

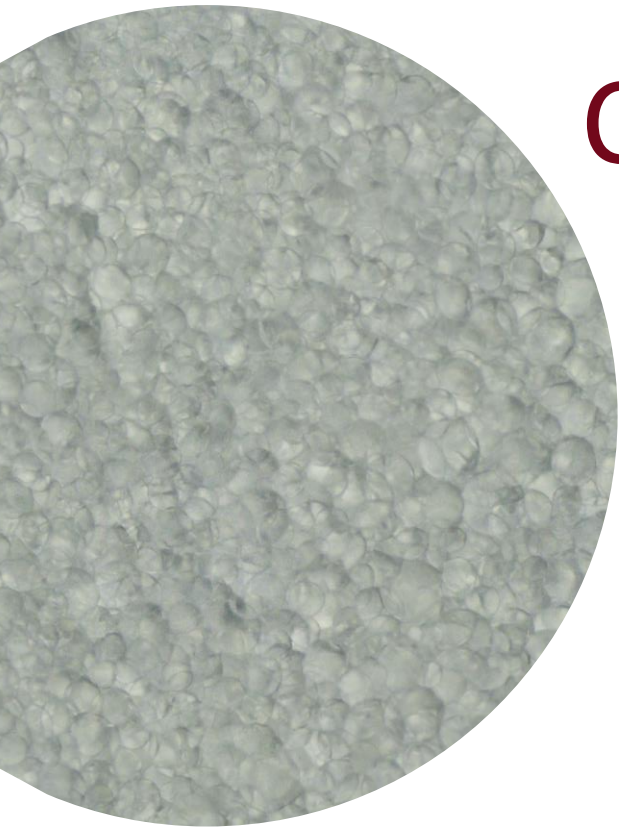


Annual European
Rheology
Conference 2022



Seville
April, 26th-28th
Meliá Sevilla Hotel

Transdisciplinary Rheology, a bridge to sustainable progress and welfare



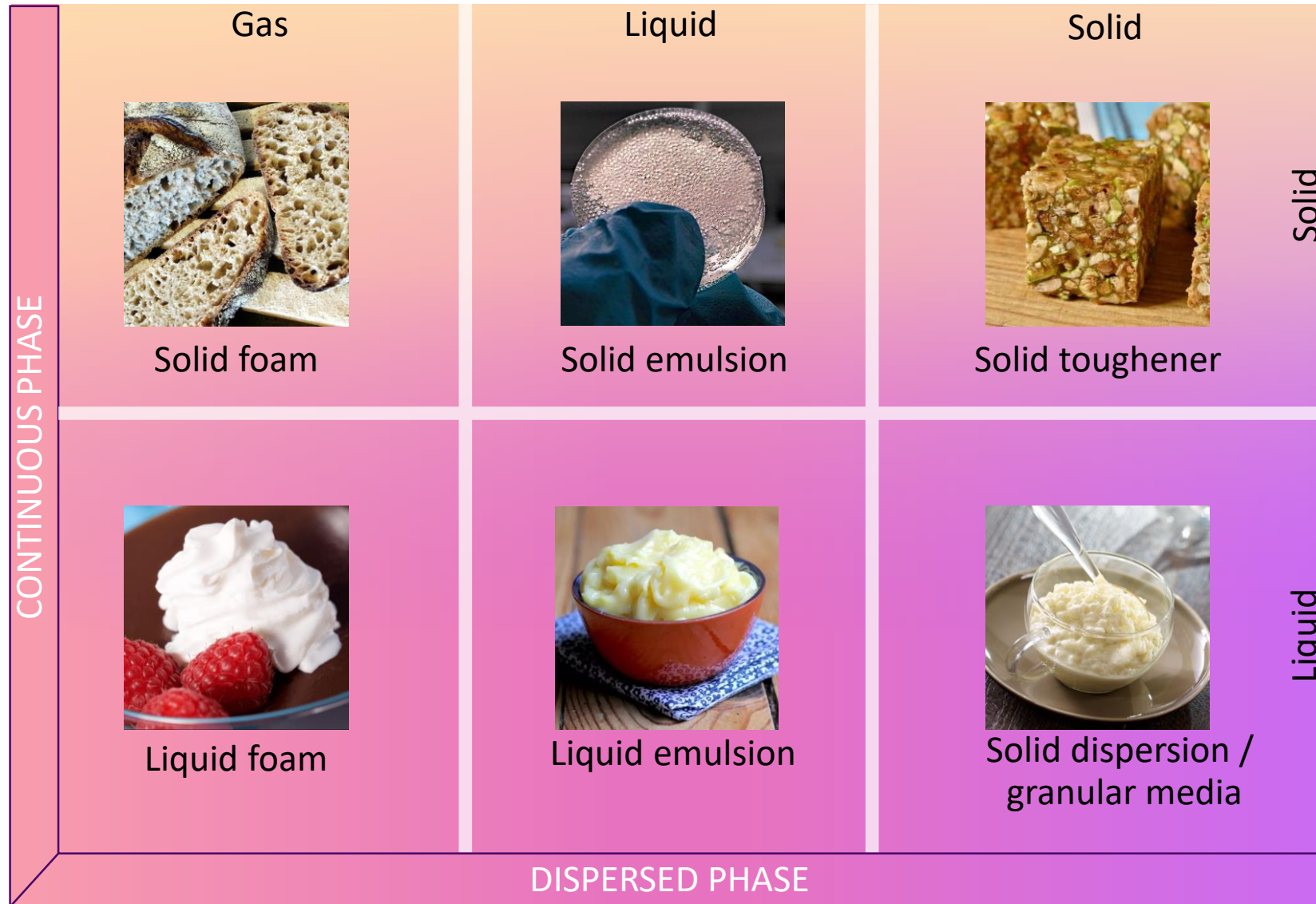
Controlling rheology of a solid emulsion with phase-changing droplets

