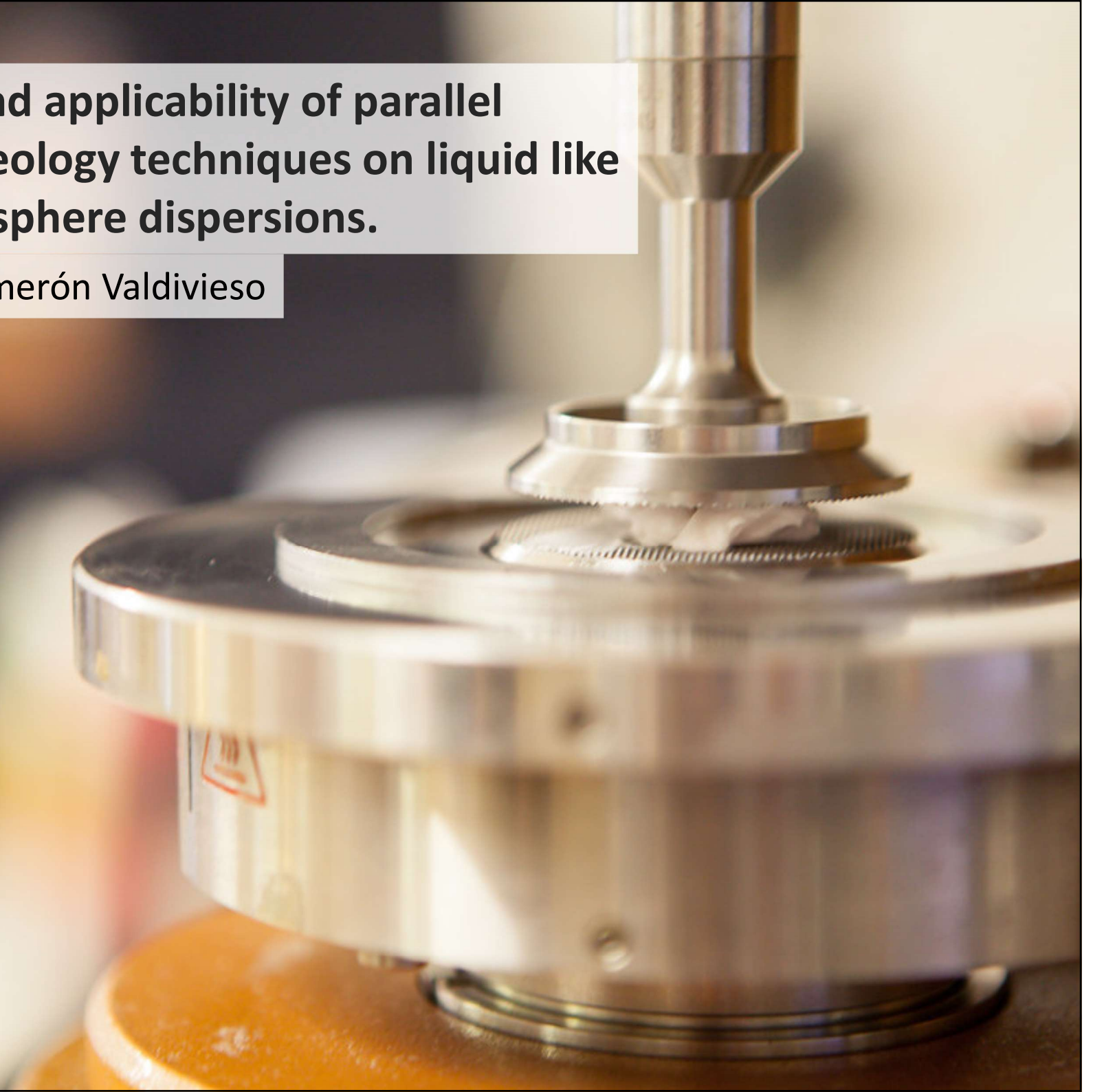
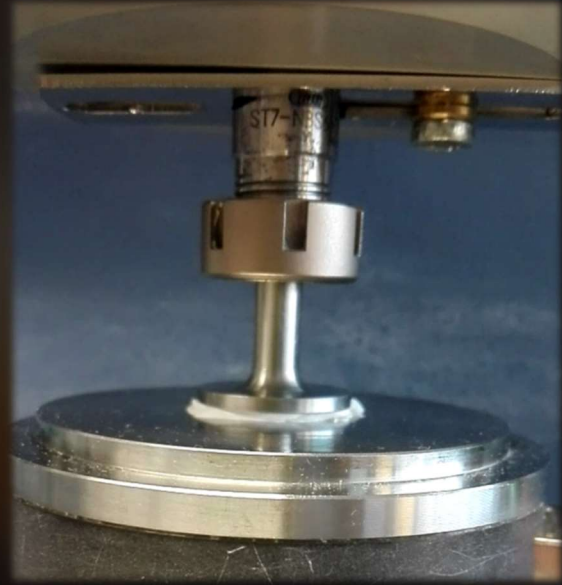


**Interpretation and applicability of parallel superposition rheology techniques on liquid like flocculated hard sphere dispersions.**

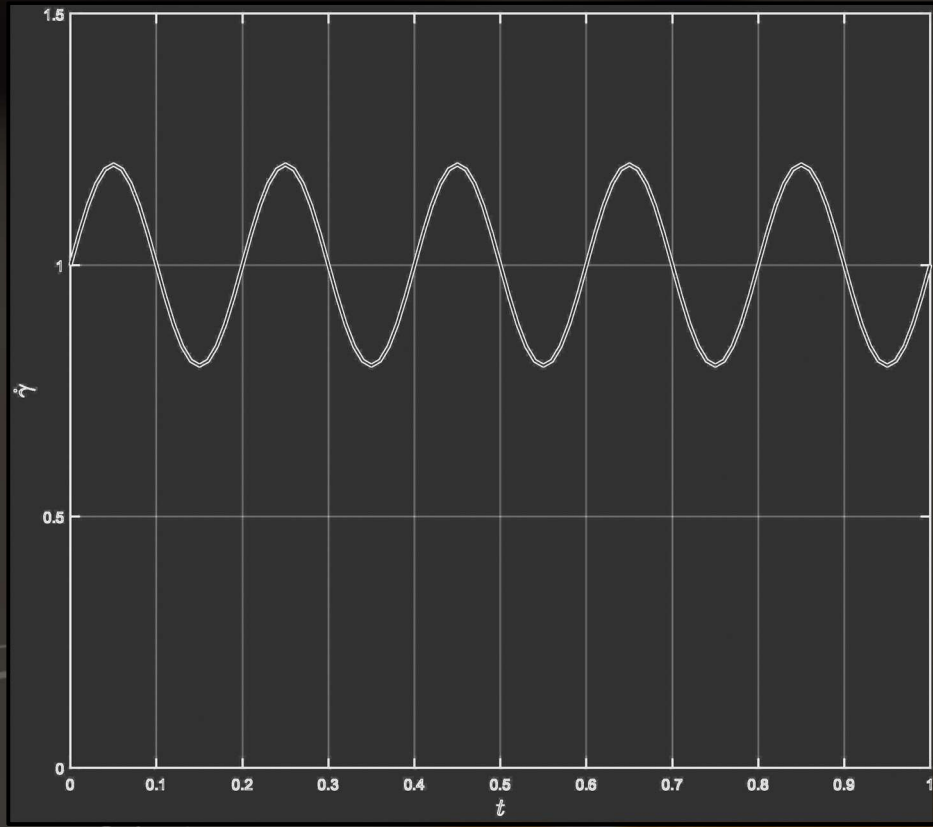
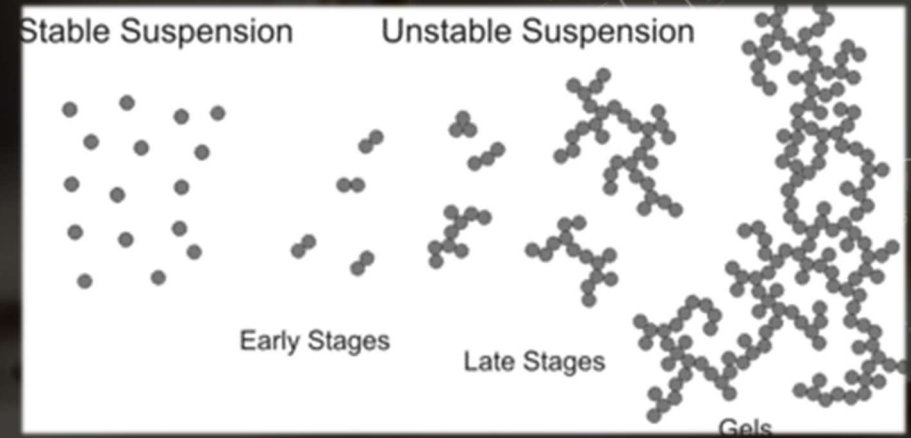
***Author:*** Honorio Salmerón Valdivieso



