Quantitative characterisation of the dispersion quality based on mechanical contrast

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KU Leuven (B), Department of Chemical Engineering
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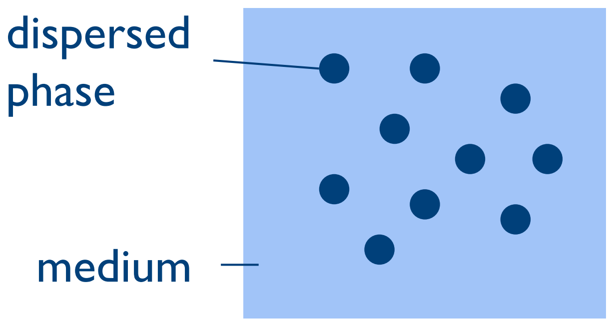
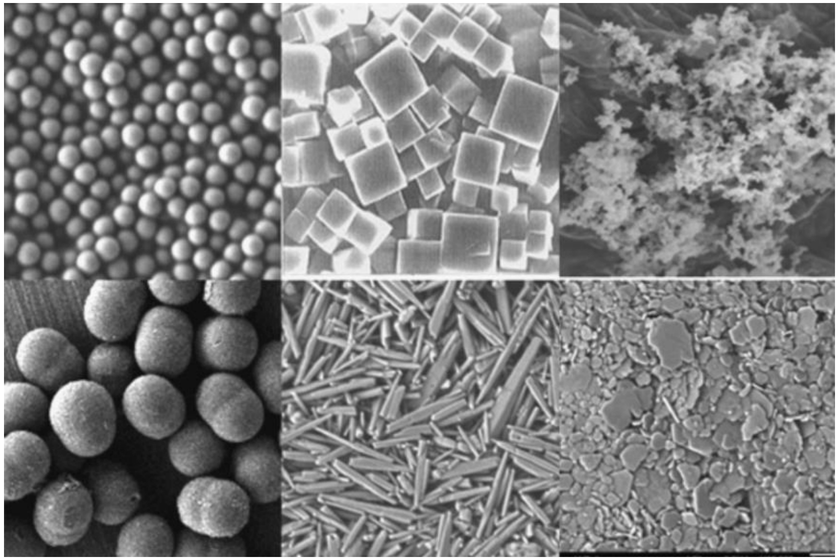
Colloidal systems



colloidal suspensions :

- dispersed phase = solid
- $F_g \leq F_B$

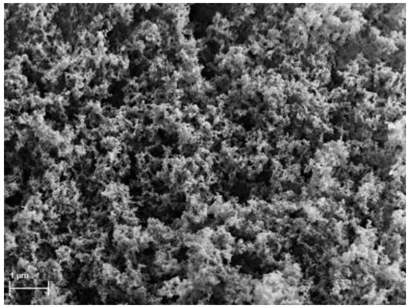


Performance of nanomaterials

nanoscale adds specific functionality ..

CEN.ACS.ORG

paints & coatings

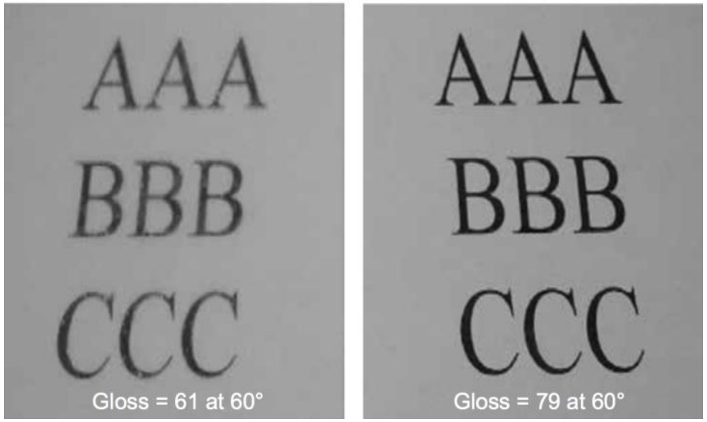


fumed silica, www.bine.info

.. importance of dispersion state

Resin
+ 1 % AEROSIL® 200

Resin
+ 5 % AERODISP® W 7520



EVONIK

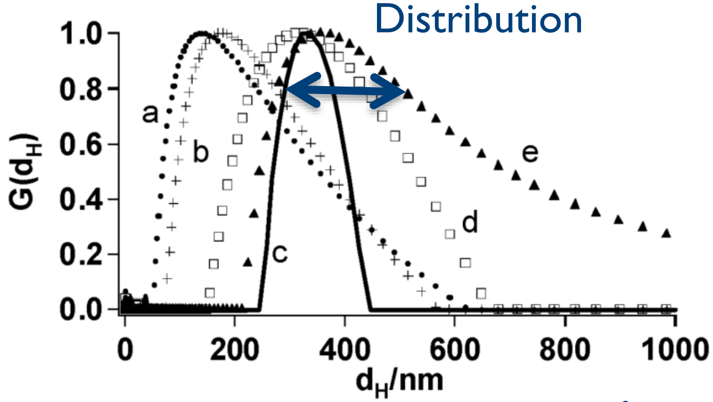
Dispersing nanoparticles ?