Elina Gilbert, Anniina Salonen, Christophe Poulard

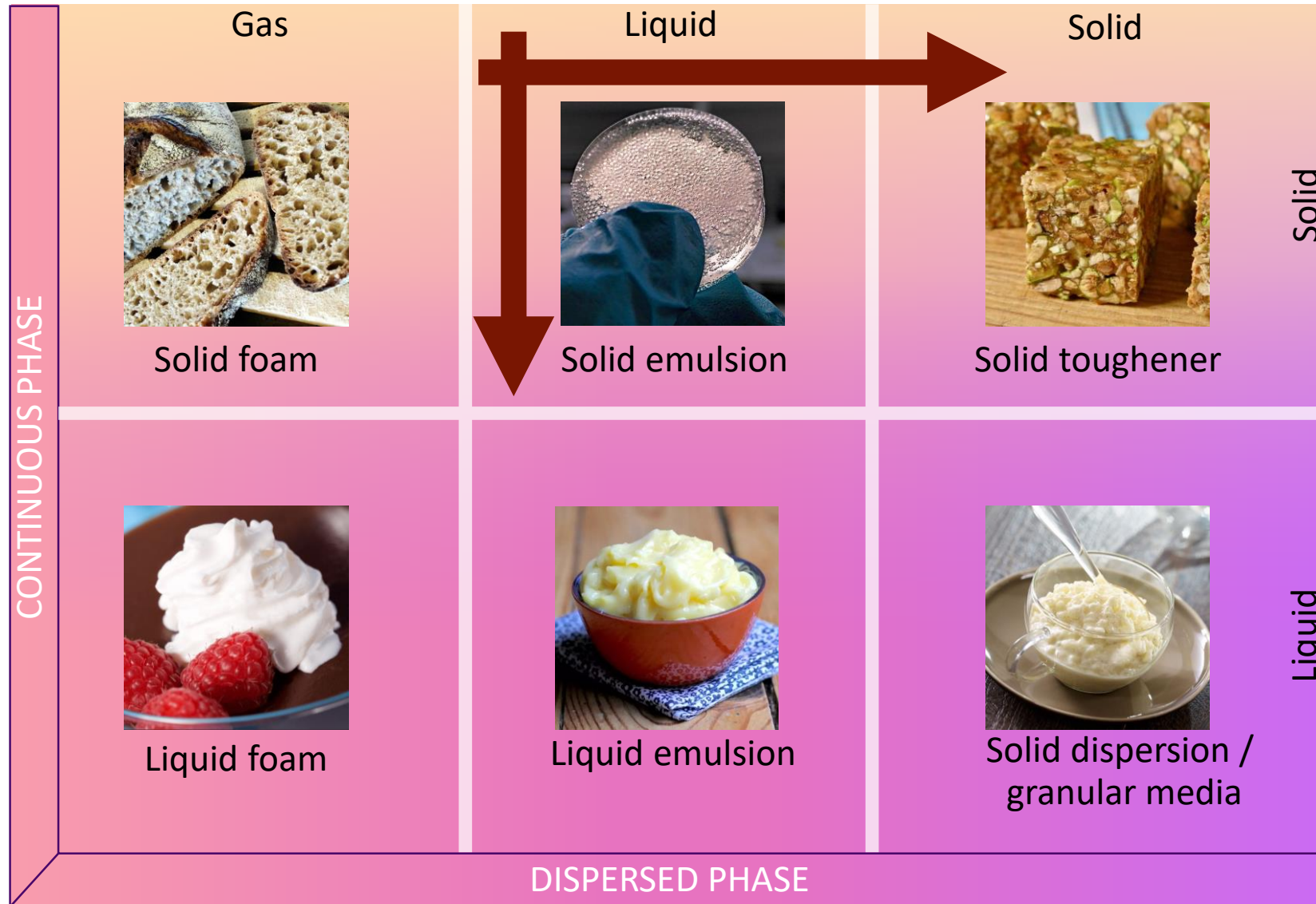
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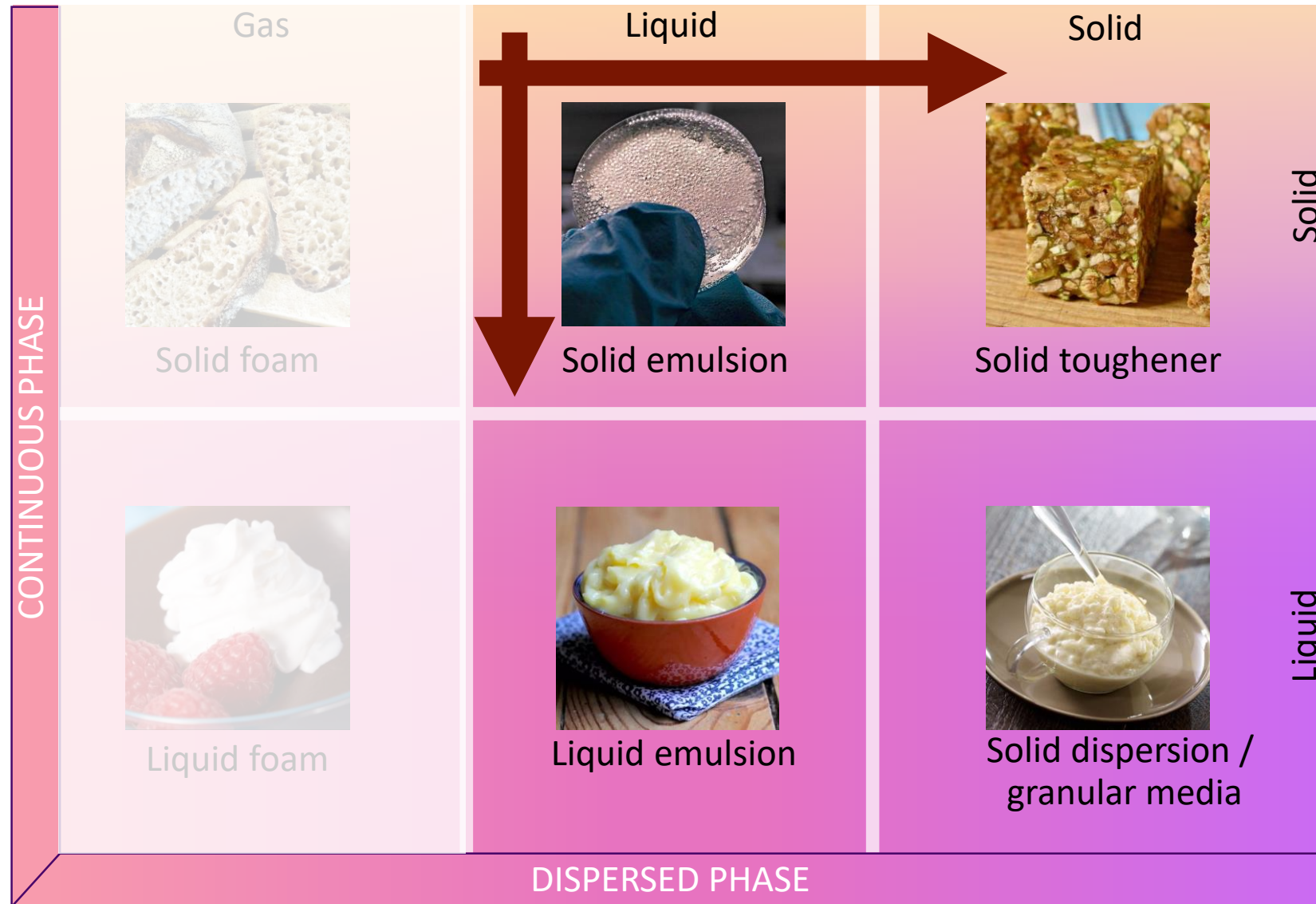
Inclusion systems