# OBJETIVE AND IMPORTANCE



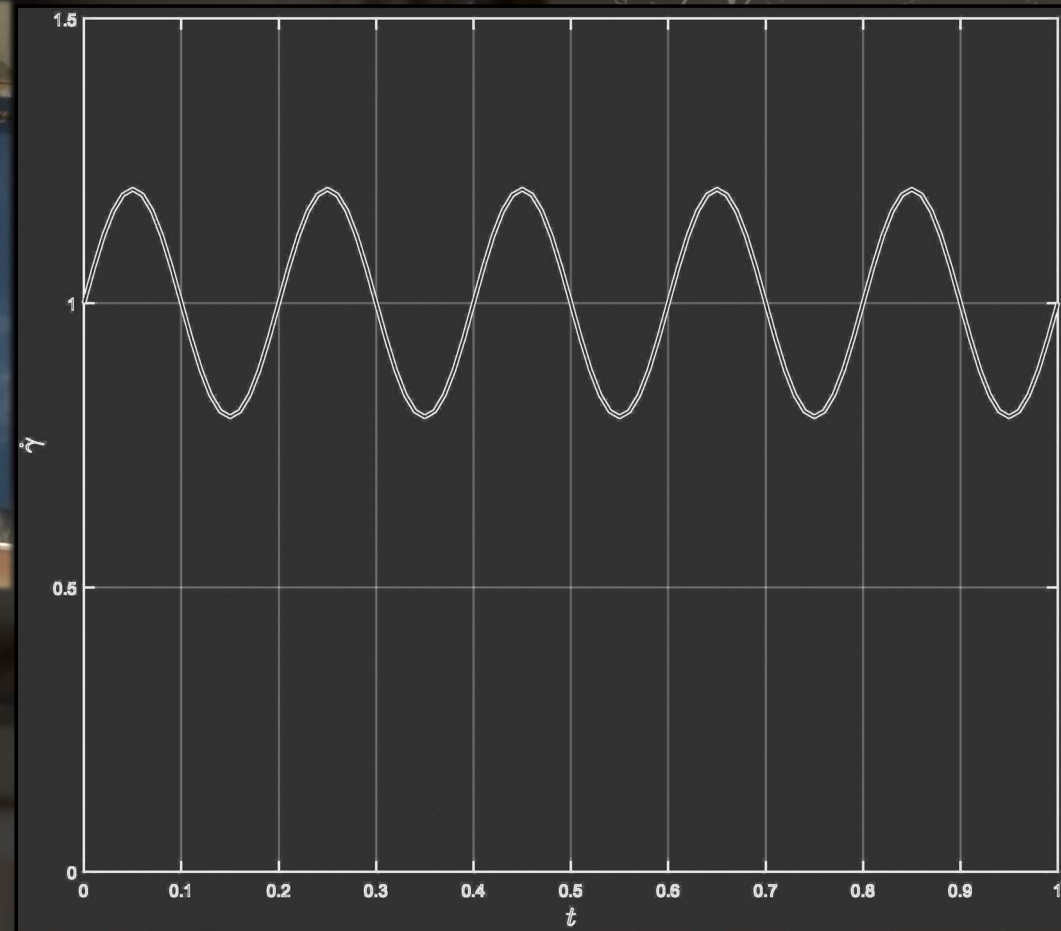
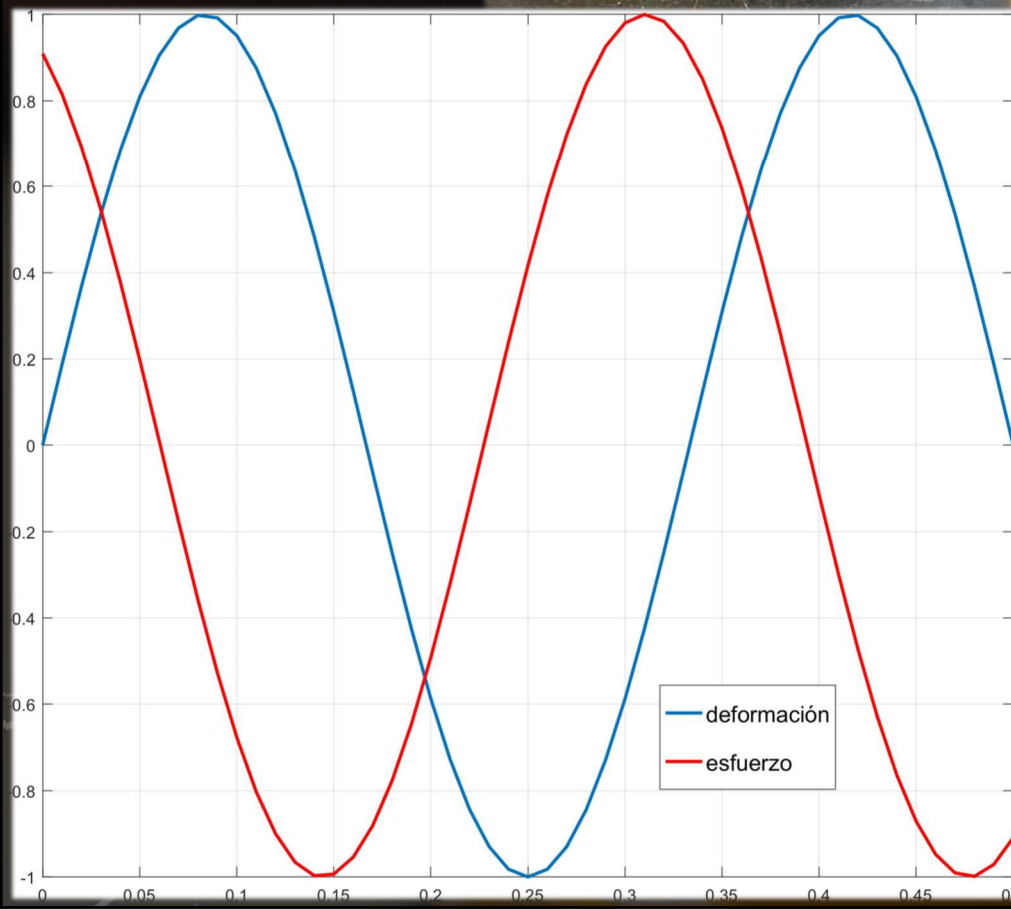
The complex behaviour of many fluids emerge from internal structures.



Stablish a link between structural reality and macroscopic behaviour may clarify the nature of some microscopic clusters.

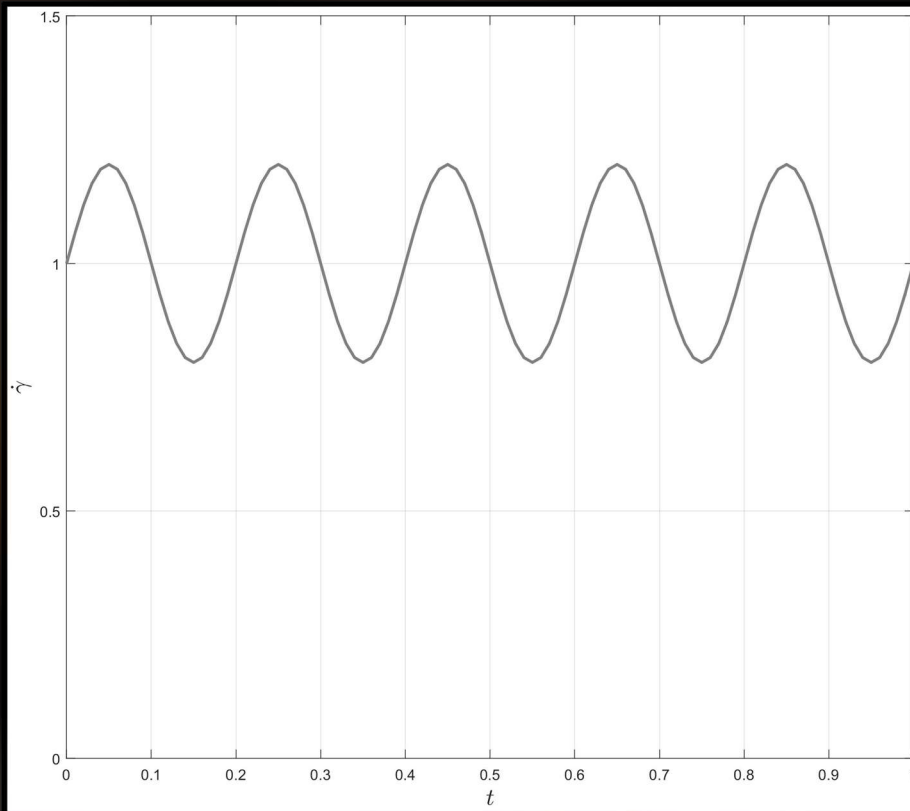
Oscillation superposition tests may be good candidate as tools to get along with that task.

# SOME INTRODUCTION



$$G' = \frac{\sigma_0}{\gamma_0} \cos(\delta)$$
$$G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta)$$
$$\tau = \frac{\eta}{E}$$

# PARALLEL SUPERPOSITION



*J. Vermant et al. (1977): description of moduli applying Yamamoto's model to a Lodge visco-elastic lineal material.*

*$H(\tau, \dot{\gamma}_{ss})$  defines de material behaviour.*

$$\lim_{\frac{\partial H}{\partial \dot{\gamma}^2} \rightarrow 0} (G'_{\parallel}, G''_{\parallel}) = (G', G'')$$

$$G'_{\parallel} = \int_{-\infty}^{\infty} \left[ H + 4 \dot{\gamma} \frac{\partial H}{\partial \dot{\gamma}^2} \frac{1}{1 + (\omega\tau)^2} \right] \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d \ln\tau$$

$$G''_{\parallel} = \int_{-\infty}^{\infty} \left[ H + 4 \dot{\gamma} \frac{\partial H}{\partial \dot{\gamma}^2} \frac{1 - (\omega\tau)^2}{1 + (\omega\tau)^2} \right] \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d \ln\tau$$

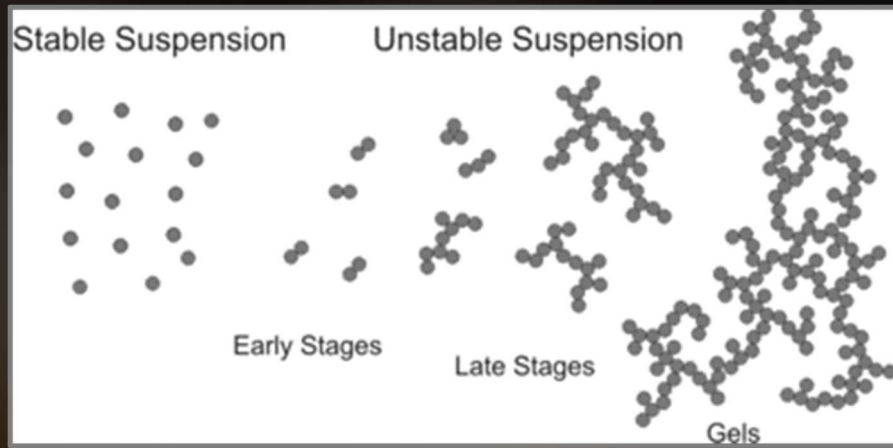
$$\lim_{\omega \rightarrow 0} \frac{G''_{\parallel}(\dot{\gamma})}{\omega} \neq \eta(\dot{\gamma})$$