partially wetted - flocculated

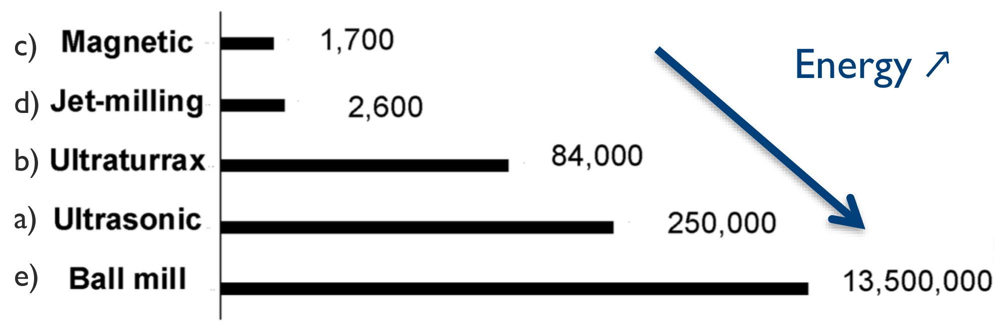
finely dispersed

- Dispersion processes

Distribution



Size ↗



Energy ↗

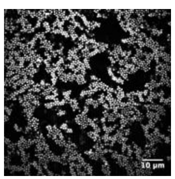
Studying nanomaterials

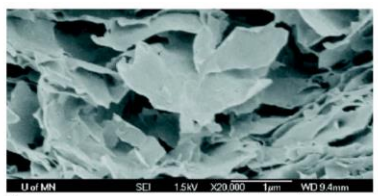
Key aspects :

- quantitative
- averaged
- in-situ ?

“local” methods

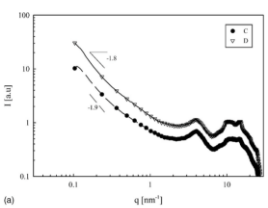
Optical : microscopy, EM





(c)

Scattering : SAXS, LS



(a)

J. Vermant, S. Ceccia, S, M.K. Dolgovskij, P.L. Maffetone, C.W. Macosko (**2007**), *J. Rheol.* 51(3) : 429-450

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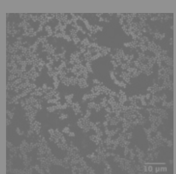
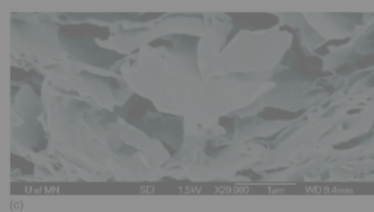
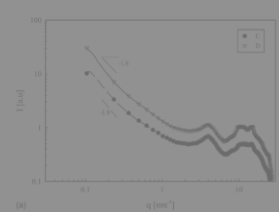




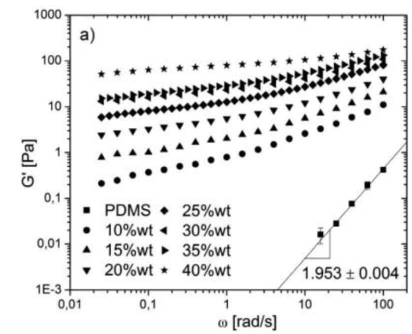
Scattering : SAXS, LS



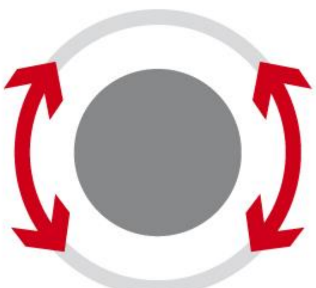
"global" methods

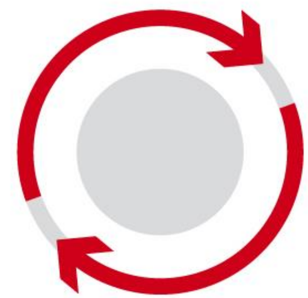
Composites : dielectric, mechanical properties

Rheology ?



