Congrès de la Société Française de Physique - 2023

Perles liquides dans une matrice solide : rhéologie des émulsions solides

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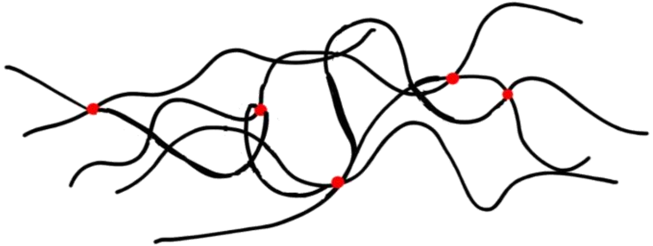
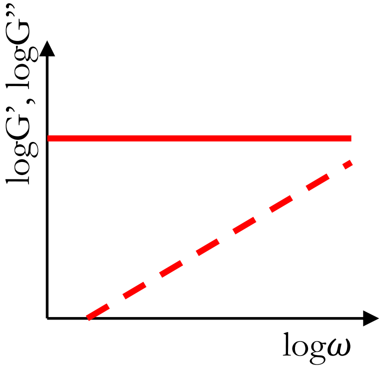
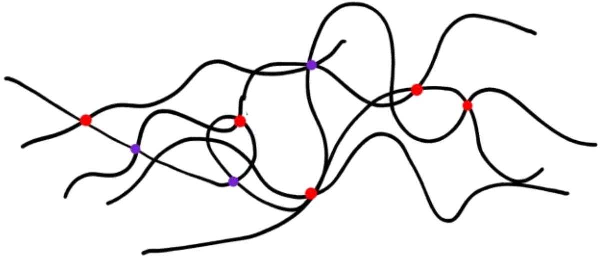
Motivation

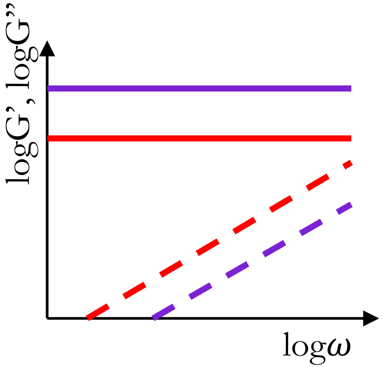




Elastomer: crosslinked polymer chains

Motivation





Elastomer: crosslinked polymer chains

→ + crosslinks = less flow, more stiffness

⇒ "coupling" of G' and G" wrt physical chemistry

Elastomer-like material with <u>separate</u> control over G' and G" ?

Inclusion systems

CONTINUOUS PHASE

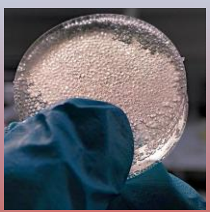
Gas

Liquid

Solid

Solid

Solid foam



Solid emulsion

Solid toughener

Liquid

Liquid foam

Liquid emulsion

Solid dispersion /
granular media

DISPERSED PHASE

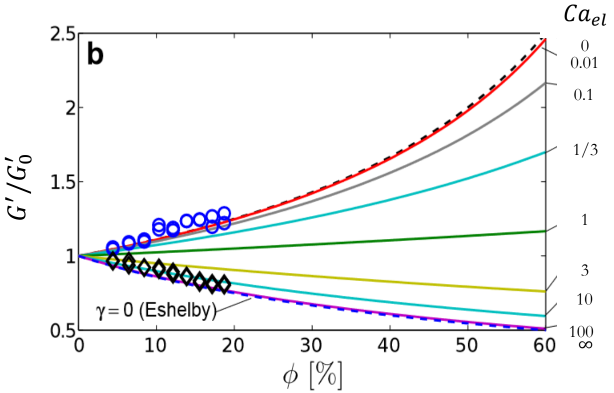
First approach for solid emulsions with liquid inclusions

- Elastocapillary number accounts for all liquid inclusions, and yield stress foamy liquids

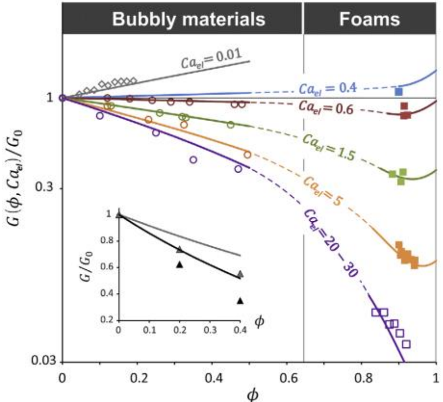
$$\phi = V_{dispersed}/V$$

$$Ca_{El} = \frac{G'R}{\gamma}$$

$$\phi = V_{void}/V$$



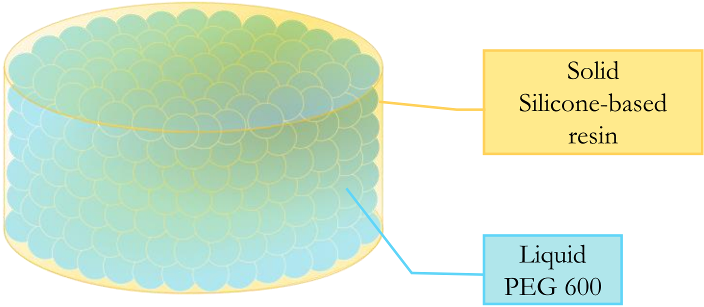
Style et al., 2014, Nature Physics, 11, 2



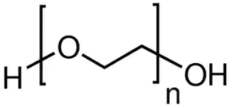
Gorlier et al., 2017, Journal of Colloid and Interface Science, 501

Experimental data for monodisperse inclusion corresponds
to the literature for elasticity:
Influence of volume fraction Φ modulated by elasto-capillary number Ca_{El}

Controlling the rheology of a solid emulsion with liquid droplets



- PEG 600 (n=15) :



melting temperature: $\sim 18°C$

- Sylgard 184 / Sylgard 527 mixture :

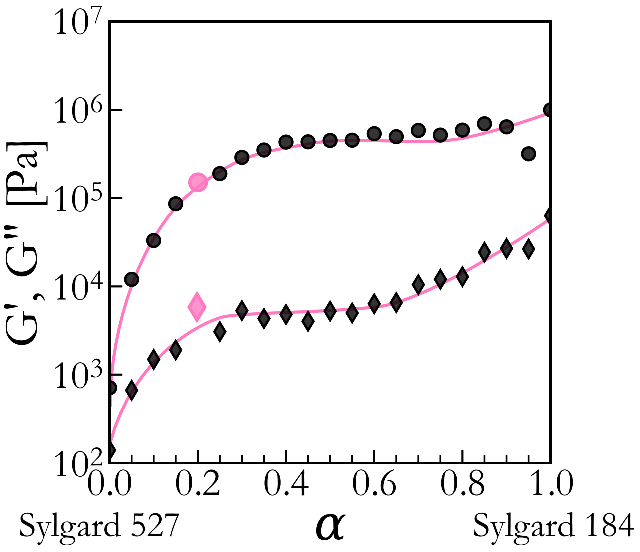
Sylgard 184: purely elastic $E \approx 1$ MPa
Sylgard 527: mainly elastic $E \approx 1$kPa