Inclusion systems



Inclusion systems: Models for emulsions

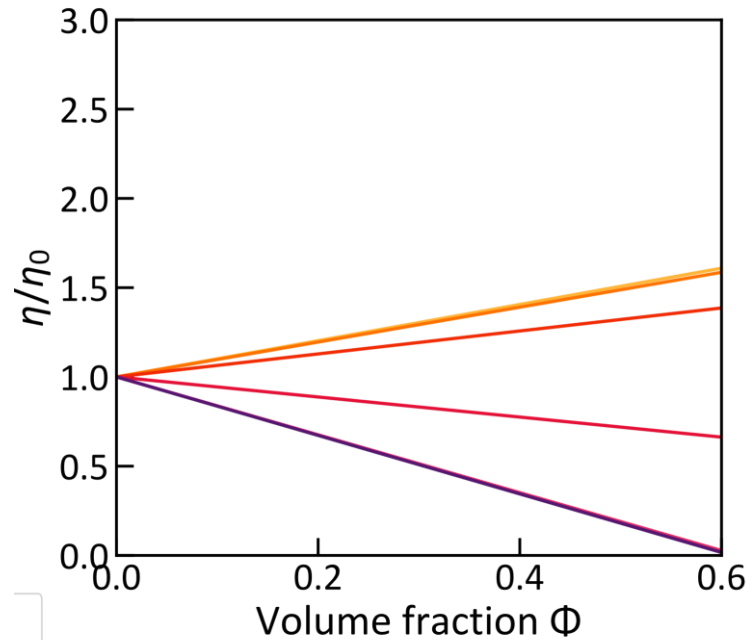
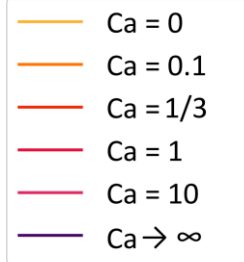


Rheology of liquid emulsions

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

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

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



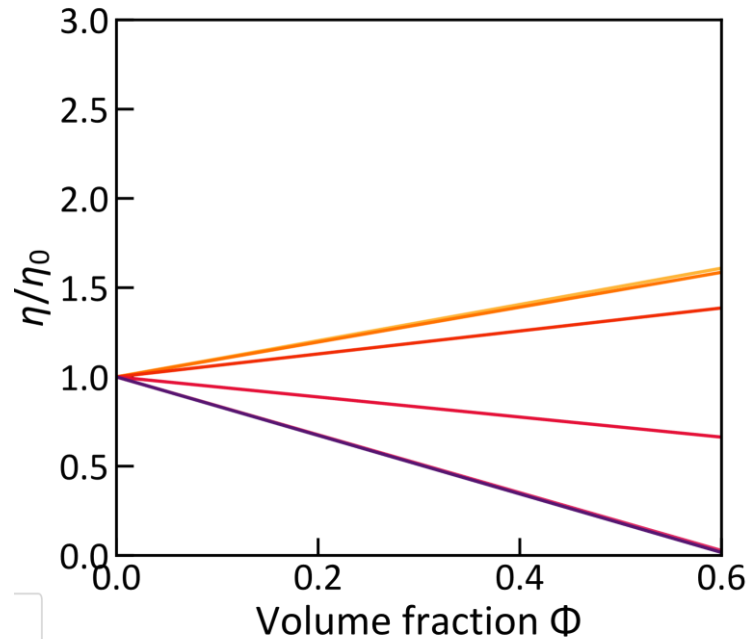
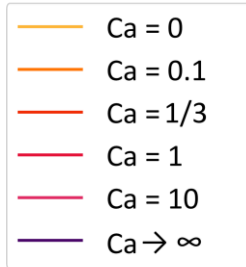
Influence of the volume fraction Φ on viscosity

Rheology of liquid emulsions

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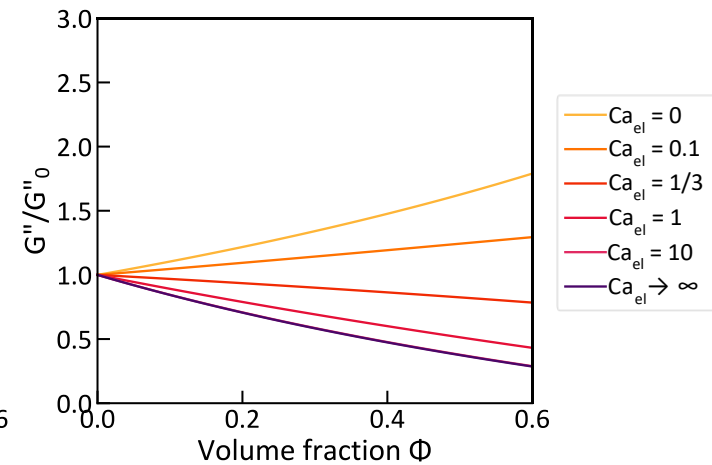
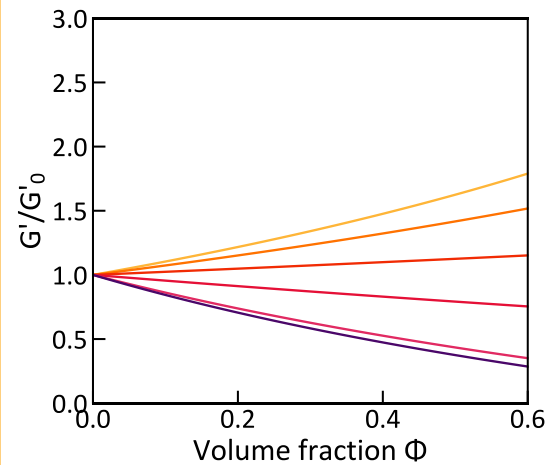
$$Ca = \frac{\eta U}{\gamma}$$



Influence of the volume fraction Φ on viscosity

- Rheology of liquid emulsions (Palierne, 1990):