Rheology

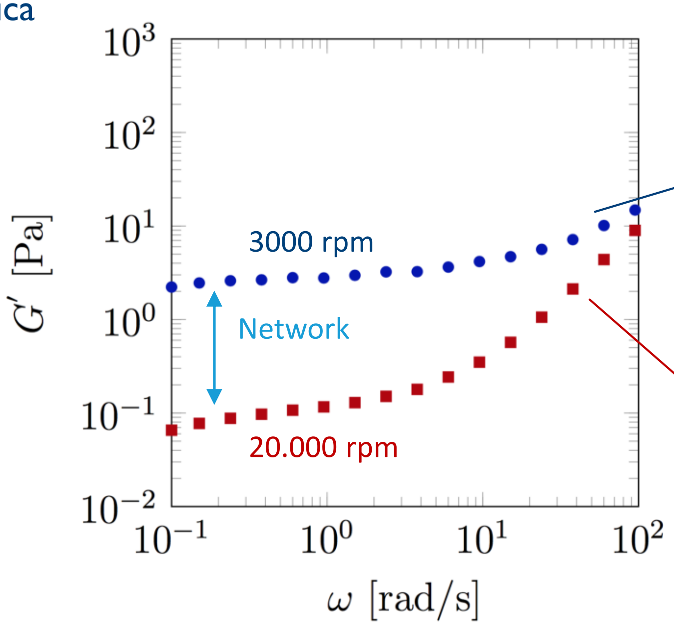


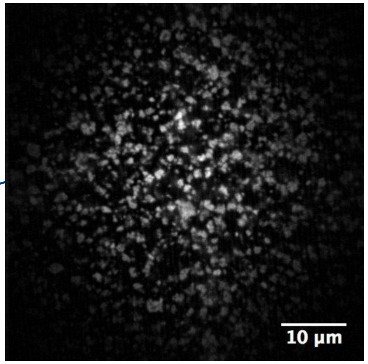


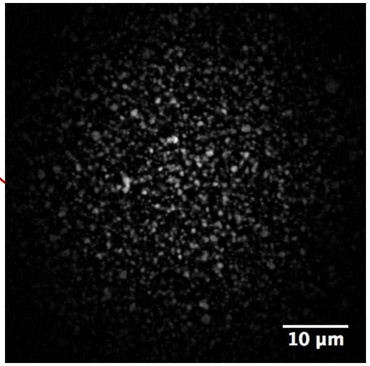
Rheology in a quantitative way

Linear viscoelastic properties of suspensions

20 wt% silica
in PDMS :





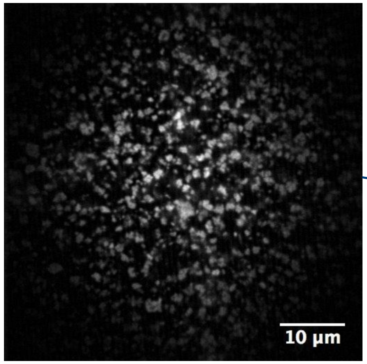


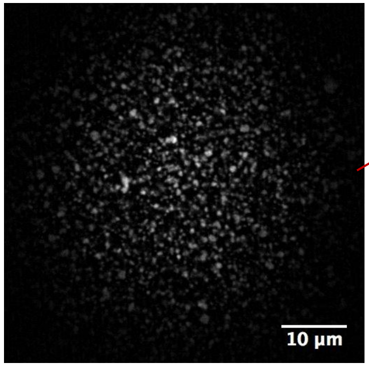
Elastic properties ?

Sensitive, but difficult to invert

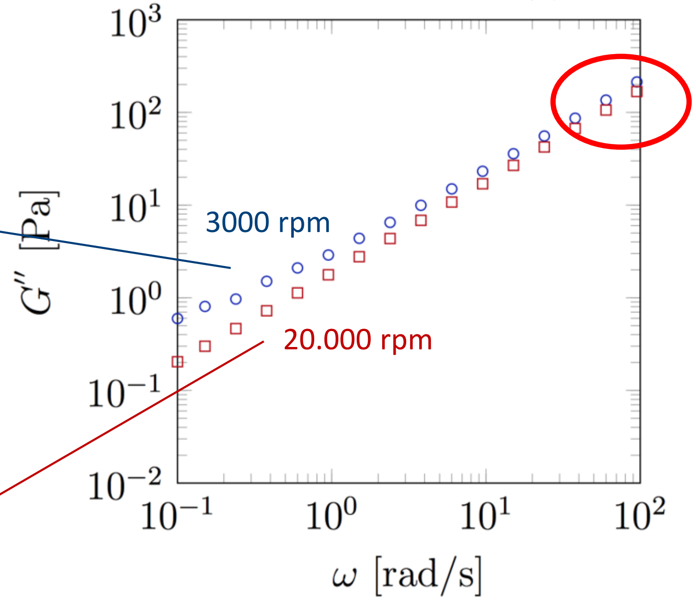
Rheology in a quantitative way

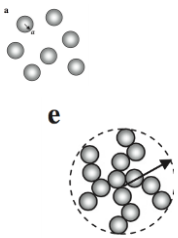
Linear viscoelastic properties of suspensions



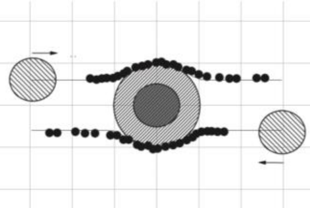


20 wt% silica in PDMS :