*Applicability conditions (?):*

$$\frac{\partial H}{\partial \dot{\gamma}^2} \ll 1 \rightarrow \frac{\gamma_0 \omega}{\dot{\gamma}_{ss}} \ll 1$$

$$Pe \gg 1$$

# REFERENCE OBSERVATIONS

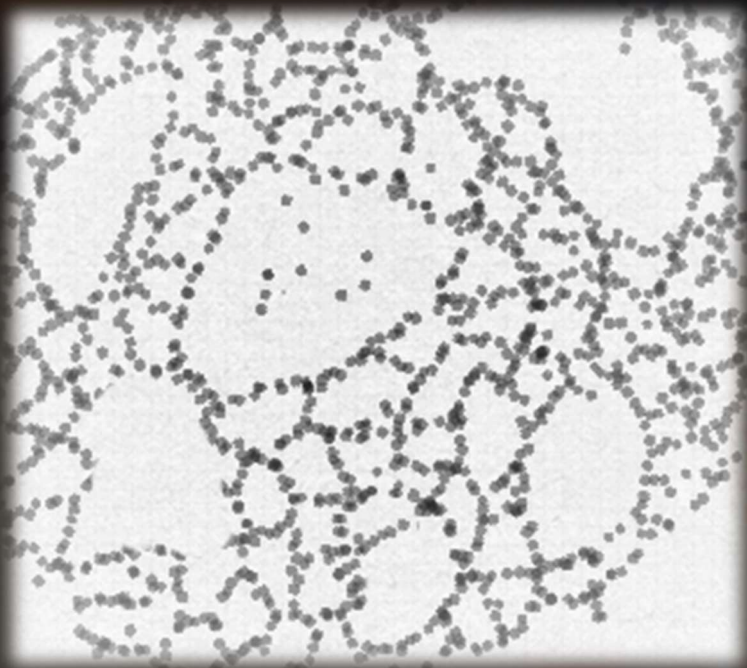


*Different structure phases.*

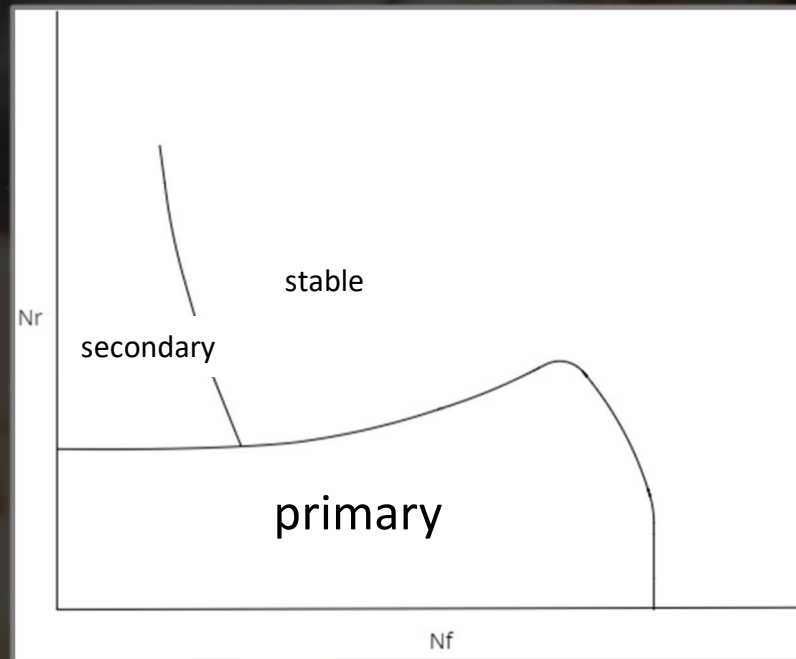
Relation between number, mass, gyration radius and floc volume.

*Ven & Mason (1977)*

$$N \propto M \propto R^{D_f} \propto \left( \frac{R_g}{a} \right)^{D_f}$$

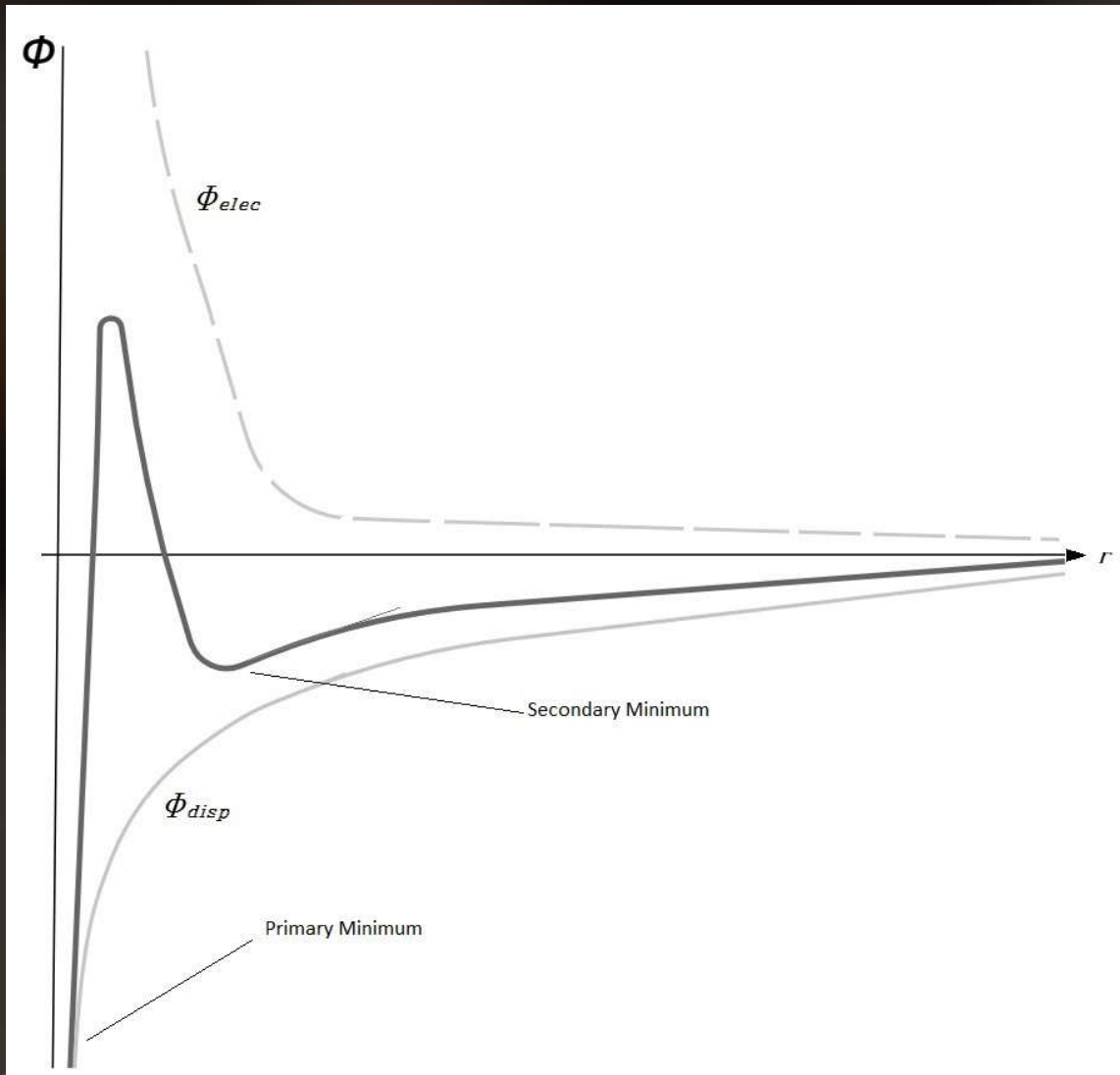


*Schematic of a colloidal floc.*



*Phase diagram for a hard sphere structure. Nr represents the relative between repulsion and attraction. Nf represents the ratio between convection and attraction.*

# THEORETICAL FOUNDATIONS: two body DLVO potential



$$\Phi_t = \Phi_e + \Phi_d$$

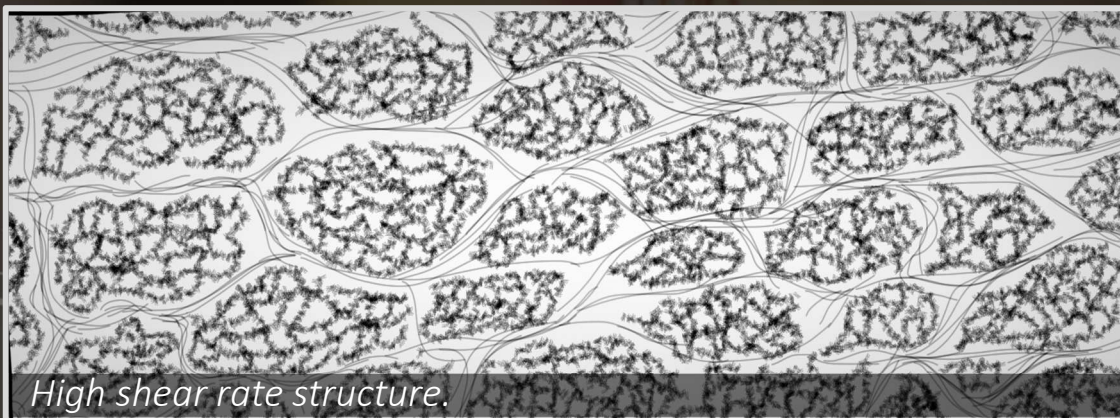
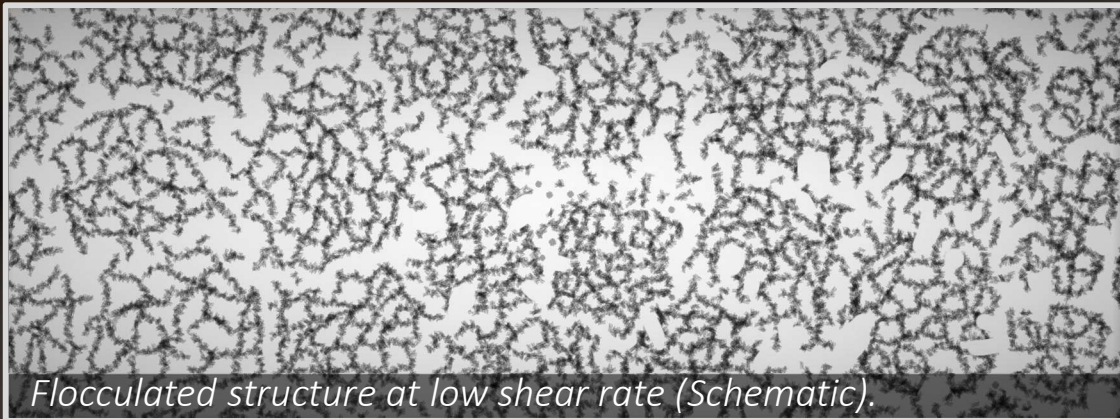
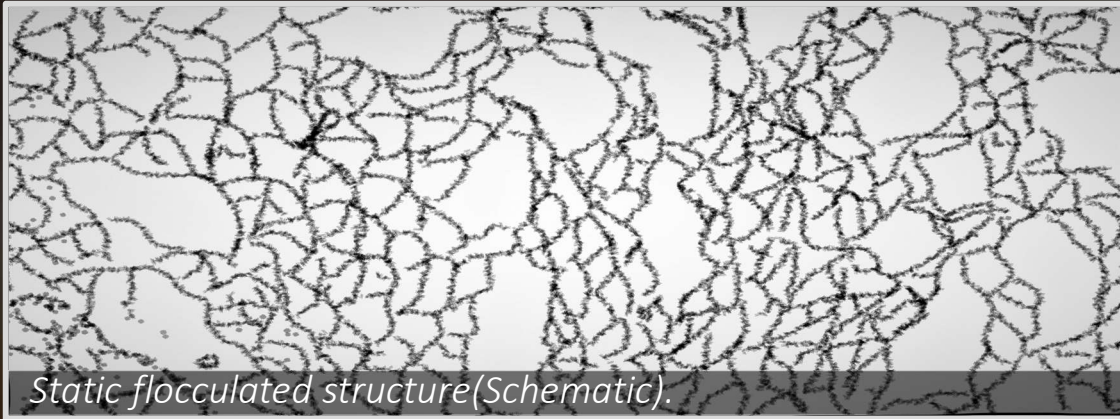
Secondary minimum:

*Gas-like and Liquid-like structures.*

Primary minimum:

*Stronger, formation of colloidal gels and colloidal crystals.*

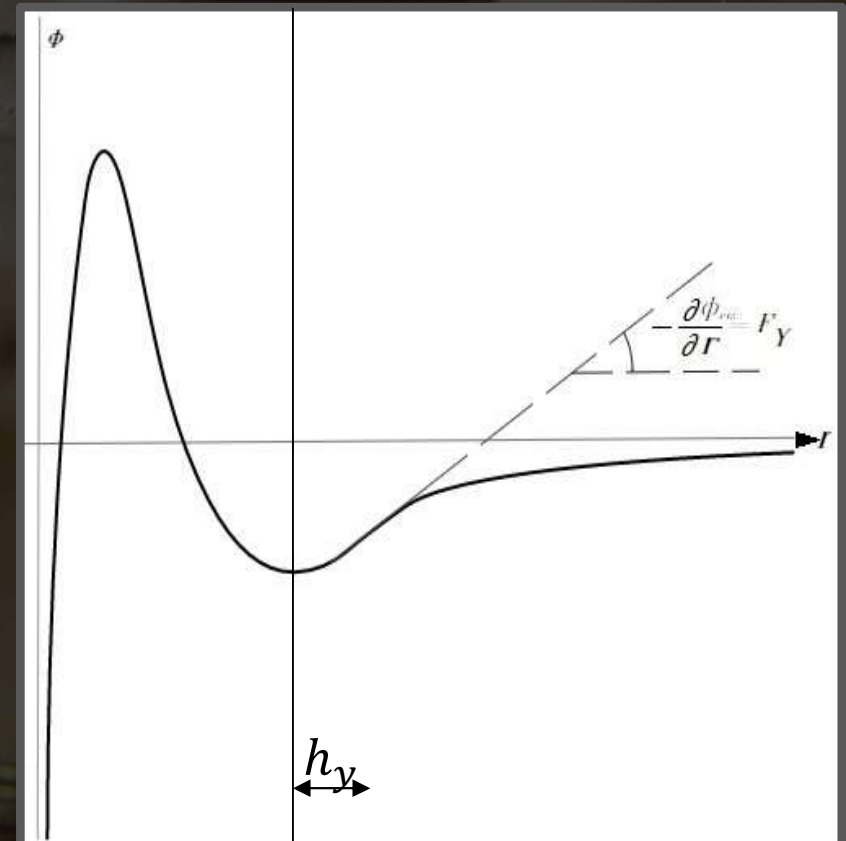
# REFERENCE OBSERVATIONS: structure and convection



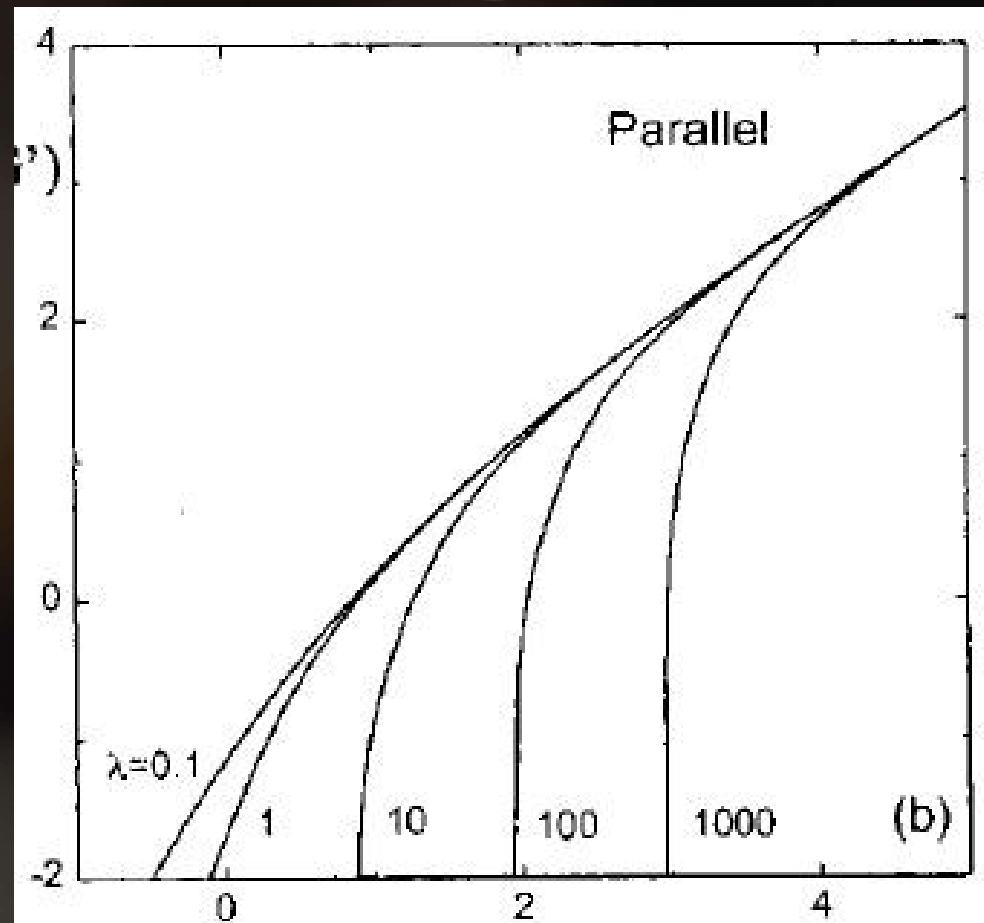
Relation between number, radius  
and convective flux on flocs.

*Sontag & Russel (1979)*

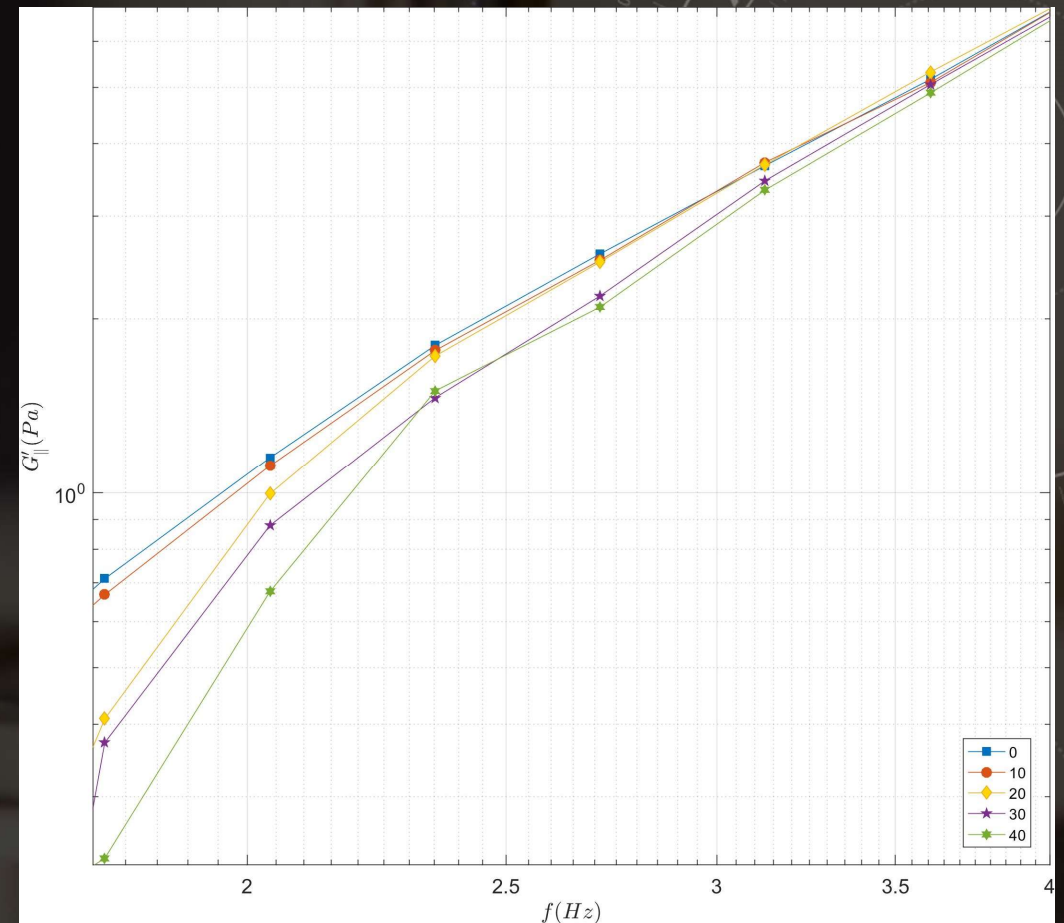
$$N_f \propto \eta_m \dot{\gamma}$$
$$\left(\frac{R_g}{a}\right)^3 \propto \frac{1}{\eta_m \dot{\gamma}}$$