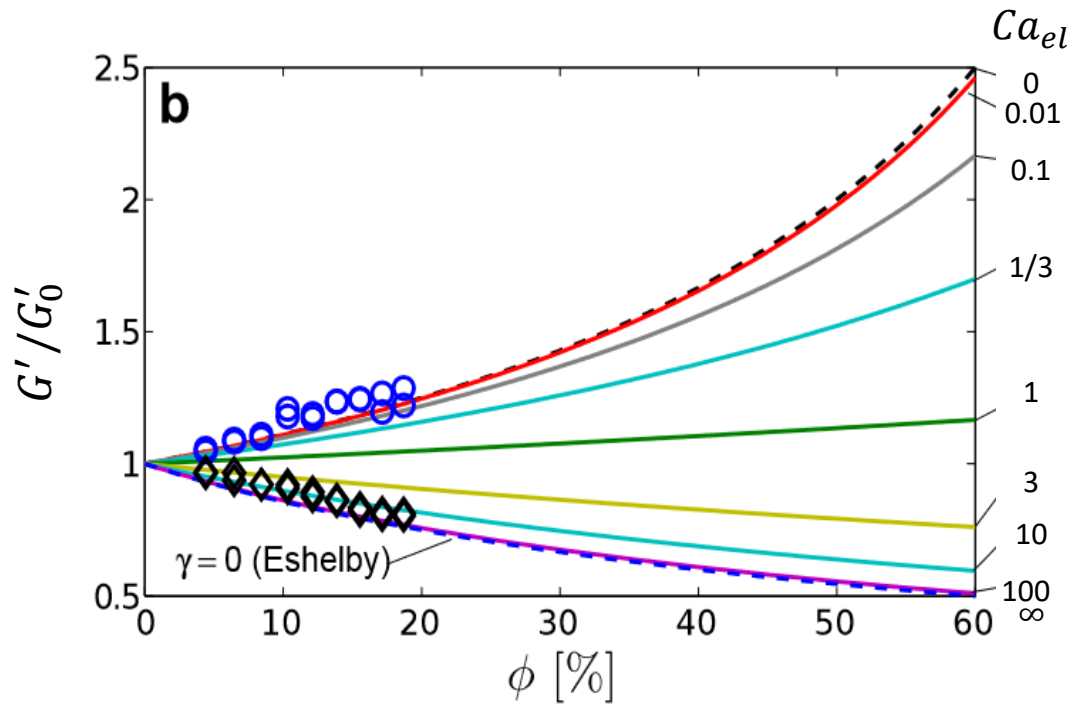
$$Ca_{el} = \frac{G'R}{\gamma}$$



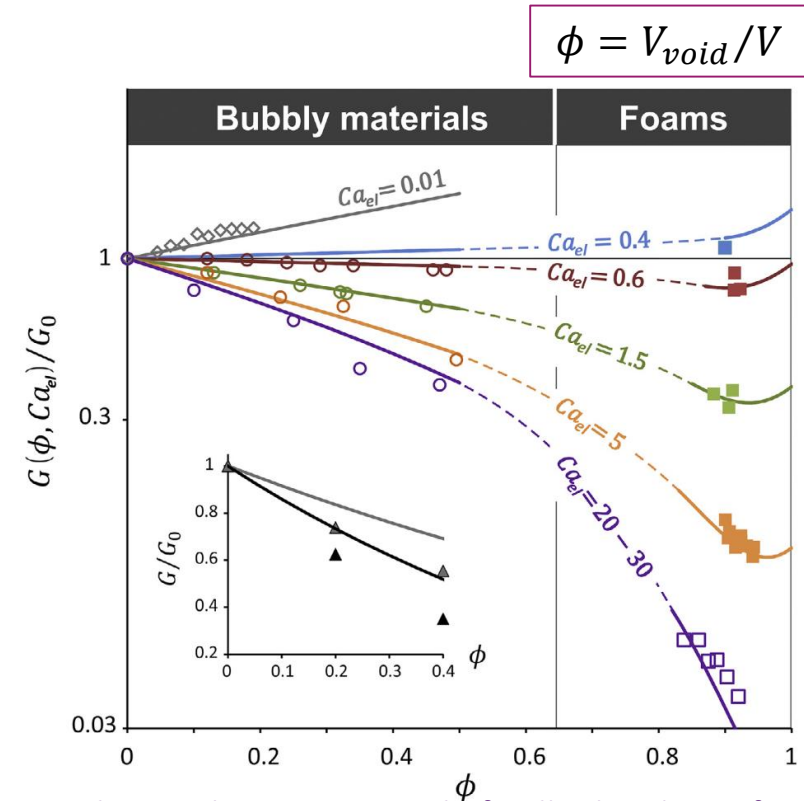
Ca_{el} influences the way Φ changes the rheological parameters

First approach for solid emulsions with liquid inclusions

- Elastocapillary number accounts also for solid emulsions with liquid inclusions and for bubbly liquids and foams



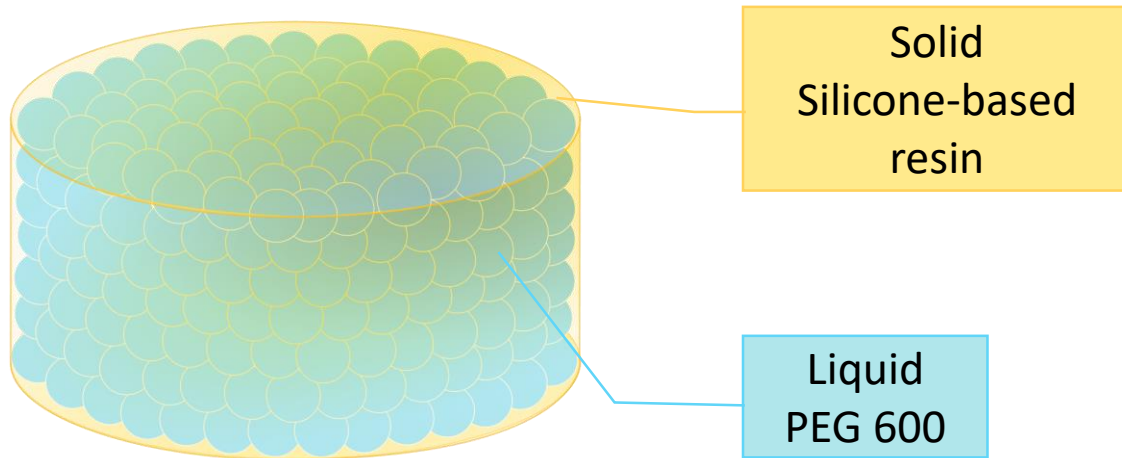
Style et al., 2014, Nature Physics, 11, 2



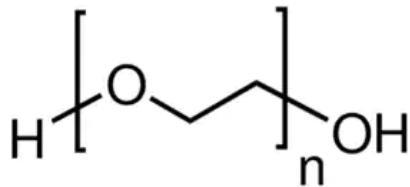
Gorlier et al., 2017, Journal of Colloid and Interface Science, 501