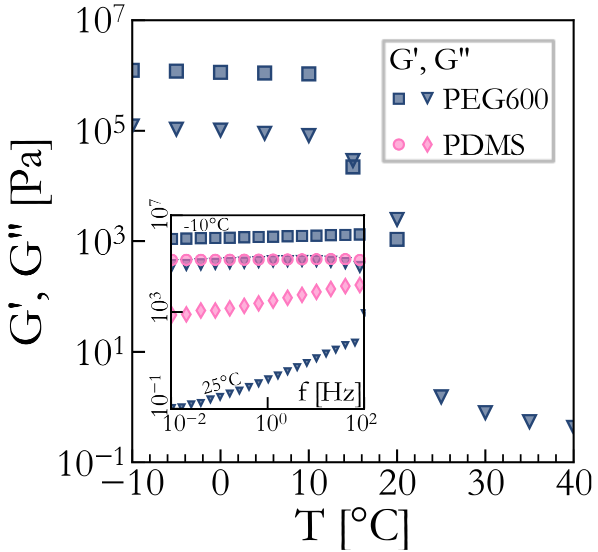
Curing at ambient temperature for 2 days

Control parameters:

$$\boldsymbol{\Phi}, \mathbf{R}, G^*_{PDMS}, \gamma, \eta_{droplets}$$

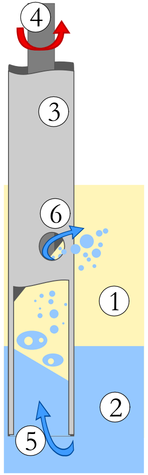
Dispersed and continuous phases



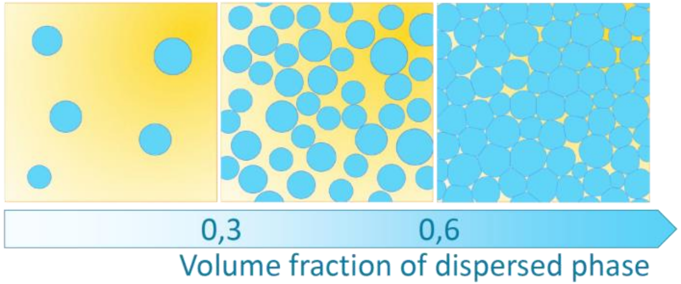


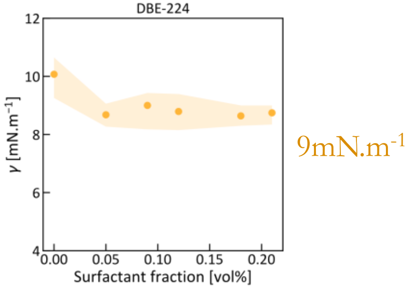
Moduli of the dispersed phase increase above the continuous phase at colder temperature

Generation of solid emulsions by breakup under shear

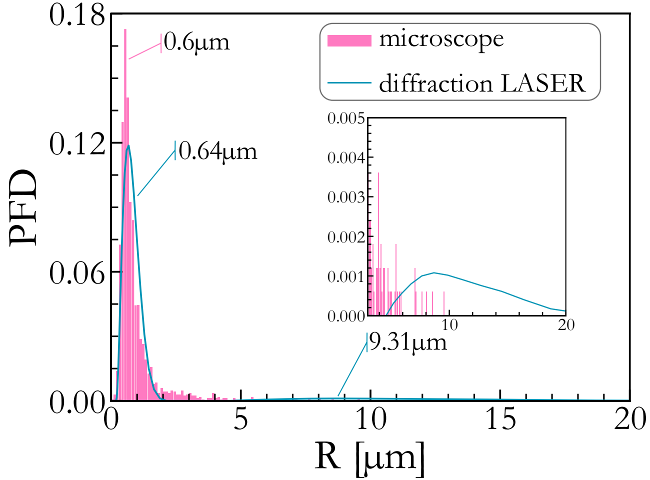


- Rotation: aspiration between rotating rod and stator
- Shearing between wall and rotor: breaking into droplets



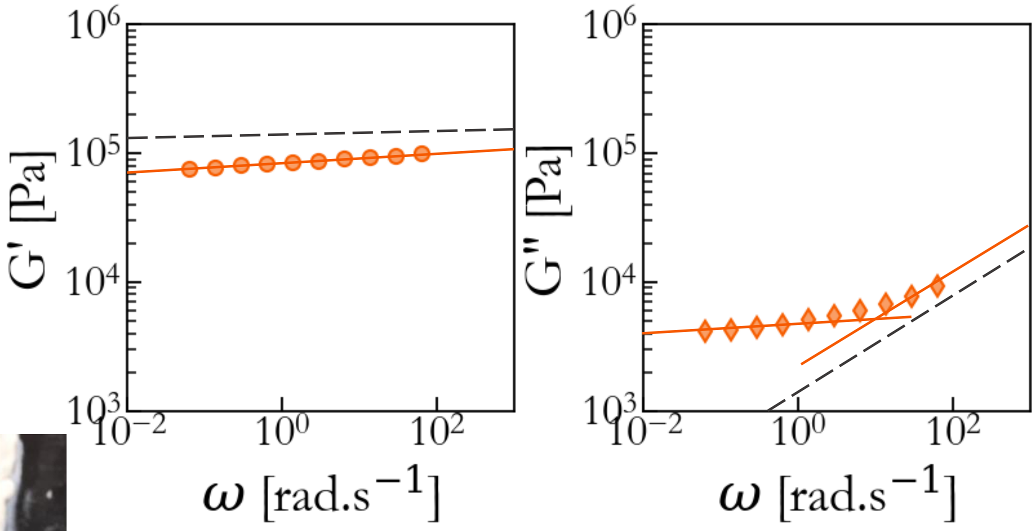


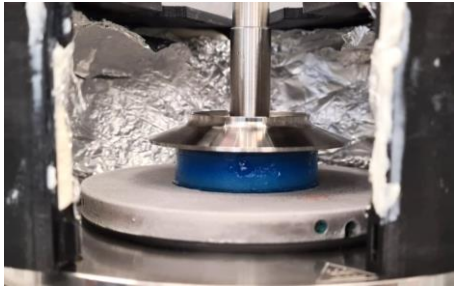
Dimethylsiloxane-ethylene glycol 70:30 block copolymer



Typical linear viscoelastic response of solid emulsions

Storage modulus:
very similar to
elastomeric plateau





Loss modulus:
2 apparent slopes

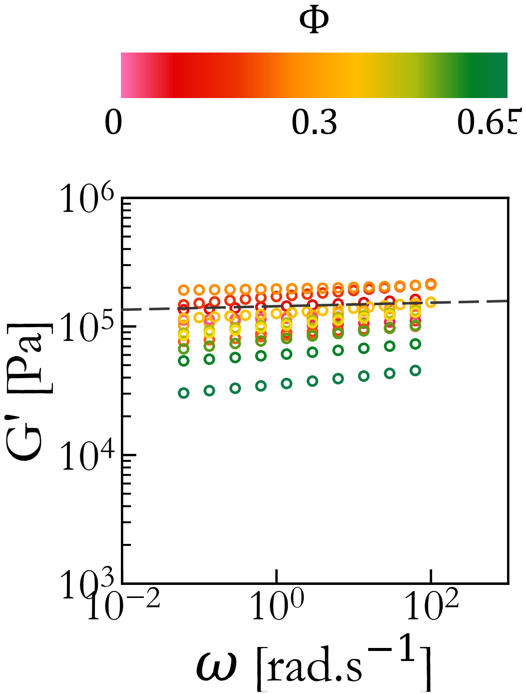
- Low frequencies: almost flat
- High frequency: same slope as continuous phase