# REFERENCE OBSERVATIONS



Storage modulus behaviour with increasing stationary flow. Figure taken without permission from reference [1]

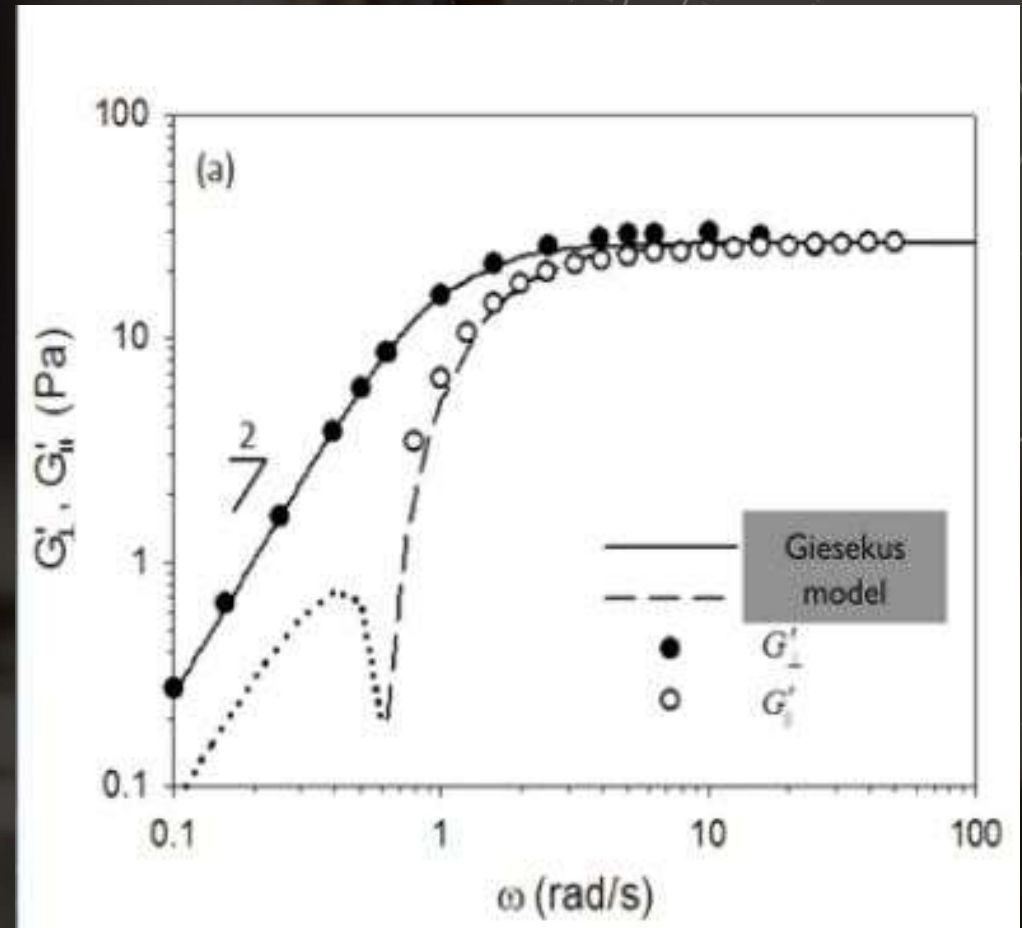


Results of oscillatory deformation test on TiO<sub>2</sub> particles with no stationary convection. Different curves correspond to different stationary shear rates.

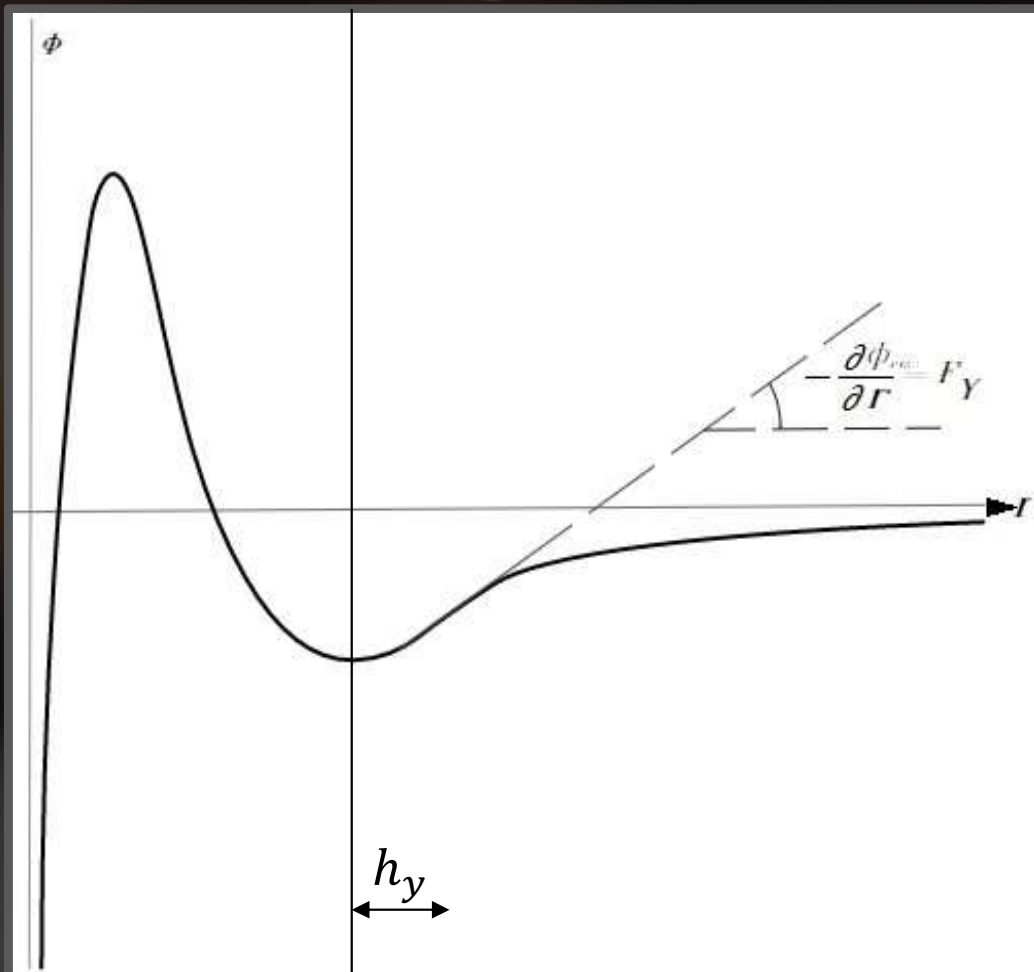


# Prediction model: foundations

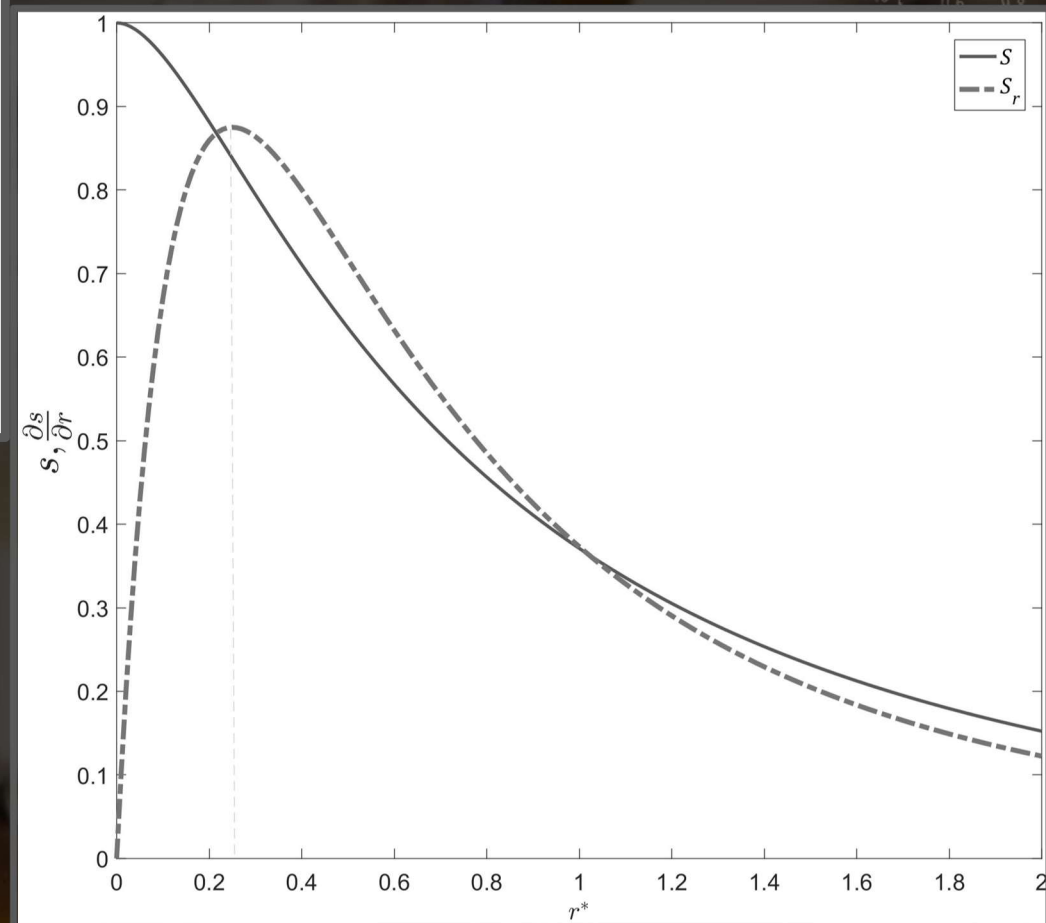
- The structural response to perturbation varies with the size of the flocs. Less radius means less resistance to convection.
- Each floc itself behaves as a viscoelastic material due to trapped fluid in the floc.
- The disaggregation of flocs causes an increase of the surrounding fluid viscosity, due to the increase of effective surface.