Experimental data for monodisperse inclusion corresponds to the literature for elasticity

Controlling the rheology of a solid emulsion with liquid droplets



- PEG 600 (n=15) :



melting temperature: $\sim 18^\circ\text{C}$

- Sylgard 184 / Sylgard 527 mixture :

Sylgard 184: purely elastic $E \approx 1 \text{ MPa}$

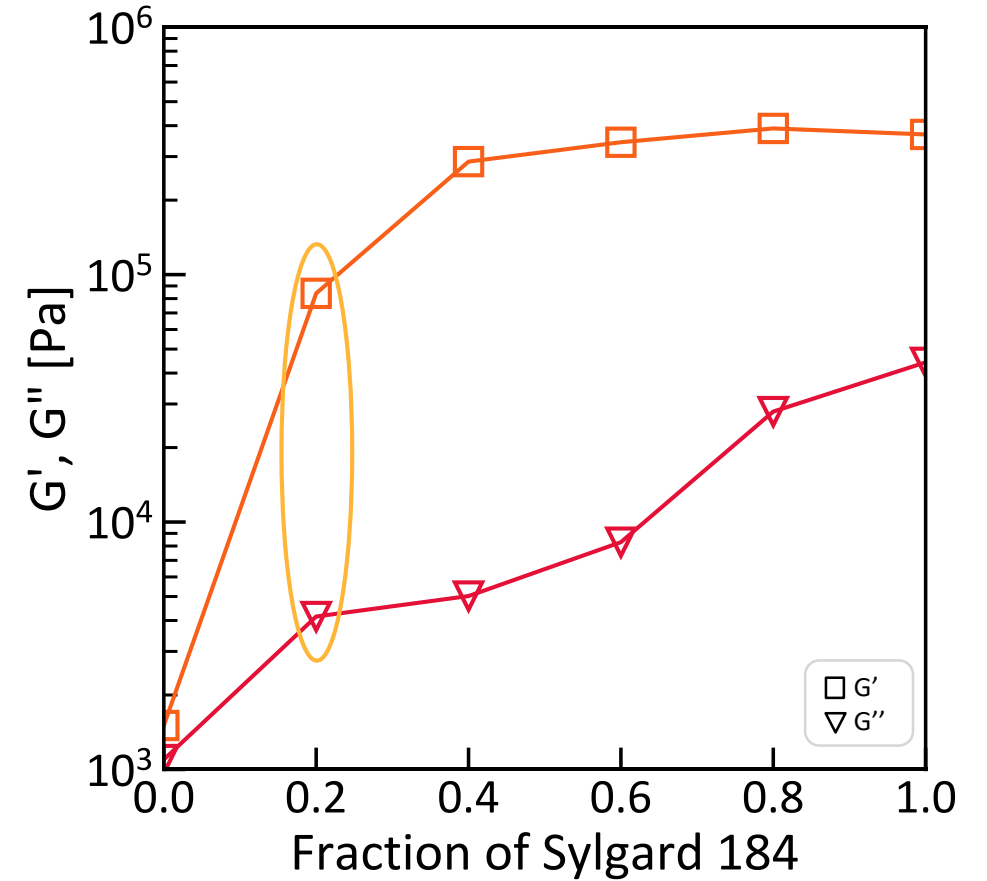
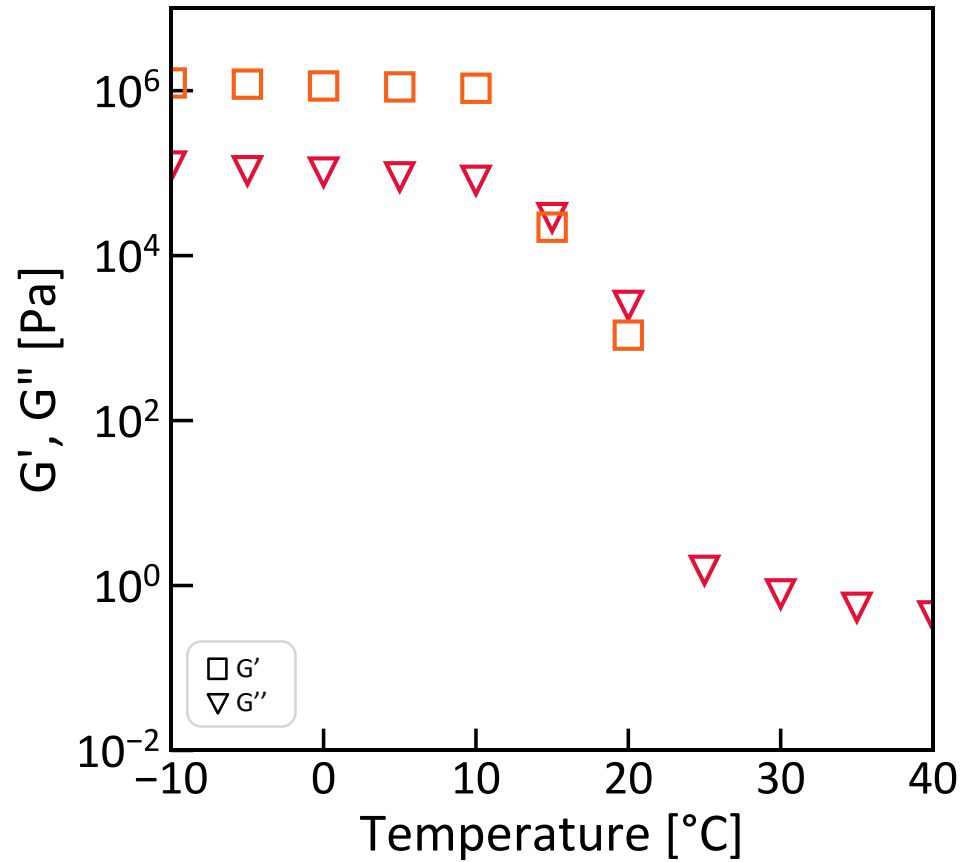
Sylgard 527: mainly elastic $E \approx 1 \text{ kPa}$