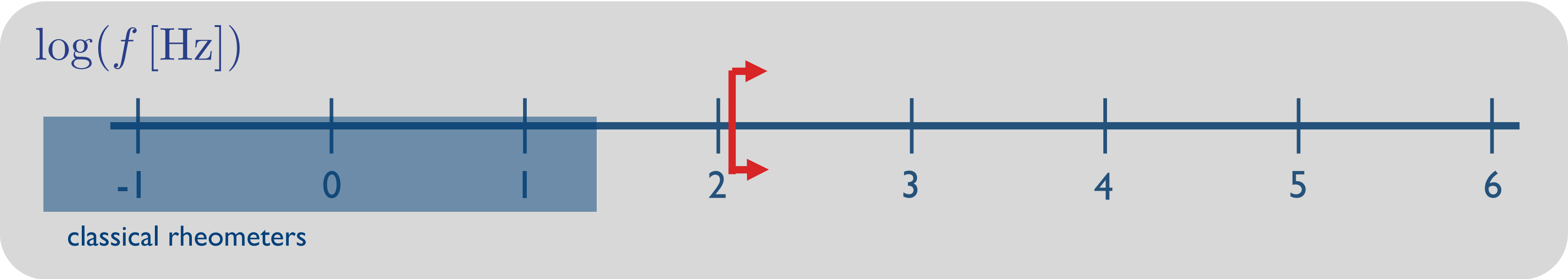




Viscous properties
@ high frequencies
=> **hydrodynamics**



Rheology in a quantitative way



hydrodynamic interactions

$$\alpha = \frac{12\pi^2 f a^3 \eta_m}{k_B T} \gg 1$$

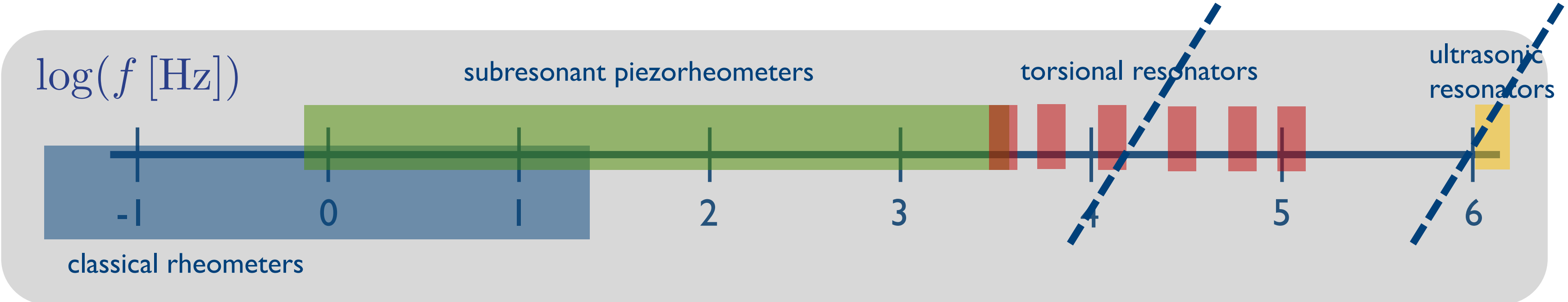
R. A. Lionberger & W. B. Russel (**1994**) *J Rheol* 38, 1885

eg. 50 nm particles in 0.1 Pas :

$$f >> 10\,\mathrm{Hz}$$

C. Beenakker (**1984**) *Physica A* 128, 48–81

Rheology in a quantitative way



2. Applicability:

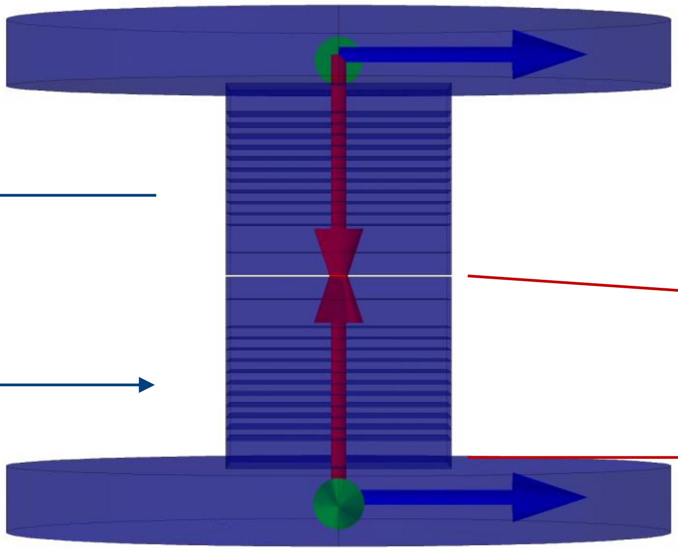
- Range η
- Range f
- Sample vol

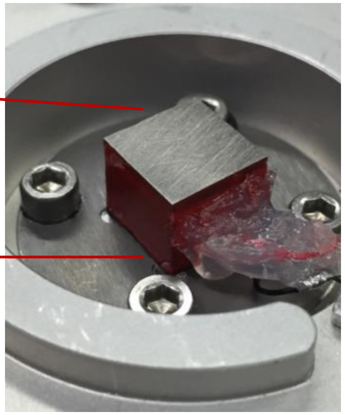
1. Penetration shear wave :

$$\delta = \frac{1}{2\pi f}\sqrt{\frac{2}{\rho}\left(\frac{G^{*2}}{G^{*} - G'}\right)}$$