Evolution of linear viscoelasticity with volume fraction

- Almost no change in the slopes of either moduli

In G':

- No tendency in plateau evolution at low volume fraction
- Decrease at higher volume fraction



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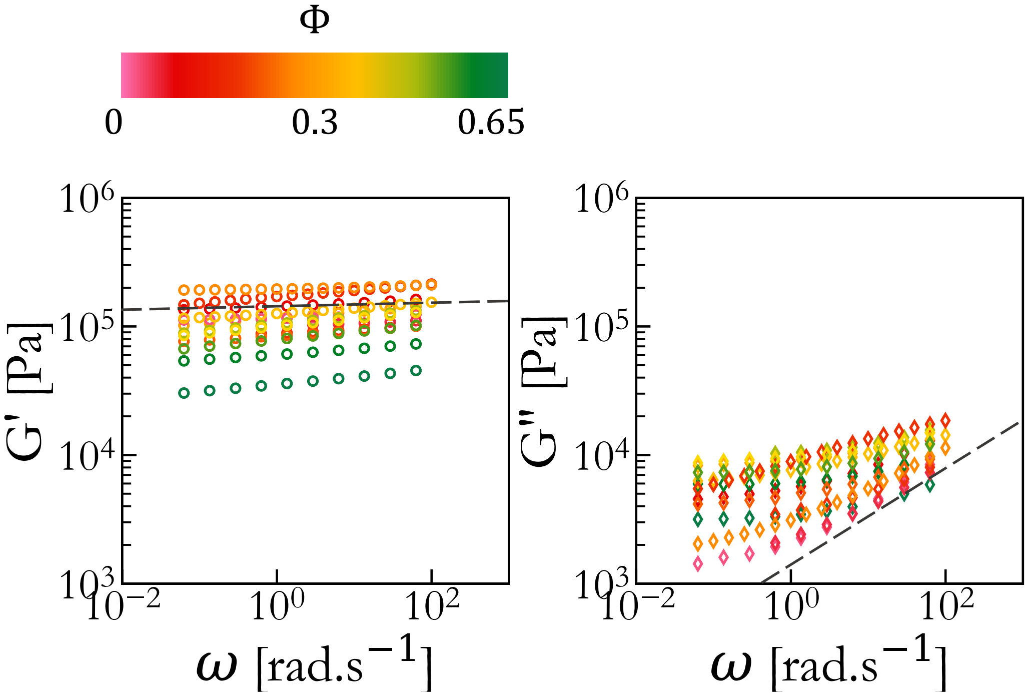

In G":

- Slope at high frequency ≡ PDMS slope
- Slope is lower than 1, close to 0.4 (usual for elastomers)
  → fractional rheology ?

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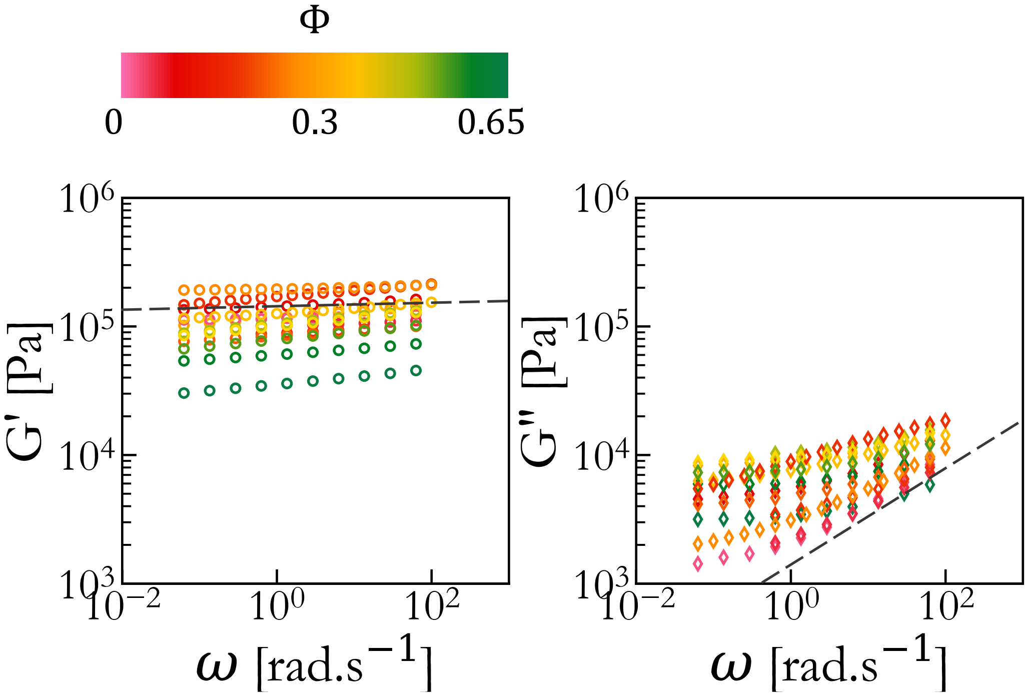
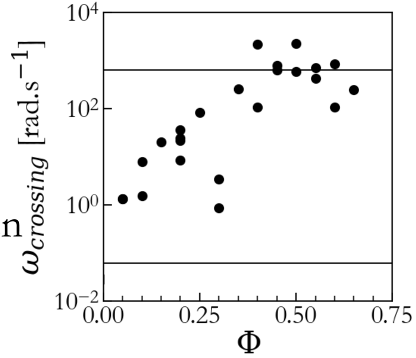


- Crossing frequency between plateau and power-law increase increases with volume fraction

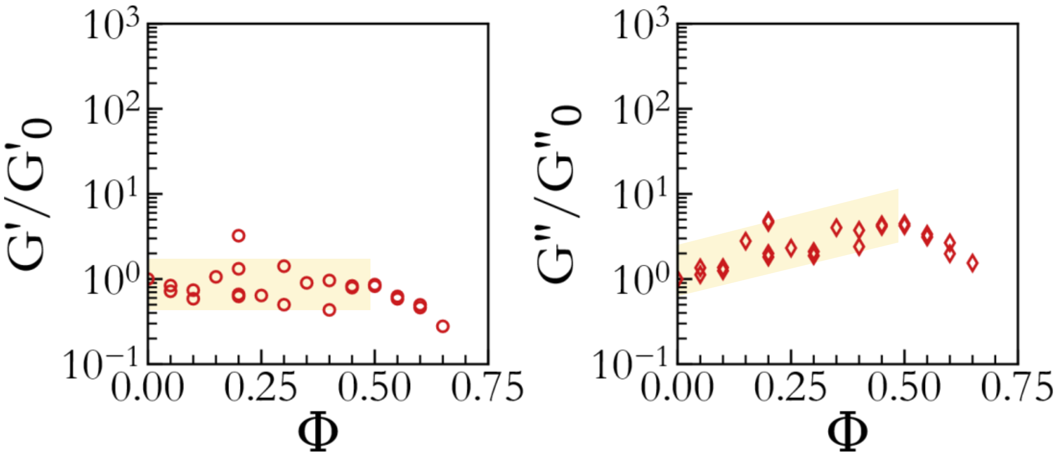
In G'':

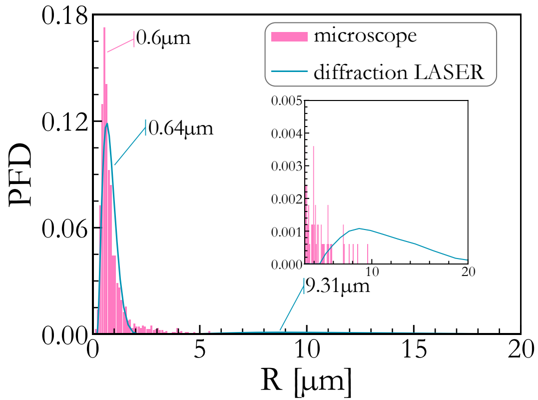
- Slope at high frequency ≡ PDMS slope
- Slope is lower than 1, close to 0.4 (usual for elastomers)

→ fractional rheology ?