Curing at ambient temperature for 2 days



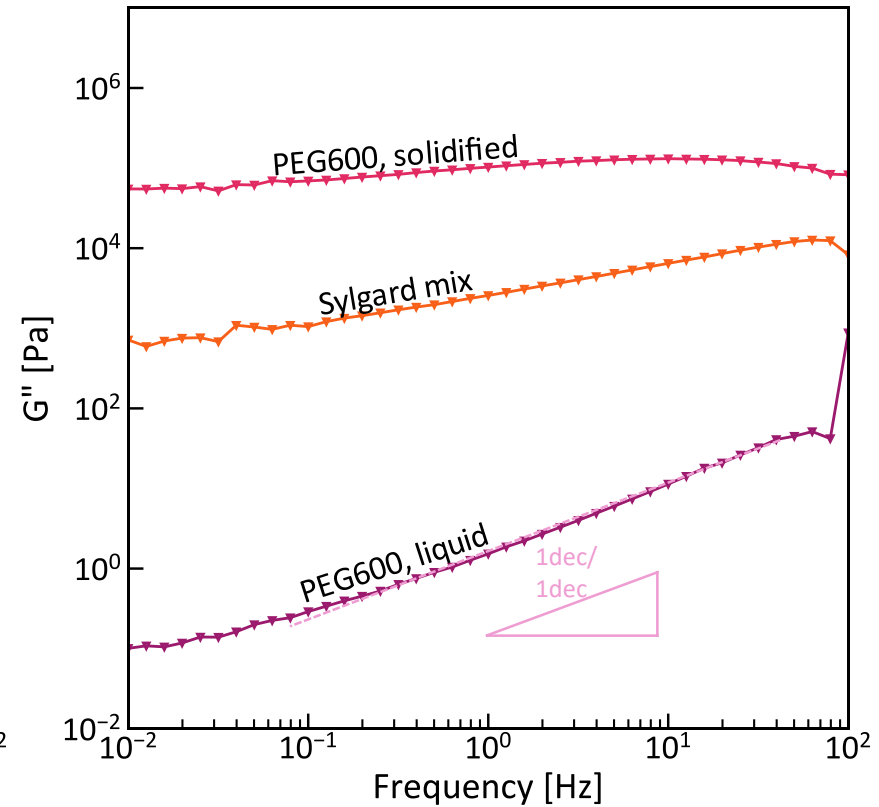
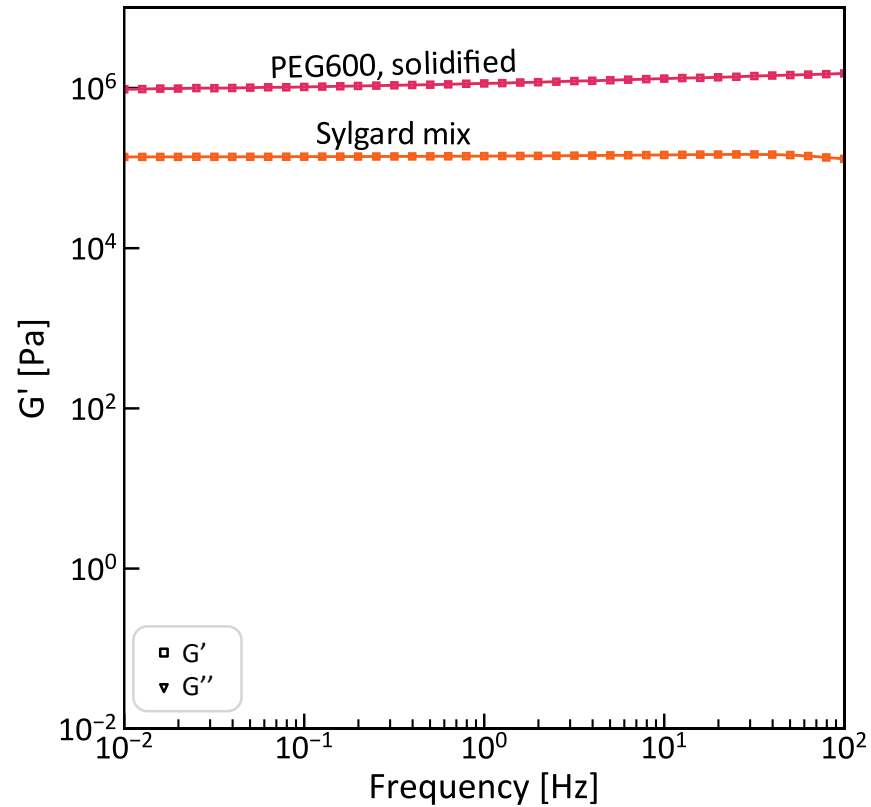
Control parameters: Φ, R

Dispersed and continuous phases



The moduli of the continuous phase is in-between the two limits for the dispersed phase

Rheological characterisation of each phase



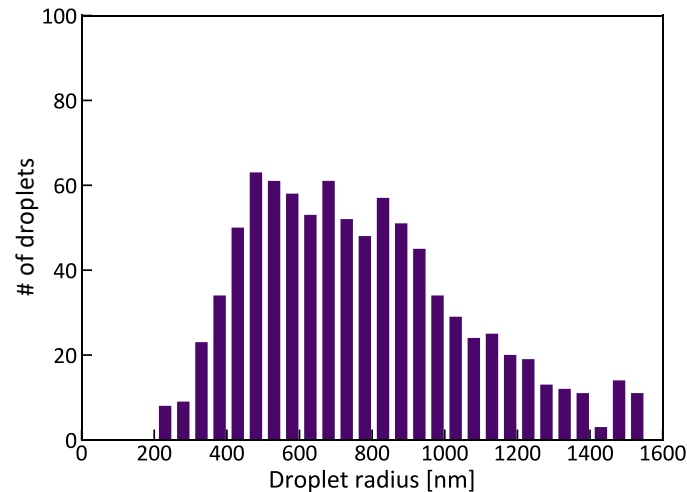
Rheological response is driven by the continuous or dispersed phase depending on temperature

Generation of solid emulsions with liquid inclusions

- Break-up under shear:
- Rotation: aspiration between rotating rod and stator
- Shearing between wall and rotor: breaking into droplets