Piezo Shear Rheometer

$$V_{out}(t) = \sigma(t) \cdot \frac{d_{15}}{C} \cdot S$$





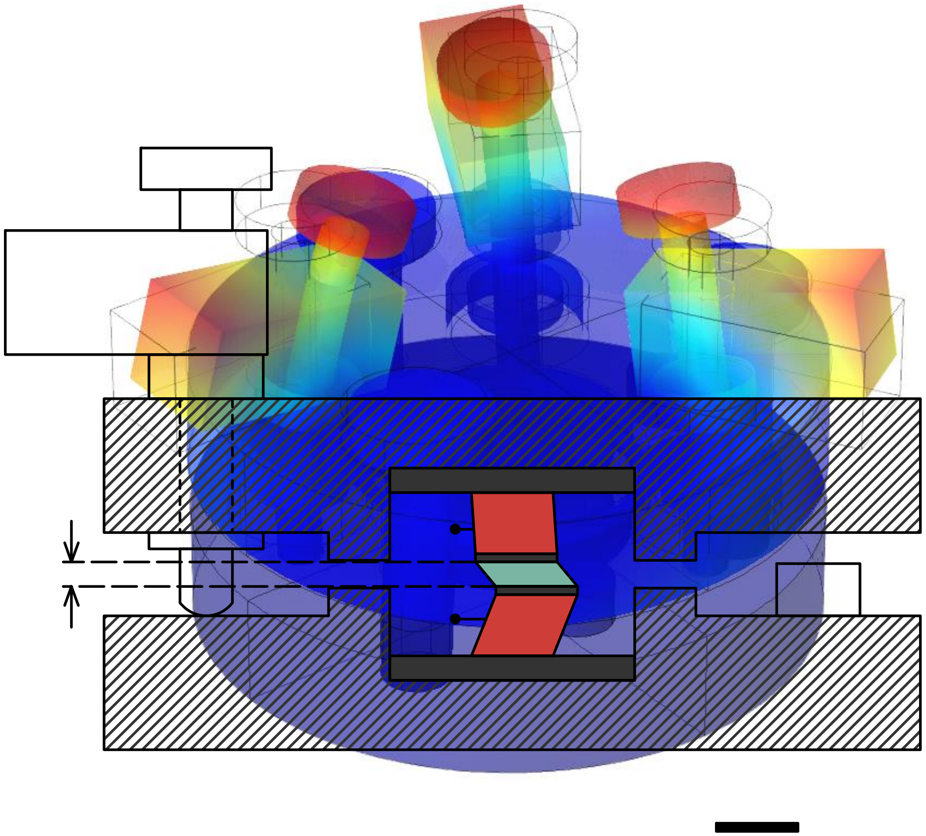
$$V_{in}(t) = \gamma(t) \cdot \frac{D}{d_{15}}$$

Piezo Shear Rheometer

- **3-point alignment**
  - Nano-positioners
  - Displacement sensors
  - Fixation screws

- **1st resonance frequency ?**

Simulation/Experiment
~ 2 – 3 kHz



Comparison different dispersion methods

Disperse silica
nanoparticles by ..

