 61.13 | 70.83 | 83.8 |
| | Oscillation | | |
| Frequency (Hz) | 0.01 | 0.1 | 1 |
| Yield stress | 58.4 | 66.1 | 82.2 |
| G' | 325 | 341 | 369 |
| | Creep | | |
| Yield stress | | 59 | |

- ▶ Yield stress is not a material constant and can depend on the conditions of the test
- ▶ One variable affecting yield stress is time.....
- ▶ Viscoelastic materials relax with time hence the test timescale or frequency can affect the result
- ▶ Some materials will show yield stress behaviour at short times but no yield stress at longer times i.e. silly putty
- ▶ Where possible stability should be related to yield stresses measured to low shear rates or frequencies

Yield stress values for a Carbopol based hair gel

| | Model Fit | | | |
|-------------------------|-----------|----------------------|--------|---|
| | Bingham | Herschel Bulkley | Casson | |
| Yield stress | 81.6 | 59.3 | 68.5 | Extrapolation of flow curves using standard yield stress models • Pick most appropriate model and use steady state data to low shear rates |
| Corr coefficient | 0.9291 | 0.9997 | 0.9861 | |
| | | Stress growth | | Apply constant strain rate and determine peak in shear stress • Low shear rates correlate with long time-scales |
| Shear rate (s^{-1}) | 0.01 | 0.1 | 1 | |
| Yield stress | 61.13 | 70.83 | 83.8 | |
| | | Oscillation | | Perform amplitude sweep and determine peak in elastic stress (stress component of G') • Low frequencies correlate with long timescales |
| Frequency (Hz) | 0.01 | 0.1 | 1 | |
| Yield stress | 58.4 | 66.1 | 82.2 | |
| G' | 325 | 341 | 369 | |
| Yield stress | | Creep | 59 | Increase stress incrementally in creep mode and look for transition to flow • Accounts for time dependent behaviour if test time is long enough |

Yield stress values for a Carbopol based hair gel

| | Model Fit | | | Extrapolation of flow curves using standard yield stress models <ul style="list-style-type: none"> • Pick most appropriate model • Use steady state data to low shear rates |
|-------------------------------|-----------|------------------|--------|--|
| | Bingham | Herschel Bulkley | Casson | |
| Yield stress | 81.6 | 59.3 | 68.5 | |
| Corr coefficient | 0.9291 | 0.9997 | 0.9861 | |
| Stress growth | | | | |
| Shear rate (s ⁻¹) | 0.01 | | | |
| Yield stress | 61.12 | | | peak |
| Frequency sweep | | | | |
| Frequency (Hz) | 0.25 | | 1 | |
| Yield stress | | 66.1 | 82.2 | Perform amplitude sweep and determine peak in elastic stress (stress component of G') |
| G' | | 341 | 369 | • Low frequencies correlate with long timescales |
| Creep | | | | |
| Yield stress | | 59 | | Increase stress incrementally in creep mode and look for transition to flow <ul style="list-style-type: none"> • Accounts for time dependent behaviour if test time is long enough |

Instabilities usually accelerated at higher temperatures so important to evaluate at temperature extremes likely to be encountered upon storage

Summary - Stable suspensions

Below *circa.* 1 μm

- ▶ Study zeta-potential.
- ▶ Create a large charge on the particle, $\pm 30\text{mV}$ (e.g. pH).
- ▶ Optimise for long range electrostatic repulsion.
- ▶ More stable with higher LOW shear viscosity (higher charge).

Above *circa.* 1 μm (depending on density)

- ▶ Now particles are sufficiently big that gravity has an effect.
- ▶ Create a stronger short range associated structure by approaching isoelectric point (zeta $\rightarrow 0\text{mV}$) OR induce a yield stress through network forming polymers or clays.
- ▶ Slow down sedimentation by increasing LOW shear viscosity through use of appropriate additives or increasing charge

The End

Any questions?

www.malvern.com

References

1. American Society for Testing and Materials (1985), ASTM Standard D 4187-8, Zeta Potential of Colloids in Water and Waste Water
2. Barnes, H A (1992), *Recent advances in rheology and processing of colloidal systems*, The 1992 IChemE Research Event, pp. 24-29, IChemE, Rugby
3. Derjaguin, B; Landau, L (1941) *Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes*, Acta Physico Chemica URSS 14, 633.
4. Hunter, R.J (1988), *Zeta Potential in Colloid Science: Principles and Applications*, Academic Press, UK.
5. Larson, R.G (1999), *The Structure and Rheology of Complex Fluids*, Oxford University Press, New York
6. Verwey, E. J. W.; Overbeek, J. Th. G. (1948), *Theory of the stability of lyophobic colloids*, Amsterdam: Elsevier
7. P. B. Laxton and J. C. Berg. Gel trapping of dense colloids. *J. Colloid Interface Sci.* **285**:152–157 (2005)