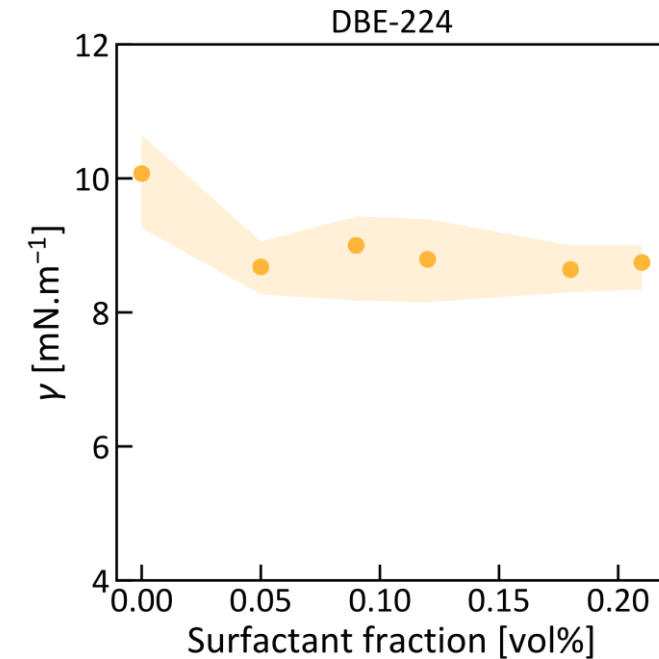


- Size distribution of droplets



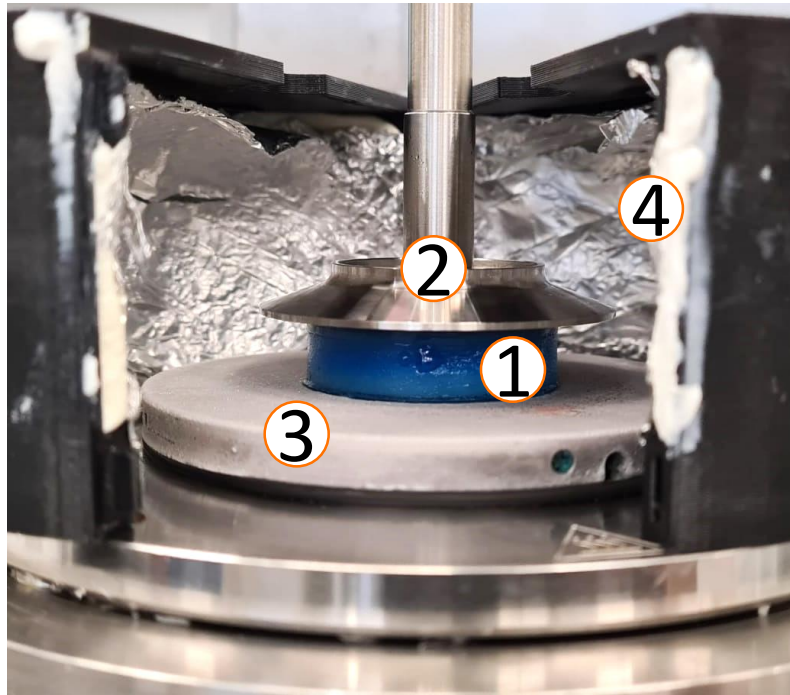
$$R_m \sim 0.85 \mu\text{m}$$
$$\langle R_{32} \rangle \approx 1.05 \mu\text{m}$$

- Variation of the interfacial free energy γ :



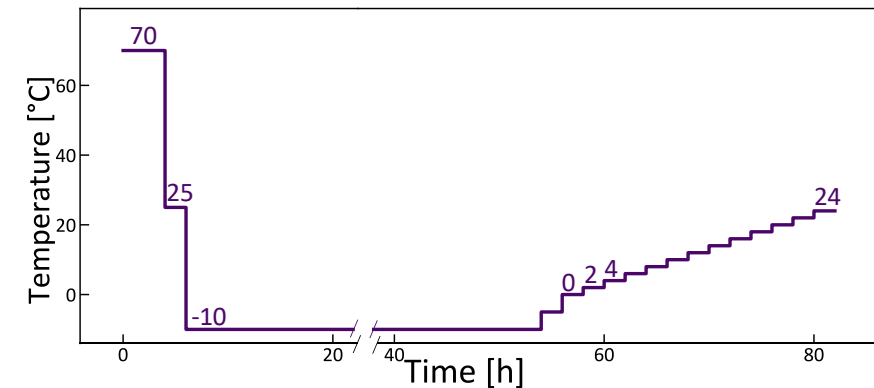
Dimethylsiloxane-ethylene glycol 70:30
block copolymer