Evolution with volume fraction for liquid inclusions



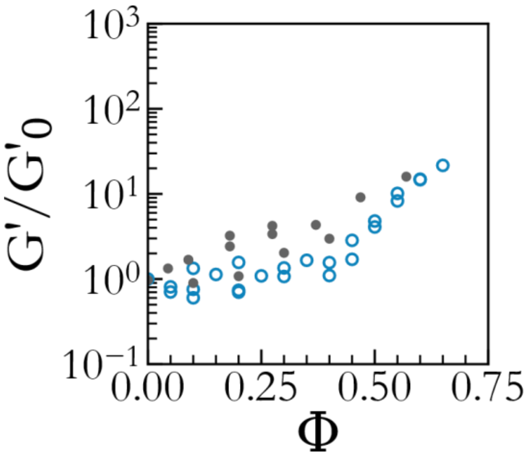


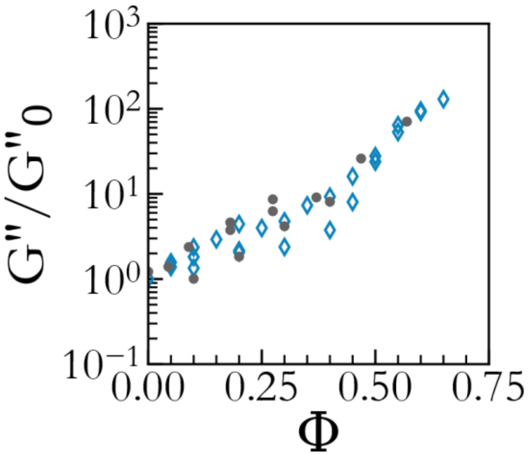
- Unexpected non-monotonous moduli
  → polydispersity ?

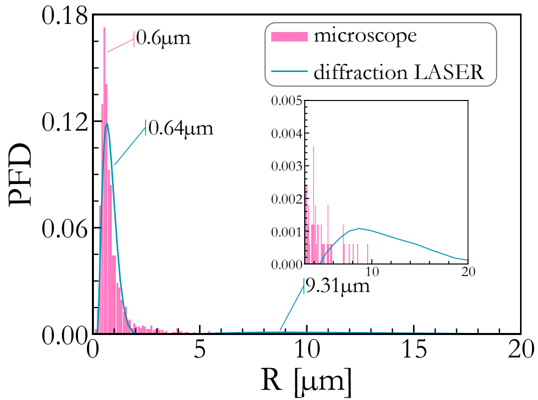
- $\Phi < 0.4$:
  - Almost constant G'
  - Increasing G''

⇒ decorrelation of G' and G'' with regards to Φ

Evolution with temperature







- Recovery of monotonous behavior

- Comparison with rigid inclusions (glass beads):
  - Similar evolution in G”
  - Discrepancy in G’

→ First hypothesis: polydispersity

Conclusions

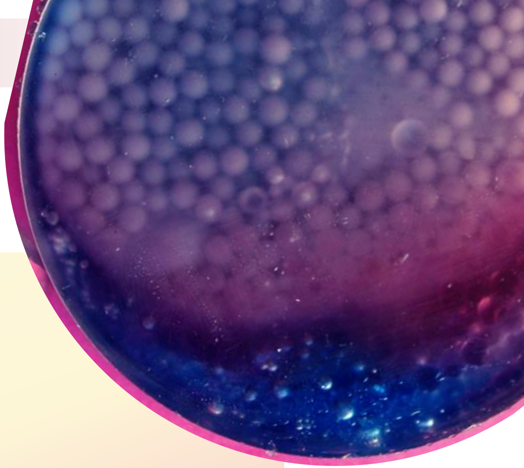
- Viscoelastic influence of liquid droplets in a soft matrix
  - ➢ Modelling work in progress with fractional rheology

- Decorrelations of storage and loss moduli with regards to volume fraction
  - ➢ Influence of polydispersity on elastocapillary number

- Interesting unexplained behavior with the temperature transition

- Discrepancy with existing models already with liquid droplets

→ Non-trivial mechanical reponse from a mix of model materials
→ Interesting for tunable materials
→ Encapsulation of a phase-transition dispersed phase: thermal energy storage



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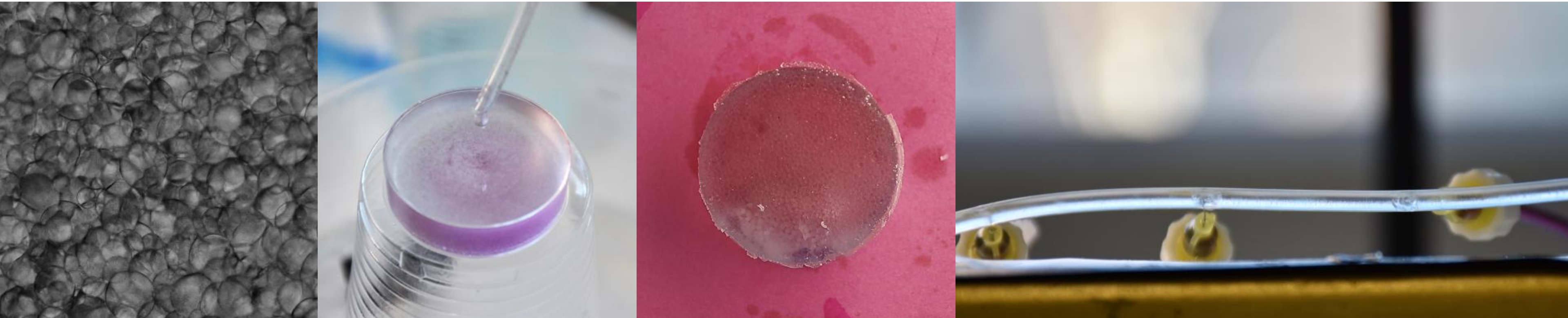
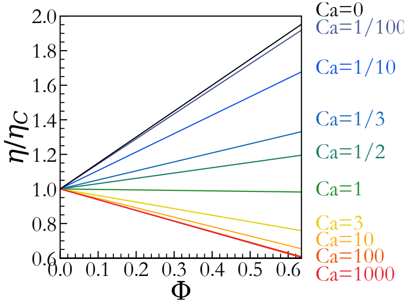