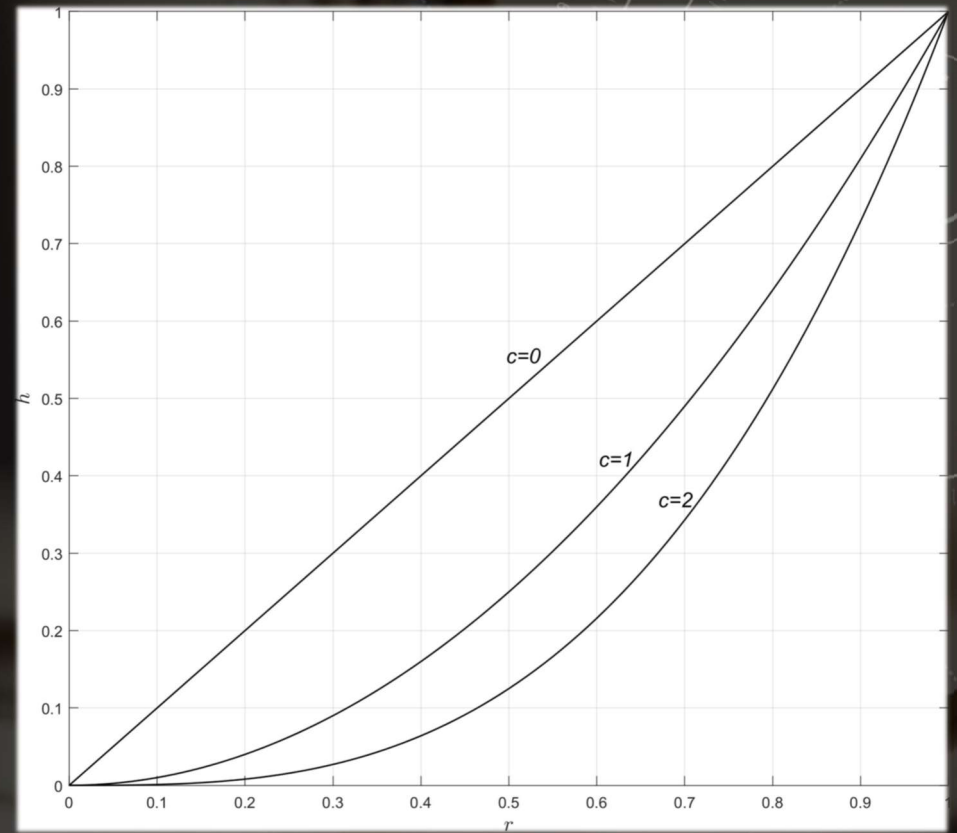
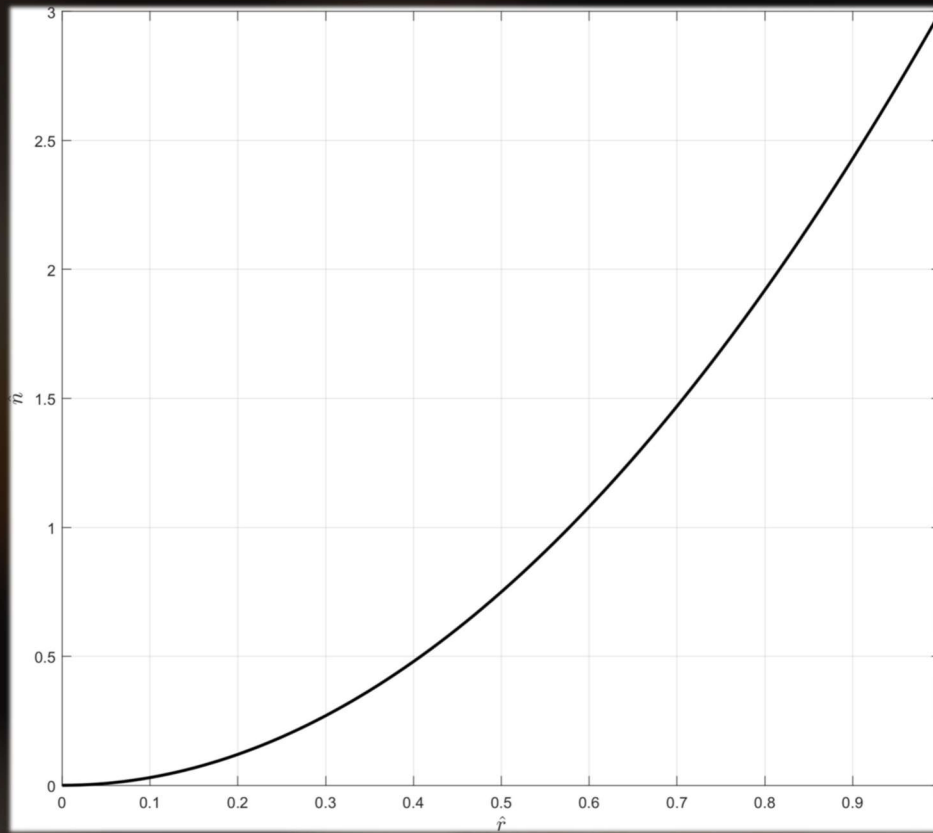
# THEORETICAL MODEL: two body potential



$$\Phi_t = \Phi_e + \Phi_d$$



# THEORETICAL PREDICTION: distribution



$$\hat{r} = \frac{r}{R_g} \quad \hat{n} = \frac{n(r)}{N_p} = 3\hat{r}^2 dr$$

$$\hat{h} = \frac{h}{h_y} = \hat{r}^{c+1}$$

$$\begin{array}{l} \dot{\gamma}_{SS} \rightarrow 0 \quad : \quad c \rightarrow 0 \\ \dot{\gamma}_{SS} \rightarrow \infty \quad : \quad c \rightarrow \infty \end{array}$$

$$S(c) = \int_0^{\hat{h}_{max}} n(\hat{h}) \cdot s(\hat{h}) d\hat{h}$$

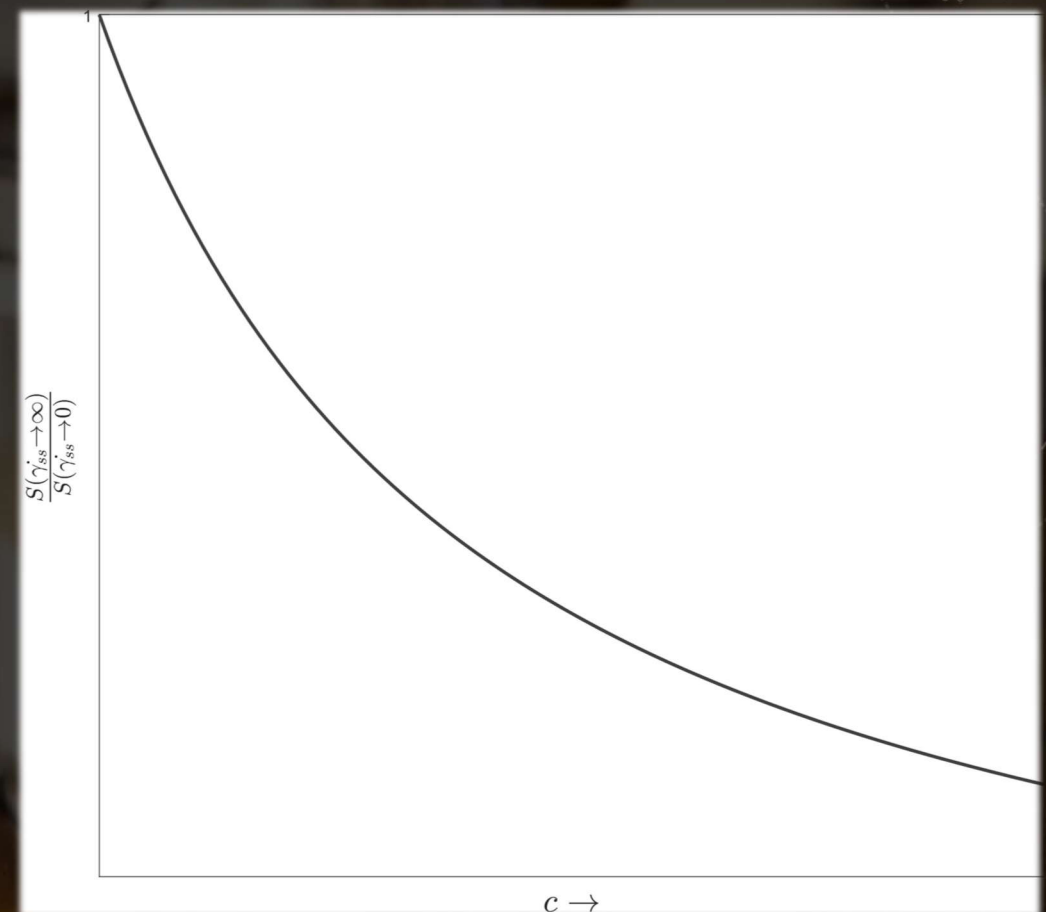
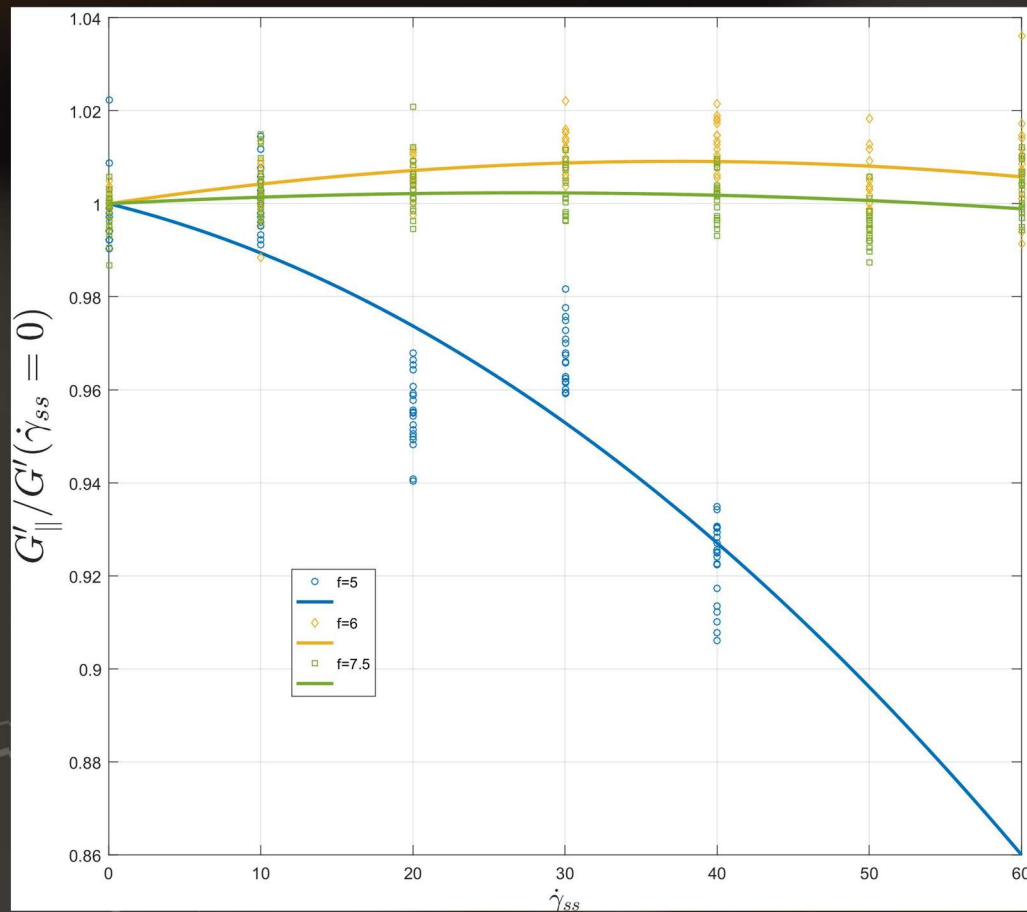
$h$  represents the av. Dispersion around each particle.  $h_{max}$  represents the maximum dispersion. (non-dimensional)