magnetic stirring

high shear mixing

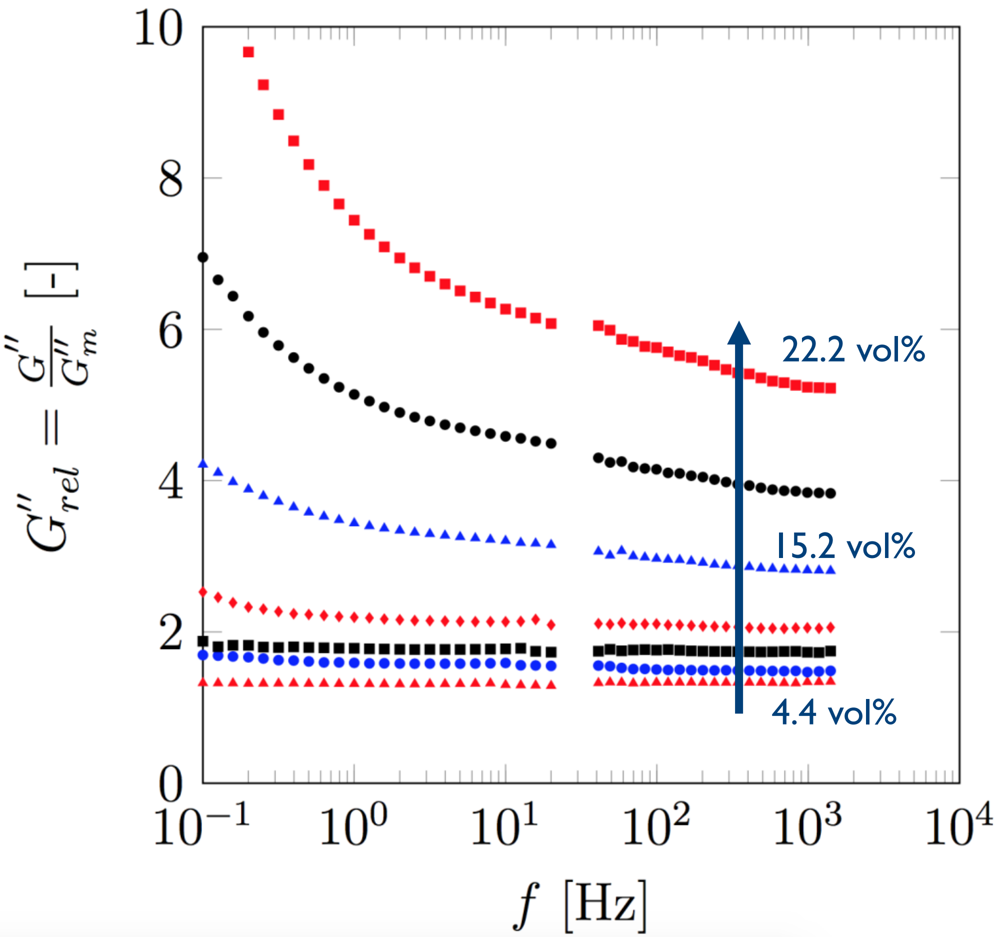
ultrasound

energy dissipation ↗

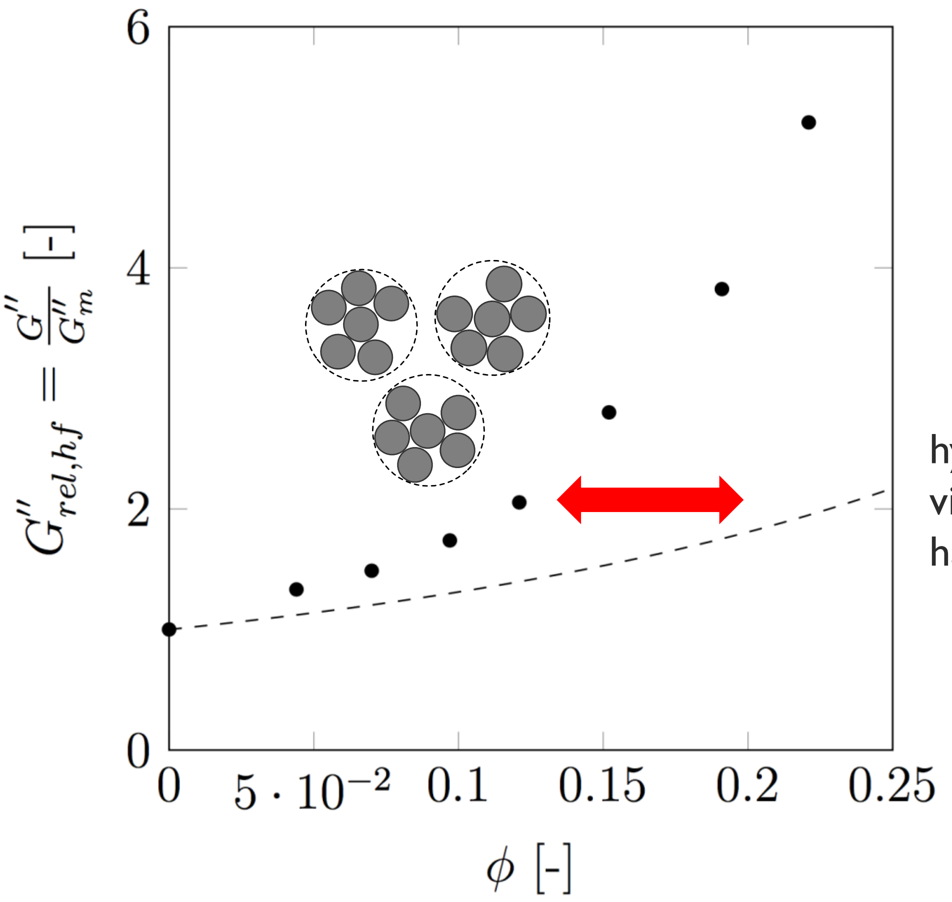
DISPERSION QUALITY ?