Rheology of liquid emulsions

- Viscosity for emulsions based on Newtonian liquids (Frankel & Acrivos, 1970):

$$\boxed{\phi = V_{dispersed}/V}$$

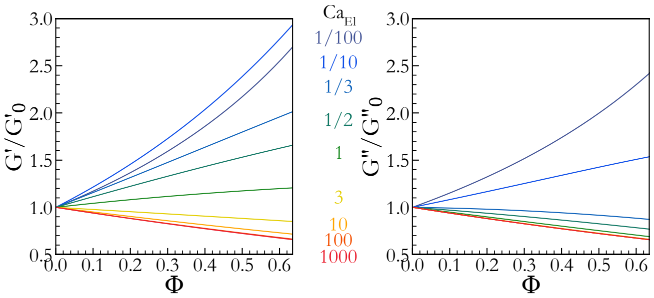
$$Ca = \frac{\eta U}{\gamma}$$



Influence of the volume fraction Φ on viscosity

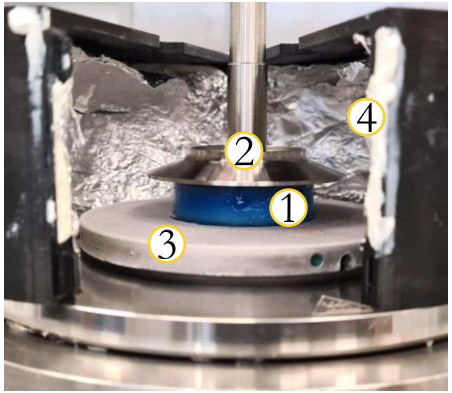
- Rheology of liquid emulsions (Palierne, 1990):

$$\boxed{Ca_{El} = \frac{G'R}{\gamma}}$$



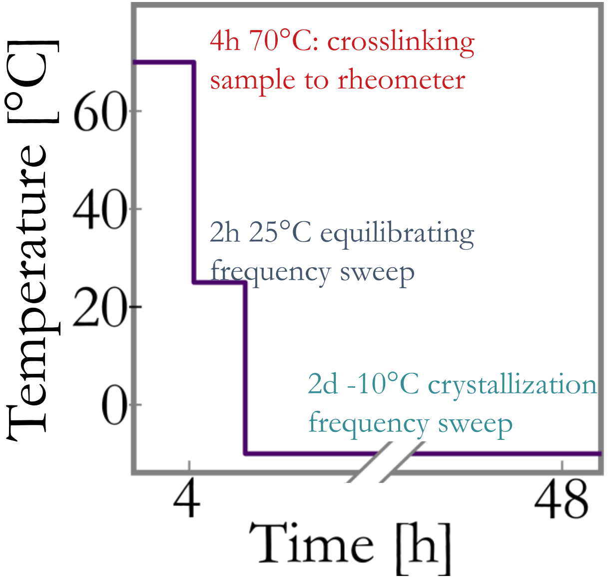
Ca_{el} influences the way Φ changes the rheological parameters

Rheological characterization

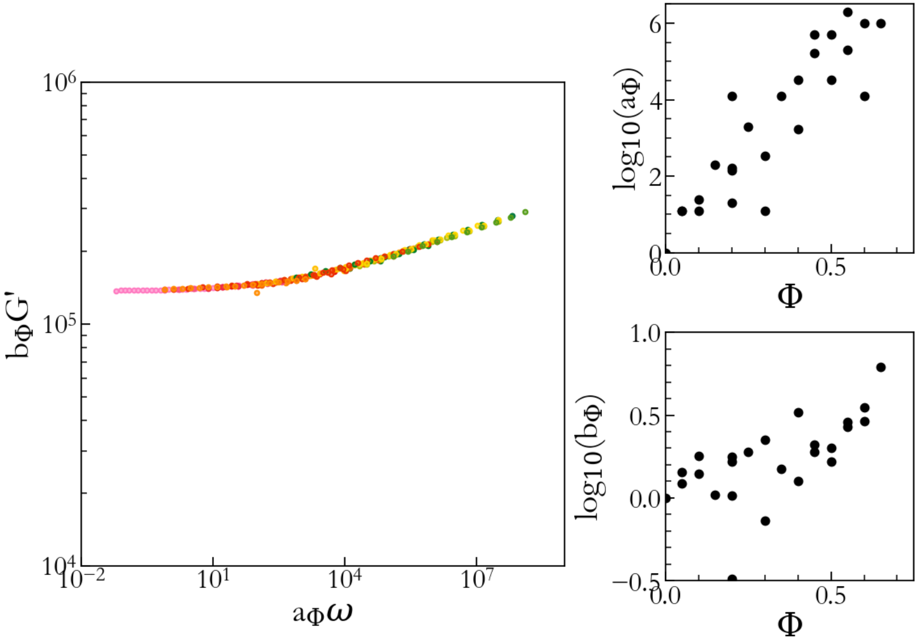


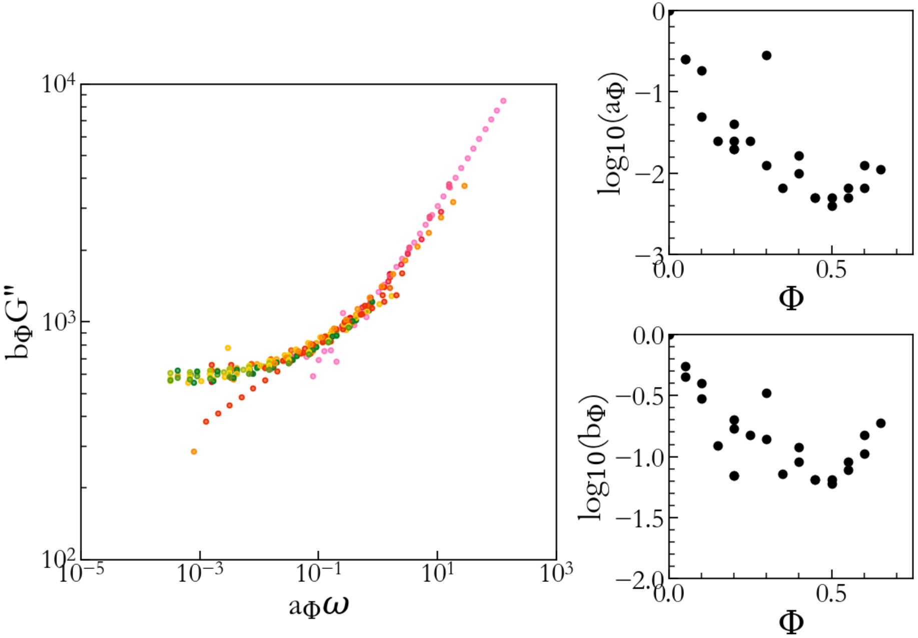
1. Sample
2. Plate-plate configuration
3. Peltier plate
4. Insulating box

- Frequency sweep between 0.01Hz and 100Hz
- Deformation $\epsilon = 0.1\%$
- Constant normal force 2N during temperature change

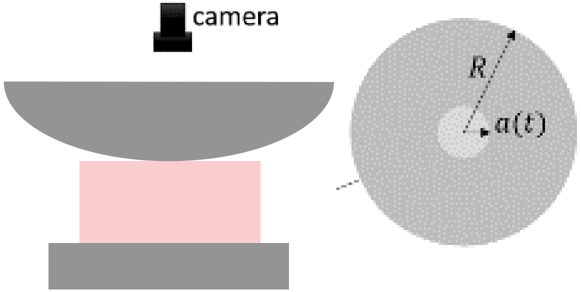


Master curve ?