# Storage on equilibrium floccs

Linearizing for equilibrium floccs:

$$\Delta s \approx \hat{h} \cdot s_Y \quad \hat{h}_{max} = 1$$

$$\hat{S}(c) = \frac{S}{N_p s_Y} = \int_0^1 \hat{n}(\hat{h}) \cdot \hat{h} \cdot d\hat{h}$$



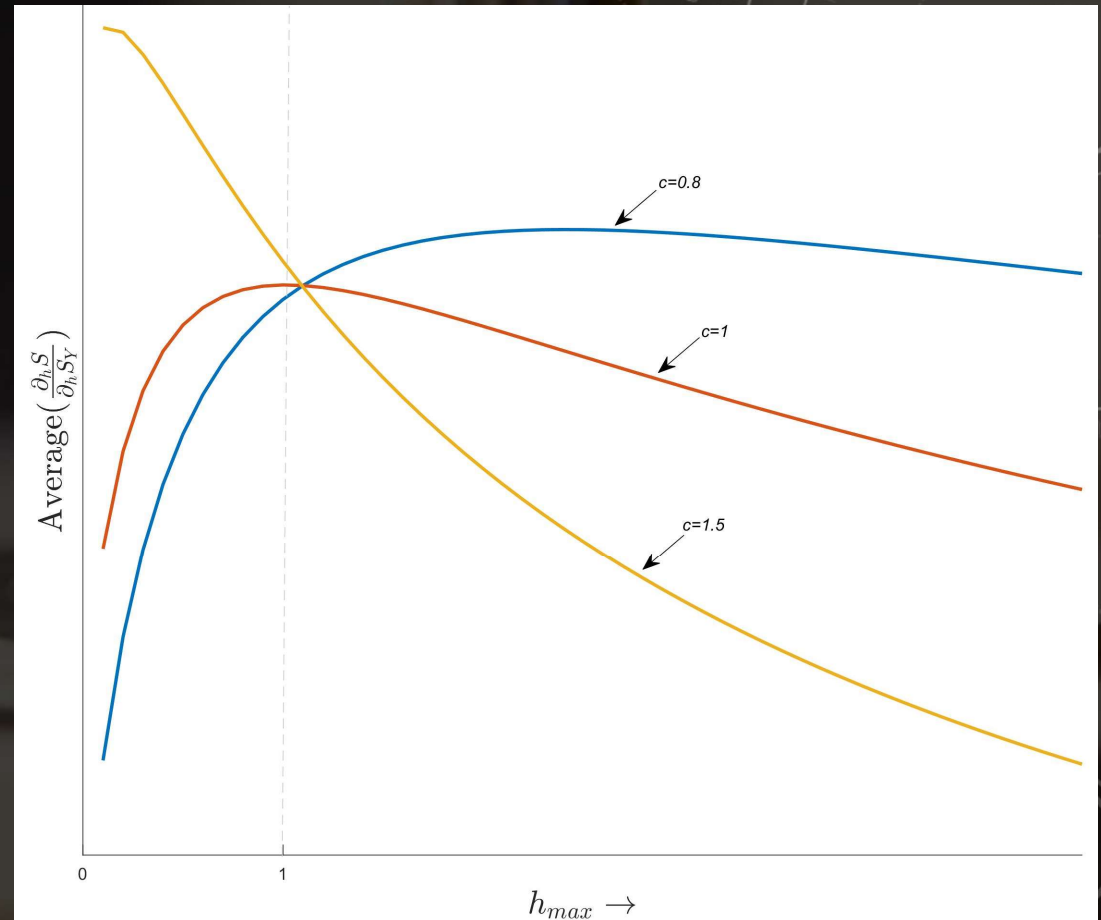
# Non-equilibrium flocs

$$\sigma = \int_0^{h_{max}} \hat{n}(\hat{h}) \cdot \partial_r \hat{s}(\hat{h}) \cdot d\hat{h}$$

The stress response of the floc decays faster with higher stationary shear rate.

*Question: How sensitive is our material?*

Bigger  $\gamma_{ss}$  → more and smaller flocs  
Bigger  $\gamma_{ss}$  → less resistance of the flocs to convection.

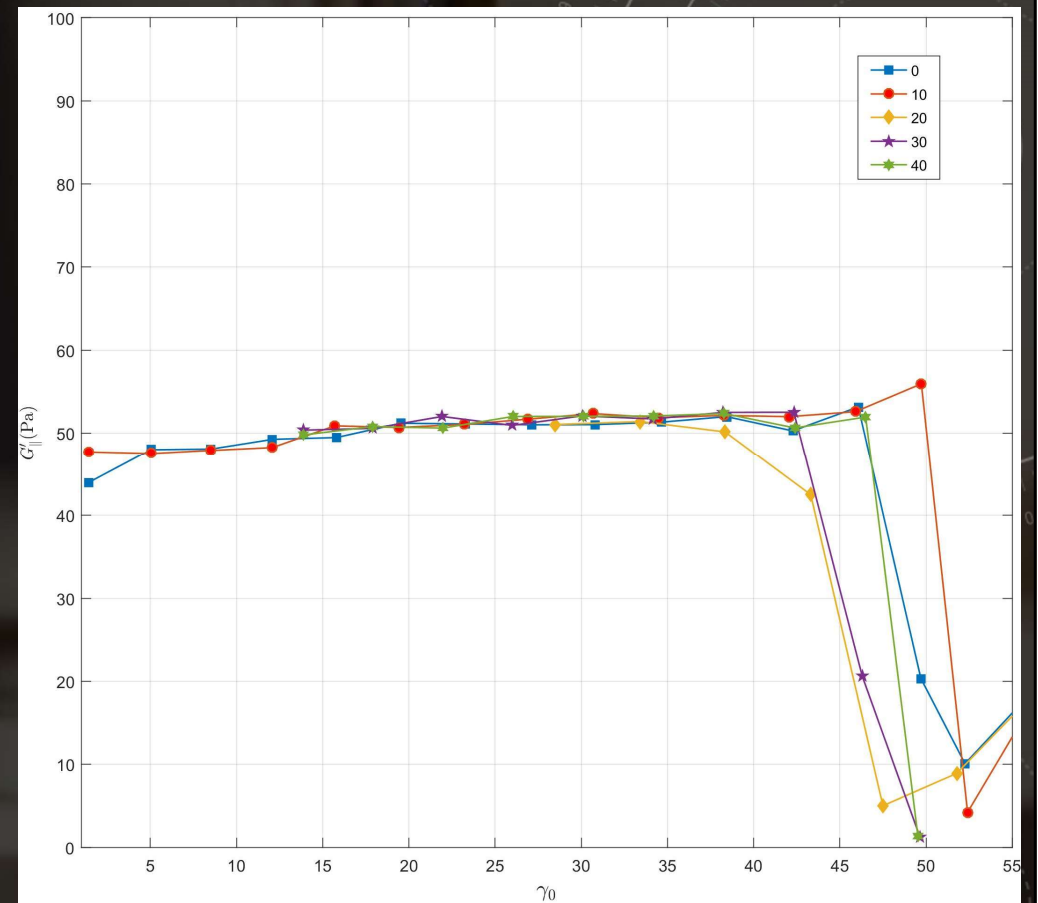
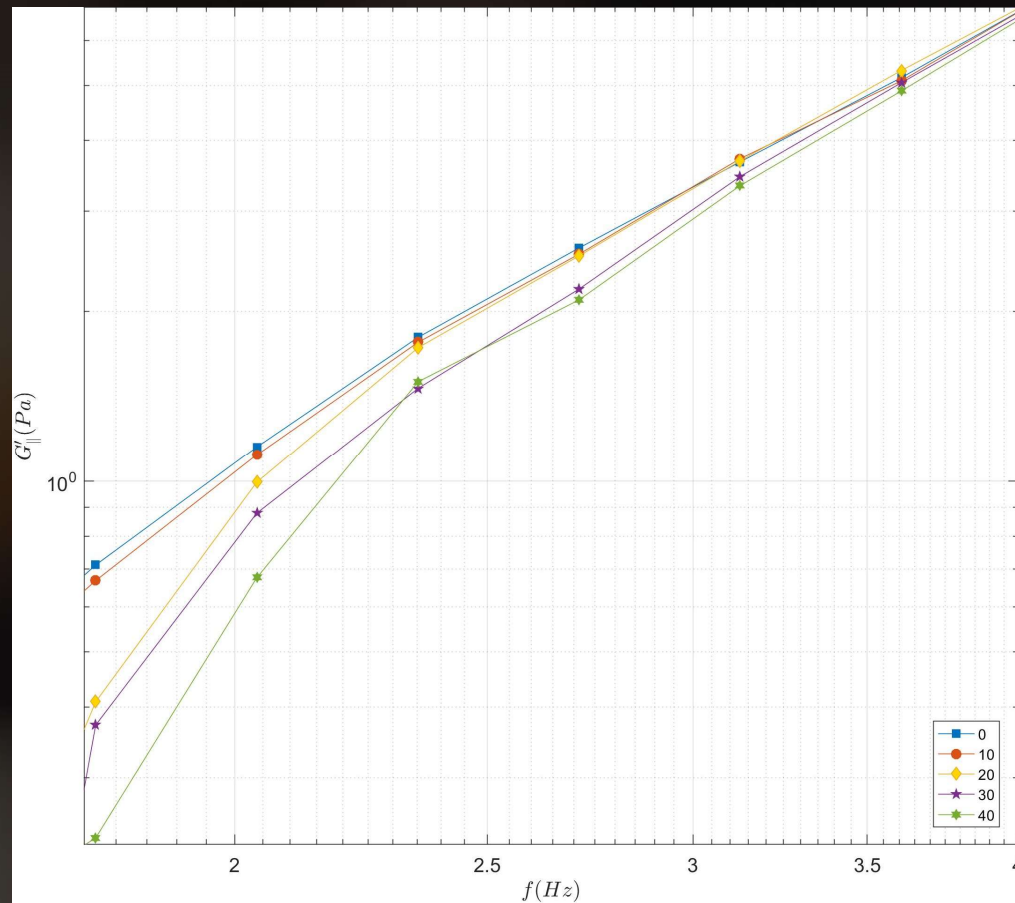