Analysis of the high frequency moduli

colloidal silica in
PDMS 0.34 Pas



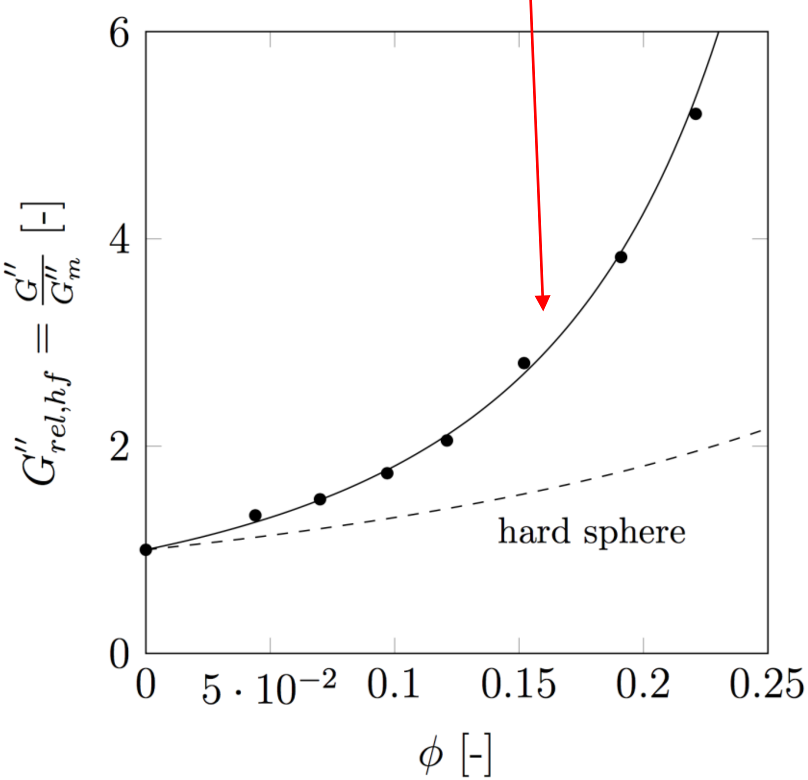
Analysis of the high frequency moduli



hydrodynamic viscosity model for hard spheres

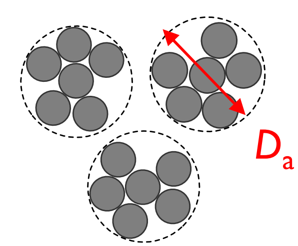
Quantification dispersion state

Quantification with viscosity model as function of

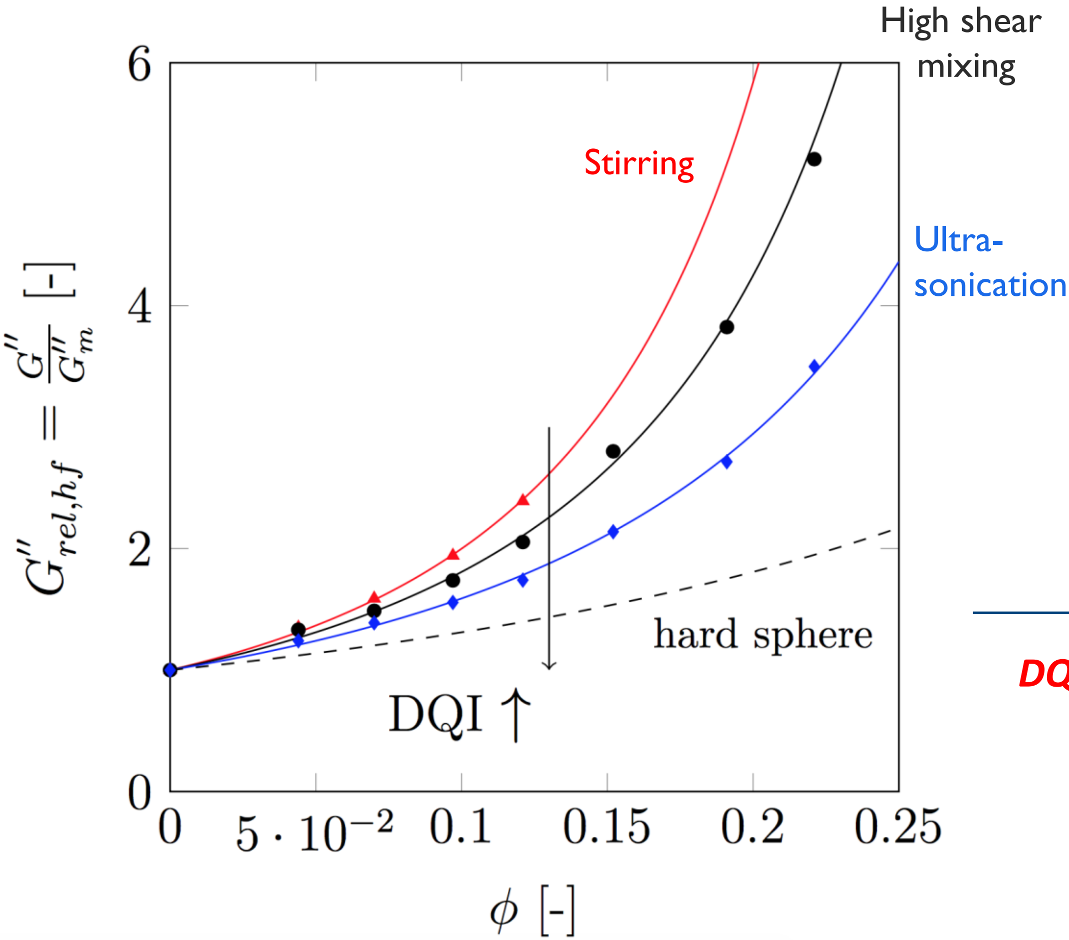


$$\phi_{eff} = \frac{\phi}{DQI}$$

=
- From 0 → 1
- Independent of colloidal interactions
- Based on "hydrodynamic size"



Quantification dispersion state: sensitivity



$$\phi_{eff} = \frac{\phi}{DQI}$$

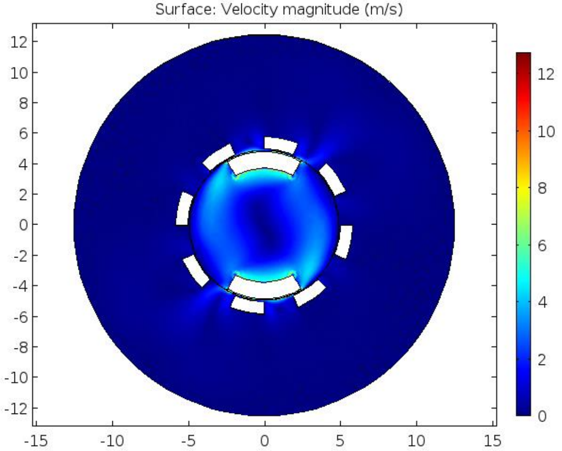
	stirring	high shear	ultra-sound	hard sphere
DQI	**0.44**	**0.51**	**0.62**	**1**

B. Schroyen, J.W. Swan, P. Van Puyvelde, J. Vermant (**2017**), *Soft Matter,* DOI: 10.1039/c7sm01690e

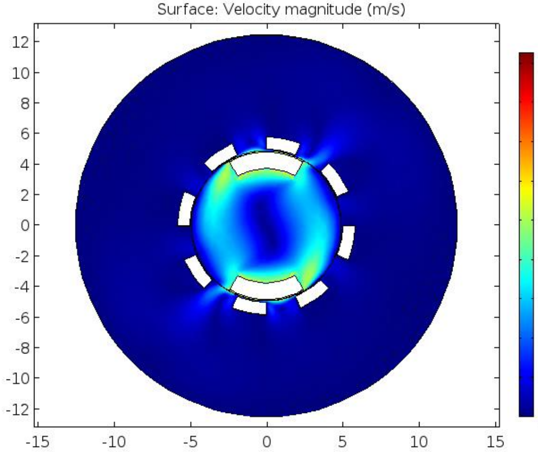
Evolution DQI during Mixing

high shear mixing

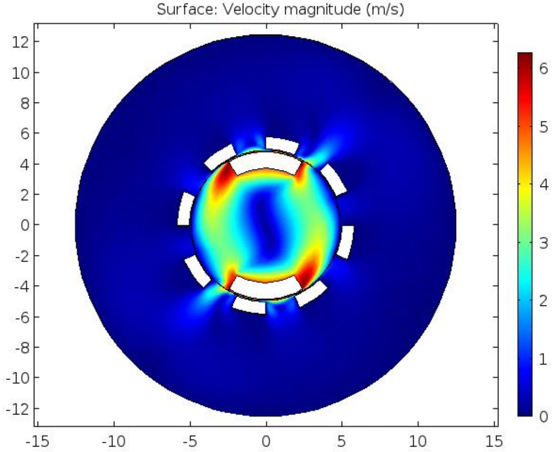
4000 rpm



8000 rpm



12400 rpm



4000 rpm

max shear rate :