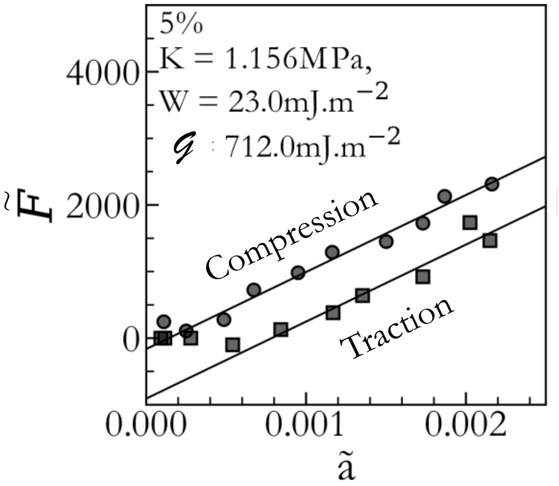




Adhesion first results with JKR experiment



Jonhson, Kendall, Roberts, 1971, RSPA, 324, pp301-313



Linearization of the force-contact relation:

Compression

$$\tilde{F} = K\tilde{a} - \sqrt{WK}$$

$$K = \frac{4}{3}\frac{E}{1-\nu^2}$$

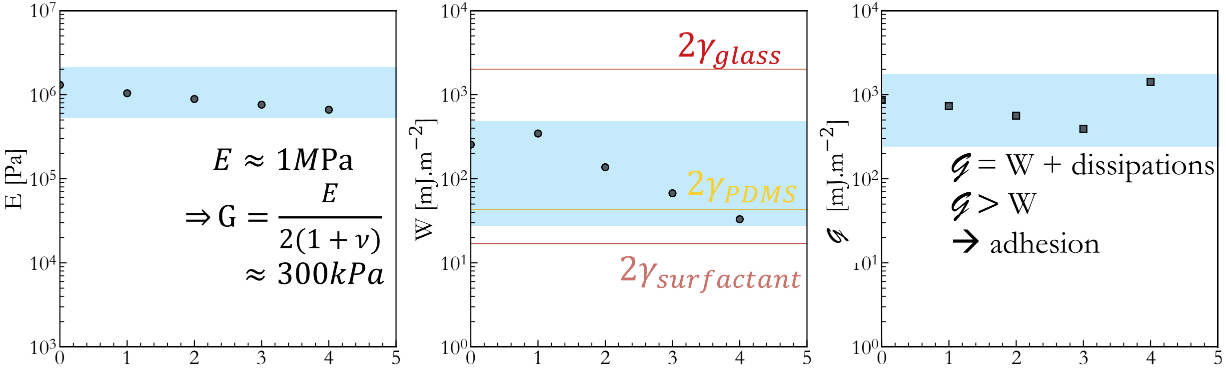
Compression work
$W = \gamma_1 + \gamma_2$

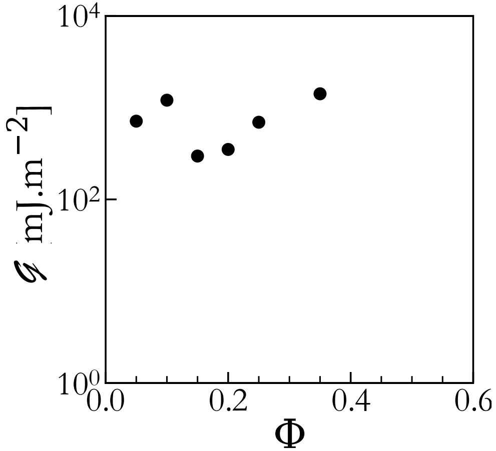
Traction

$$\tilde{F} = K\tilde{a} - \sqrt{\mathcal{G}K}$$

Energy release rate
$\mathcal{G}$ = W + dissipations

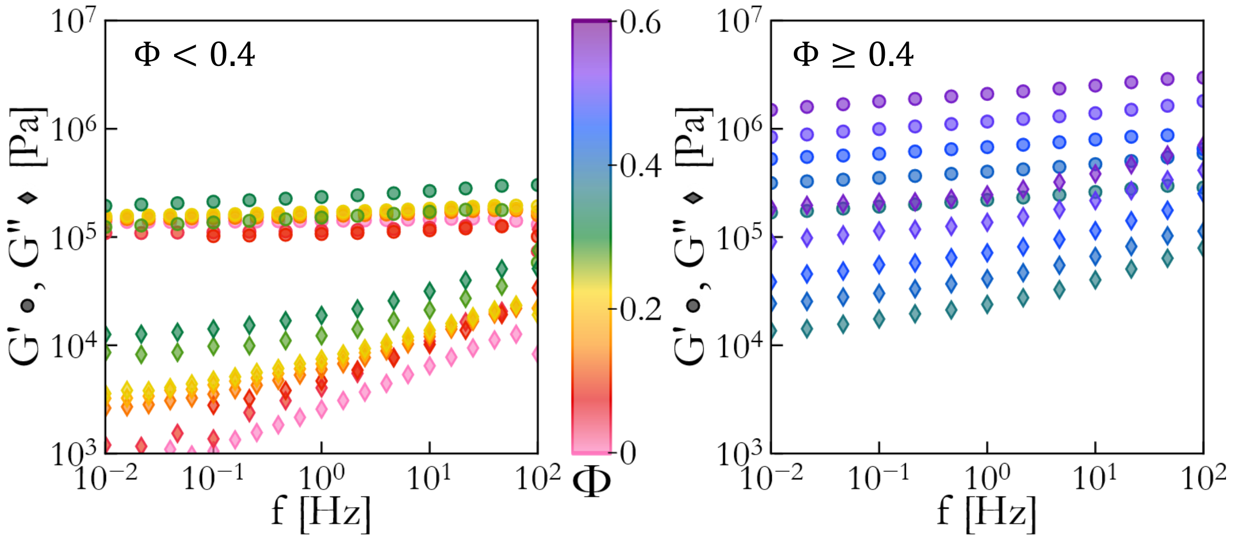
Preliminary JKR results





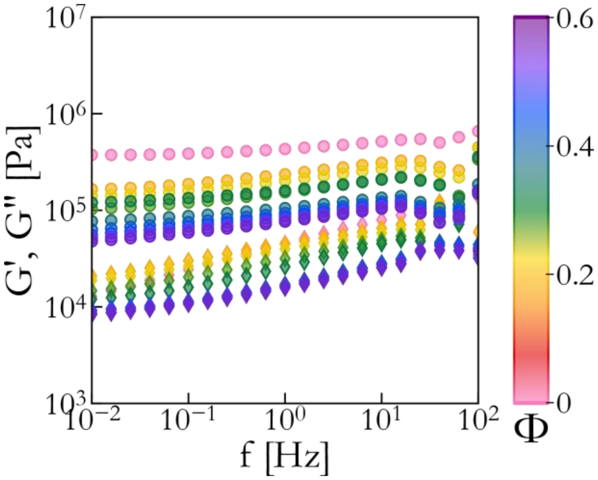
- **Adhesion in all the samples**
- **Preliminary data shows apparent influence of volume fraction**

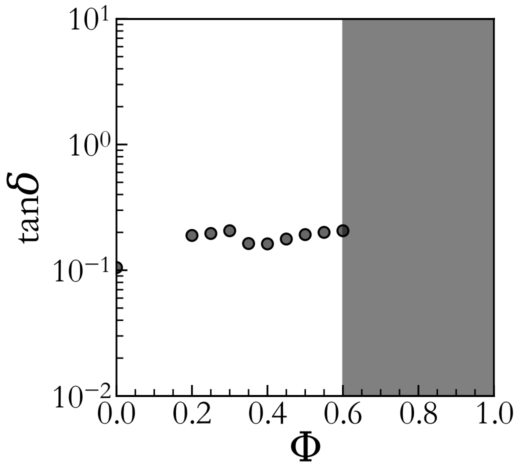
Typical rheometry for solidified inclusions (T=-10°C)