Different “stress” curves vs maximum dispersion. The bigger  $h_{max}$ , the bigger strain rate ( $\omega \gamma_0$ ). The bigger  $c$ , the bigger stationary shear rate ( $\dot{\gamma}_{ss}$ ).

Similar shapes observed on LAOS experiments:

*K. Hyuna et al. A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS). Progress in Polymer Science pp1697-1753 (2011)*

# Observations:



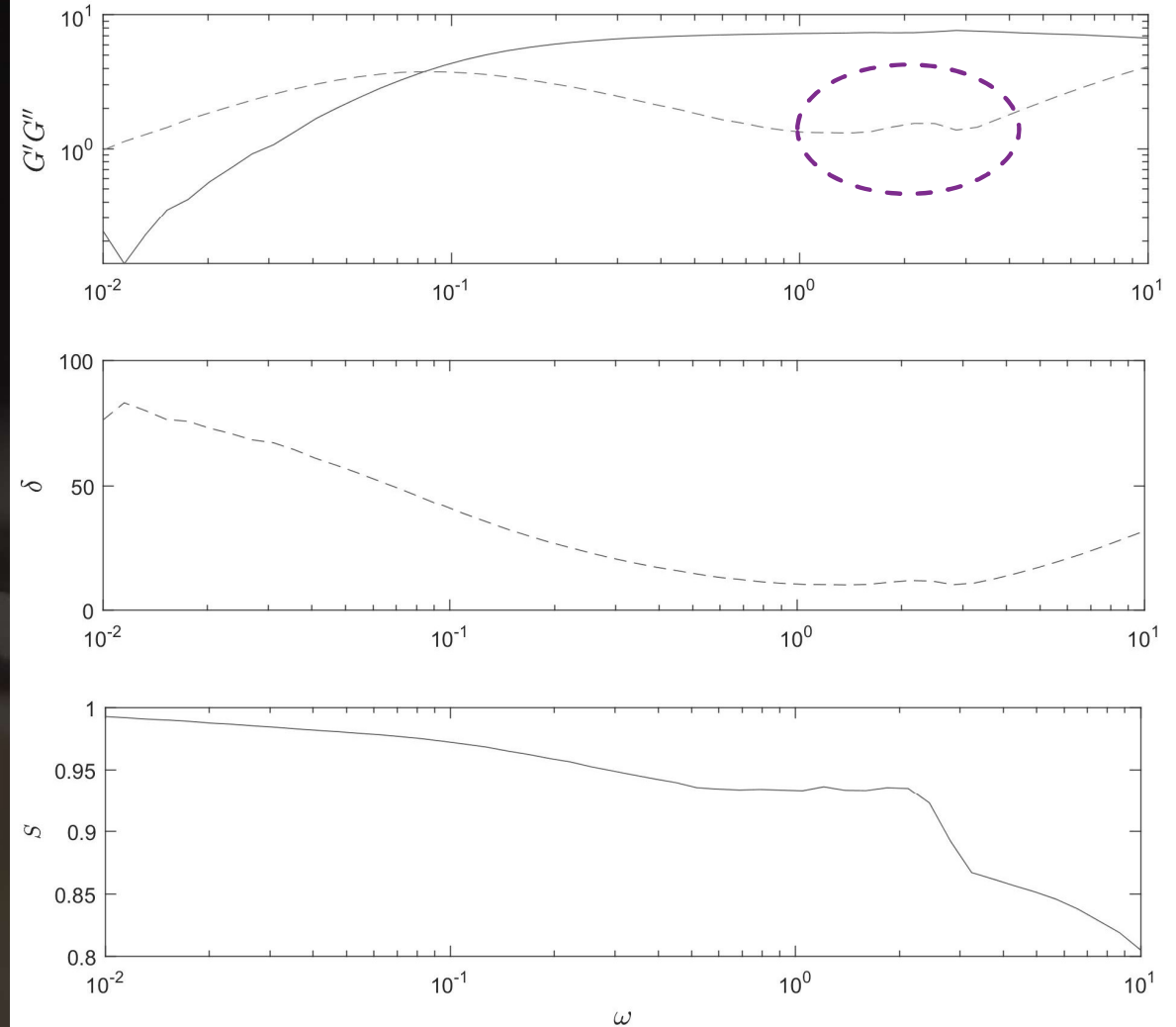
Our material responds little sensitive to stationary shear rate variations (at high frequencies).

Hypothesis:

- 1-This model does not represent the physical reality.
- 2-The internal structure is very self-conservative .
- 3-The volume concentration is to high and the structure is not able to evolve.

# Simulation

The structure behaves very self-preservative until a critical point where the viscosity modulus grows greatly due to the increase of free particles on the medium.

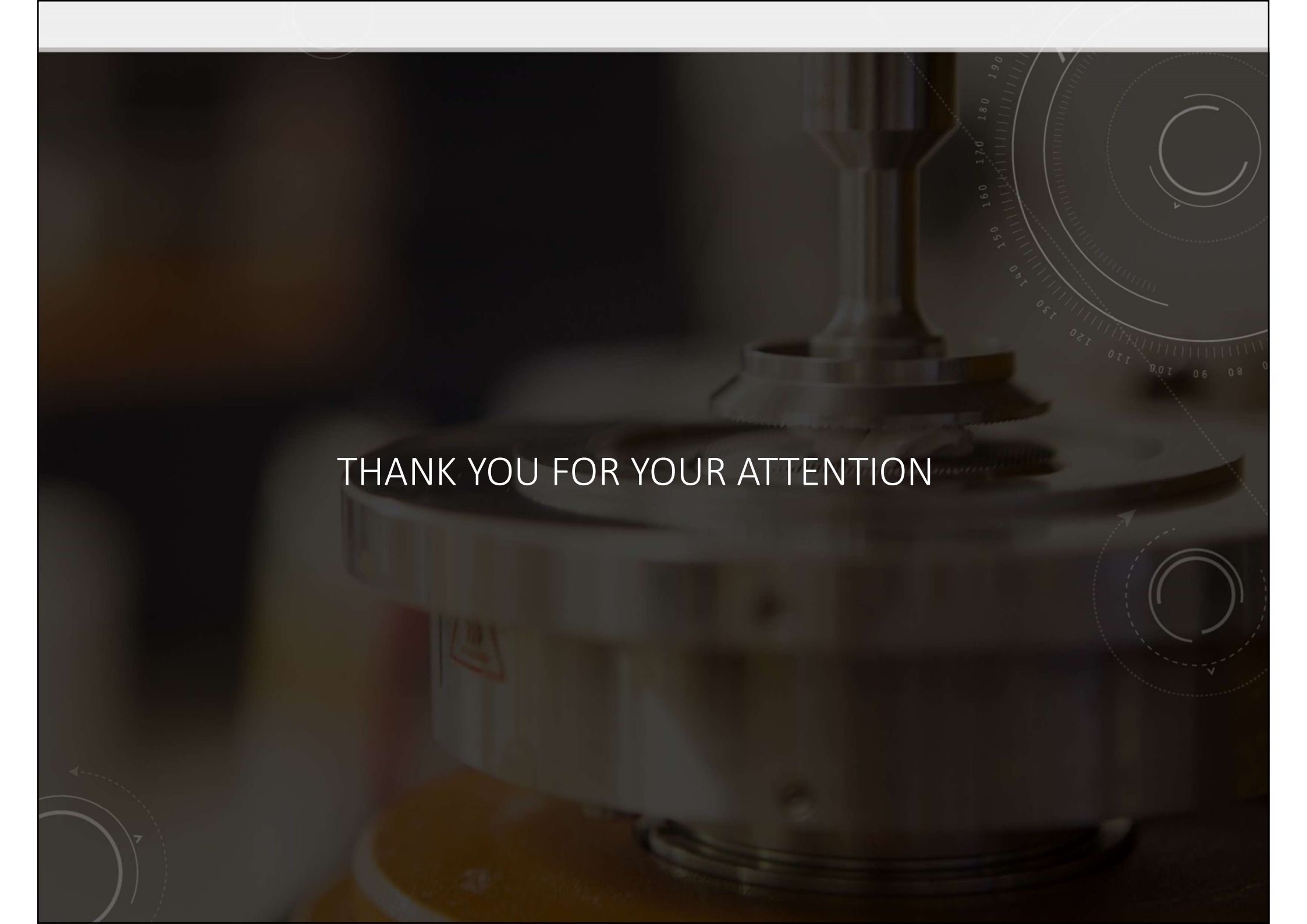


# CONCLUSION AND FURTHER WORK

- The linear, structure consistent zone has been isolated if the predictions are correct.
- Due to the difficulties modelling the interaction rheometer-dispersant-flocs, trying to connect quantitative variations on measurements with the cluster structure seems to be a non efficient research path.
- It may be on critical points as the one mentioned where the structure manifest itself the most. However it requires the rheometer to be able to measure on high strain rates.
- This work may have shown how self consistent the cluster structure is.

The dependence of those critical point with the stationary shear rate should be observed in further work to stablish if the prediction is correct and if the individual colloid properties are related with it.





THANK YOU FOR YOUR ATTENTION