$$\dot{\gamma}_{max} \approx 15.000 \ 1/\mathrm{s}$$

specific dissipation rate :

$$Q_v = 2 \cdot 10^5 \frac{\mathrm{J}}{\mathrm{m^3 s}}$$

12400 rpm

max shear rate :

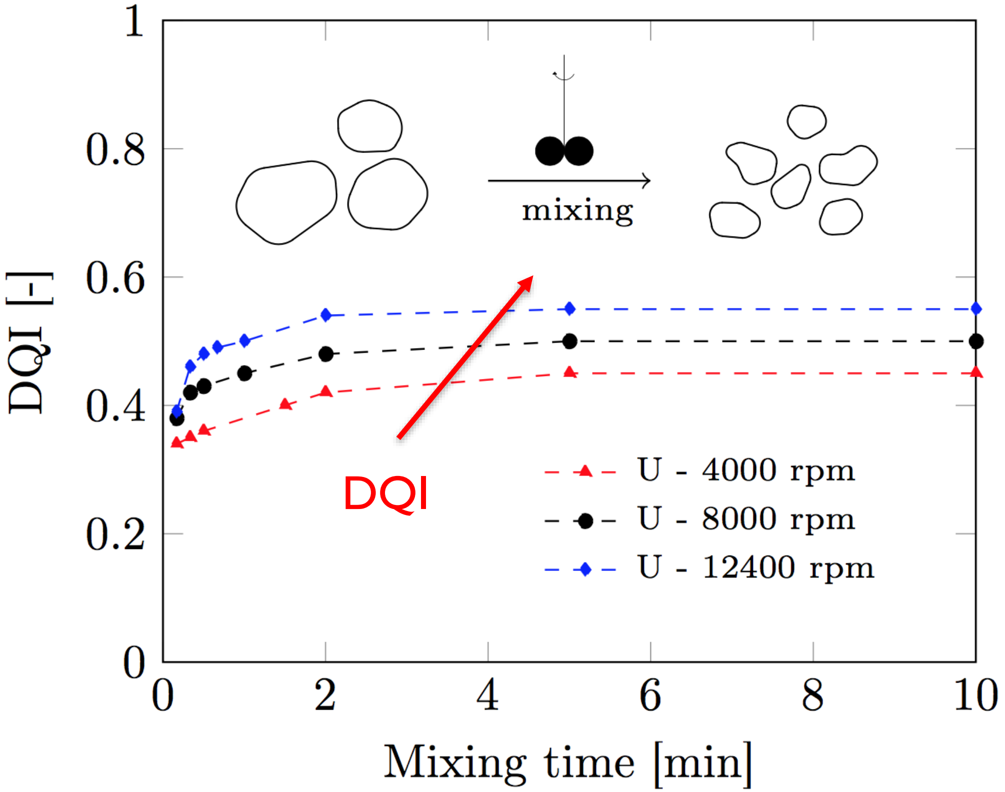
$$\dot{\gamma}_{max} \approx 52.000 \ 1/\mathrm{s}$$

specific dissipation rate :

$$Q_v = 2 \cdot 10^6 \frac{\mathrm{J}}{\mathrm{m^3 s}}$$

Evolution DQI during Mixing

Degree of dispersion induced by dispersion process



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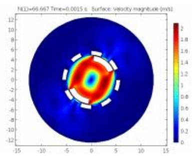
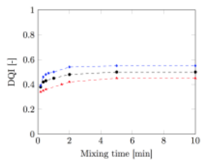
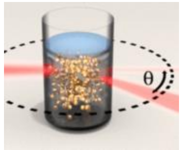
Evolution DQI during Mixing

Equilibrium state in high shear mixing :

	Shear rate (1/s)	DQI (-)	D_a (nm)
			
4000 rpm	15 000	0.45	440
8000 rpm	31 500	0.5	360
12400 rpm	52 000	0.55	265

improved degree of dispersion

Conclusion & Outlook

- Rheological approach to assess dispersions
  - Development *piezo-rheometer*
  - Quantitative assessment *dispersion quality*

⇒ Evaluation different **dispersing techniques**

⇒ Evaluation DQ during **mixing operation**

- Outlook
  - Towards nanocomposites
  - Towards in-line sensoring

Acknowledgements

- SIM Flanders

- G.K. Auernhammer

  MPI Polymer Research, Physics of Interfaces

- W. Schmidheiny & K. Feldman

  ETH Zürich, Department of Materials

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Operating window of the PSR

	Freq [Hz]	Gap [μm]	Displacement [nm]	AR [N/m]	Phase error [°]	Alignment error [μm]
Min	1	1	0	20 – 100		
Max	2500	400	54		2	1

Viscoelastic standard

11.4 wt% PIB in Pristane