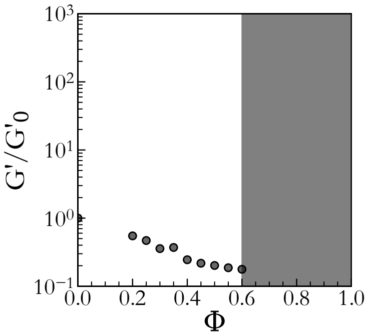


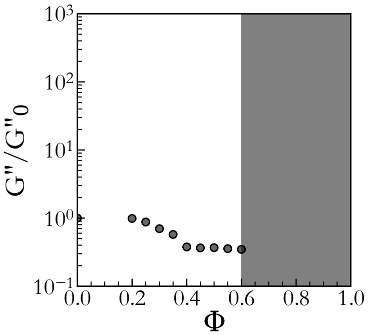
G' almost constant for $\Phi \leq 0.4$, increasing with Φ above $\Phi = 0.4$
G'' increases strongly with Φ

Sylgard 184 continuous phase



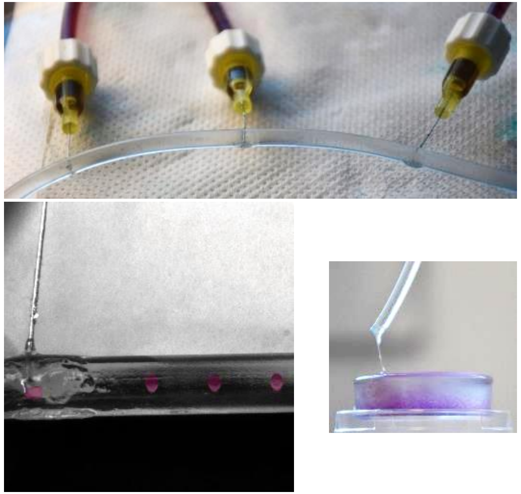




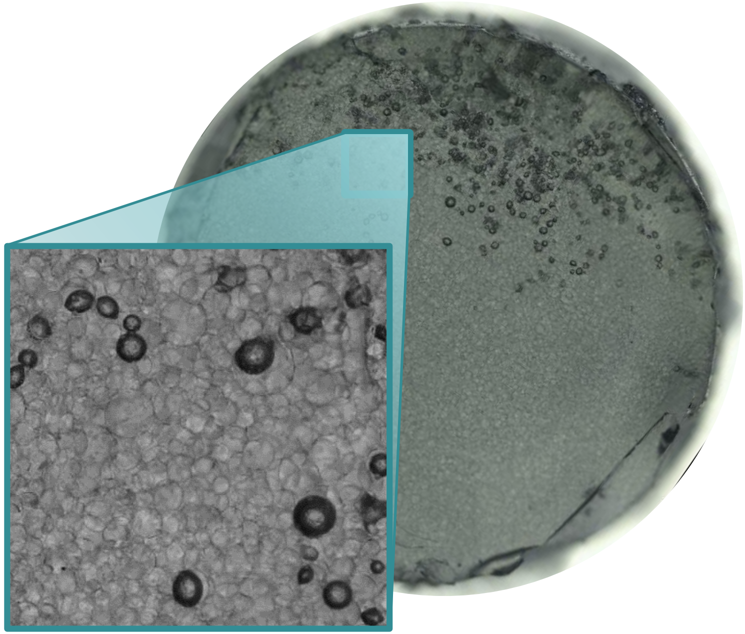


- → Little variation compared to the continuous phase: dominated by elasticity
- → Modulus decreases as thin films are formed
- → Same variation for G’ and G”

Microfluidics-generated samples

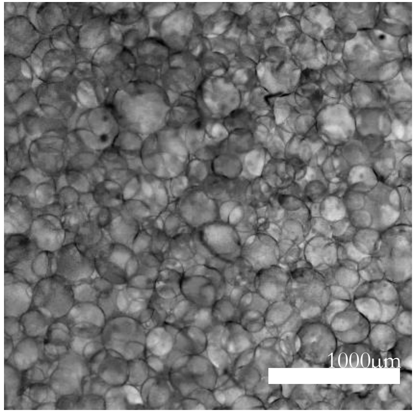


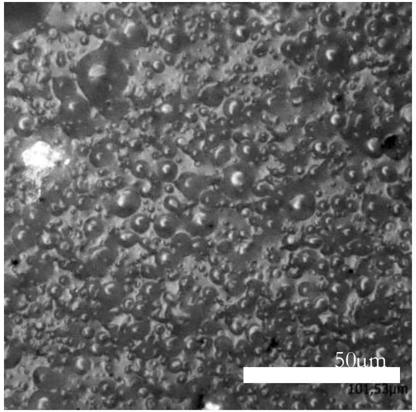
- PDMS cooled down and pushed through a peristaltic pump, allowing for reuse on the excess oil
- PEG600 pushed through 10 syringes in the flow of PDMS
- Sedimentation of the droplets leading to $\Phi \approx rcp$ and curing at room temperature

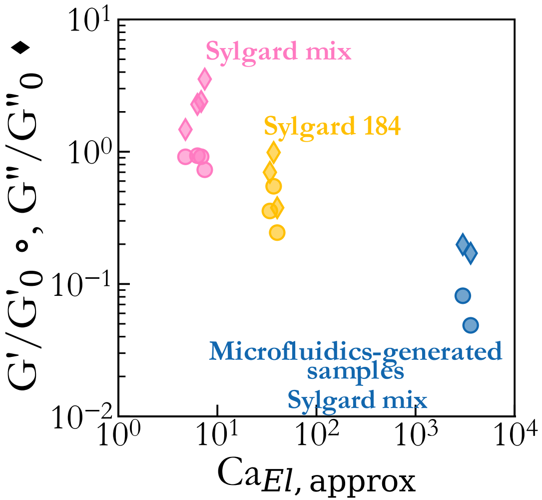


R≈150μm

Influence of the elastocapillary number

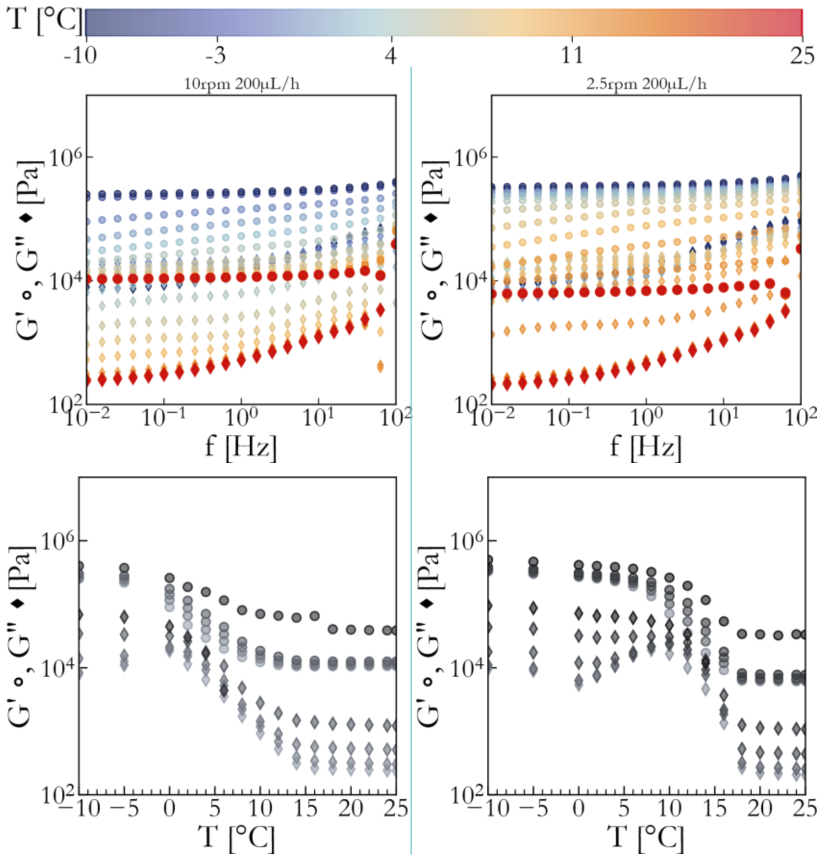






→ Coherent : much larger droplets lead to a larger elastocapillary number, thus softening the sample

Temperature transition for the larger droplets



- Much clearer transition

- Sample with smaller droplets shows a flatter curve

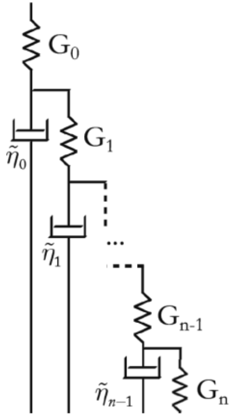
- Multiple behaviors in frequency sweep depending on the temperature showing the influence of the progressive solidification of the dispersed phase

Fractional rheology model

« spring-pot » with intermediate behavior:

$$\tau = V\frac{d^{\alpha}\gamma}{dt^{\alpha}}$$

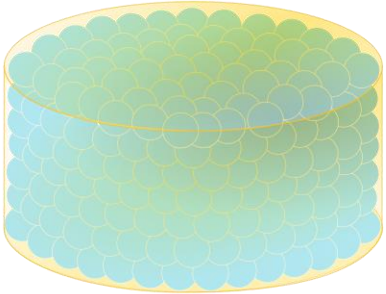
$$\tau^{*} = V(\mathrm{i}\omega)^{\alpha}\gamma^{*}$$



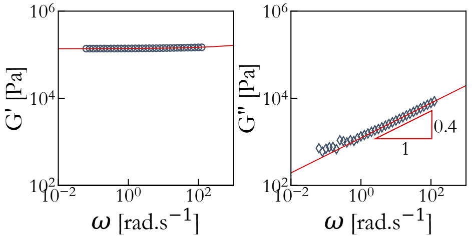
Another way to view it:

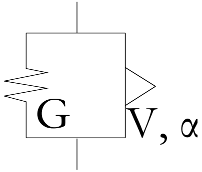
Infinite amount of relaxation times from small statistical events

How can we model a solid emulsion ?



→Elastomeric continuous phase: already a power-law material





$$G^{*}_{PDMS} = G_0 + V(\mathrm{i}\omega)^{\alpha}$$

$$\alpha \approx 0.4$$

→Droplets: modelized as an ensemble

$$G^{*}_{droplets} = C(\mathrm{i}\omega)^{\delta}$$

Solid emulsion: simple mixing model

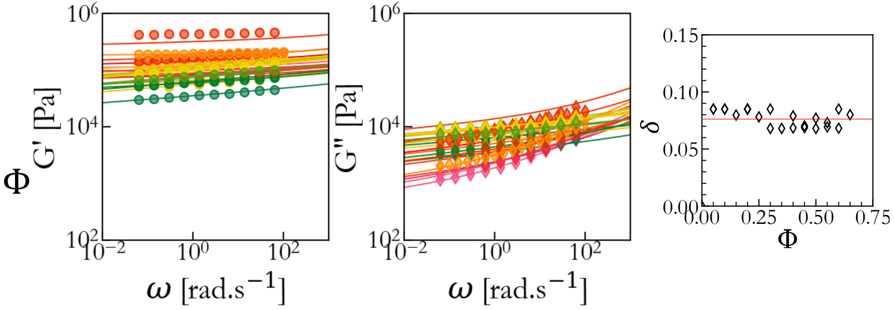
$$G^{*}_{emulsion} = f(\Phi)\ G^{*}_{PDMS} + g(\Phi)\ G^{*}_{droplets}$$

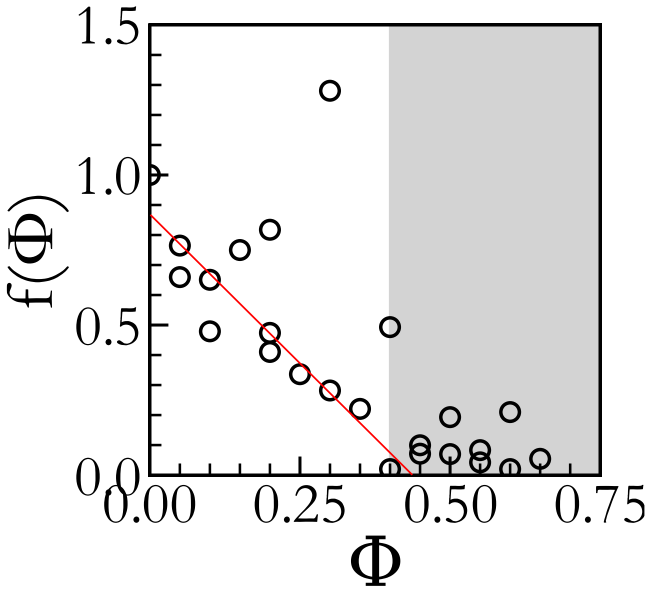
Preliminary fit results

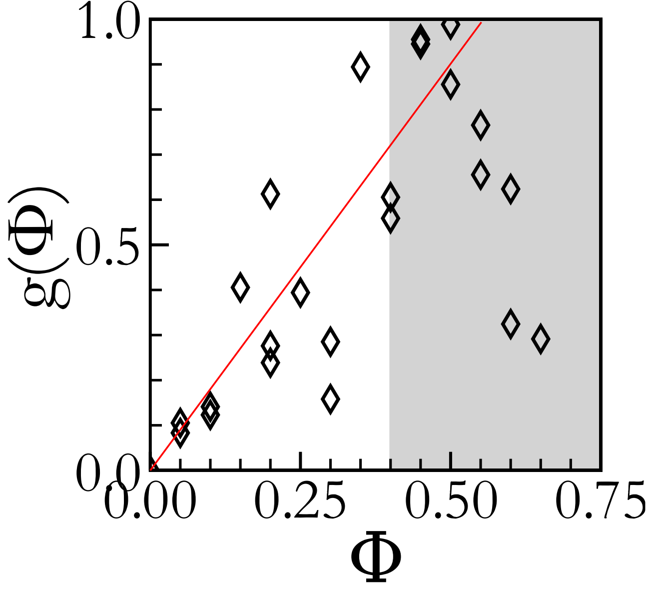
$$G^*_{emulsion} = f(\Phi)\ G^*_{PDMS} + g(\Phi)\ G^*_{droplets}$$

$$G^*_{PDMS} = G_0 + V(\mathrm{i}\omega)^{\alpha}$$
$\alpha \approx 0.4$

$$G^*_{droplets} = C(\mathrm{i}\omega)^{\delta}$$
δ constant across all Φ
$\delta \approx 0.75$







- Change from linear behavior around $Phi = 0.35$ van also be lack of high frequency information

- Similar frequency behavior across volume fraction

⇒ let's compare the samples at a given frequency