Rheological characterization

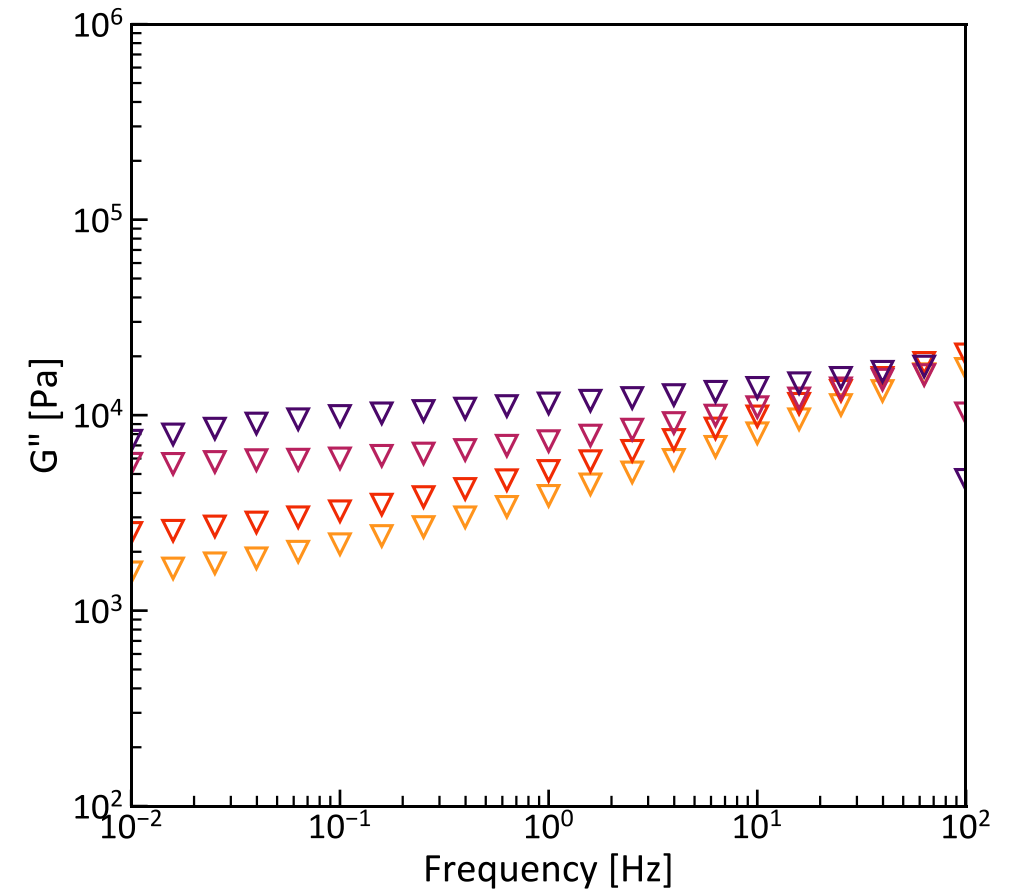
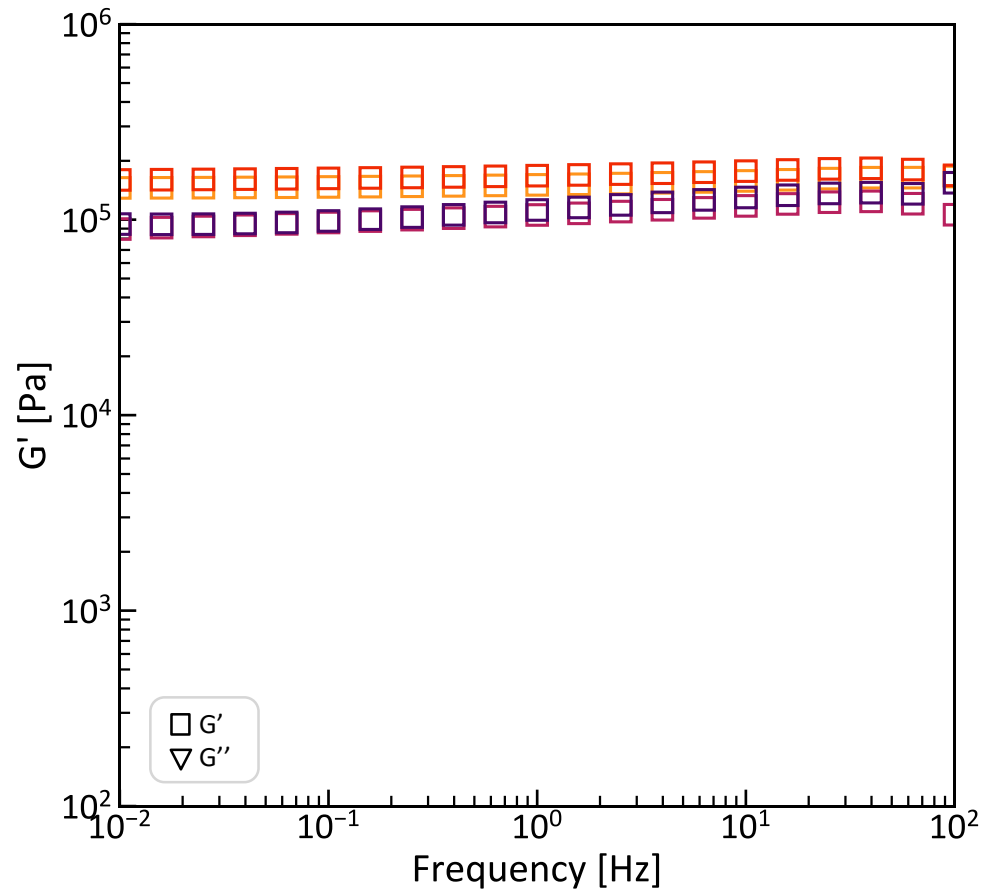


1. Sample, fixed to the rheometer with a layer of crosslinked PDMS
2. Rotating plane measuring system
3. Peltier plate for temperature control
4. Insulating box for better temperature control

- Frequency sweep between 0.01Hz and 100Hz
- Deformation $\gamma = 0.01\%$
- Temperature steps:
 - Crosslinking at 70°C
 - First study at 25°C
 - Solidification at -10°C for 2 days
 - First step at -5°C then 2°C steps between 0°C and 24°C→ Frequency sweep performed for each step
- Constant normal force 2N during temperature change



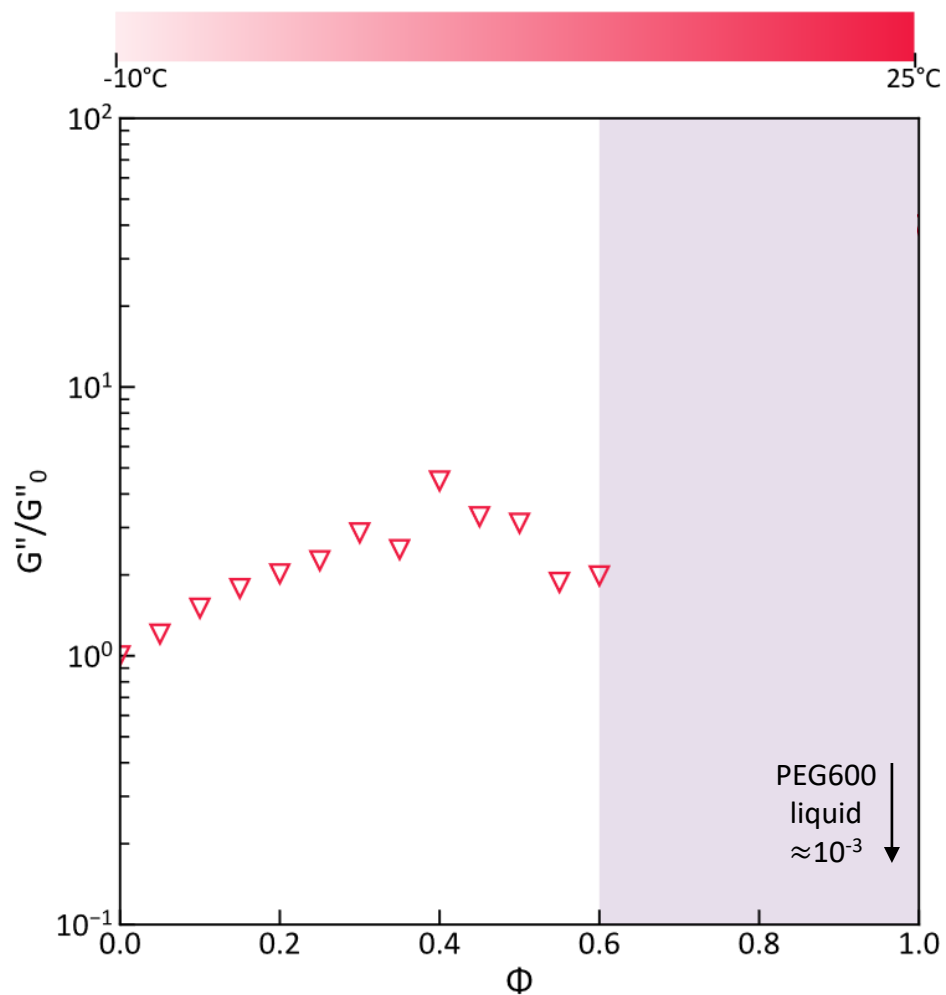
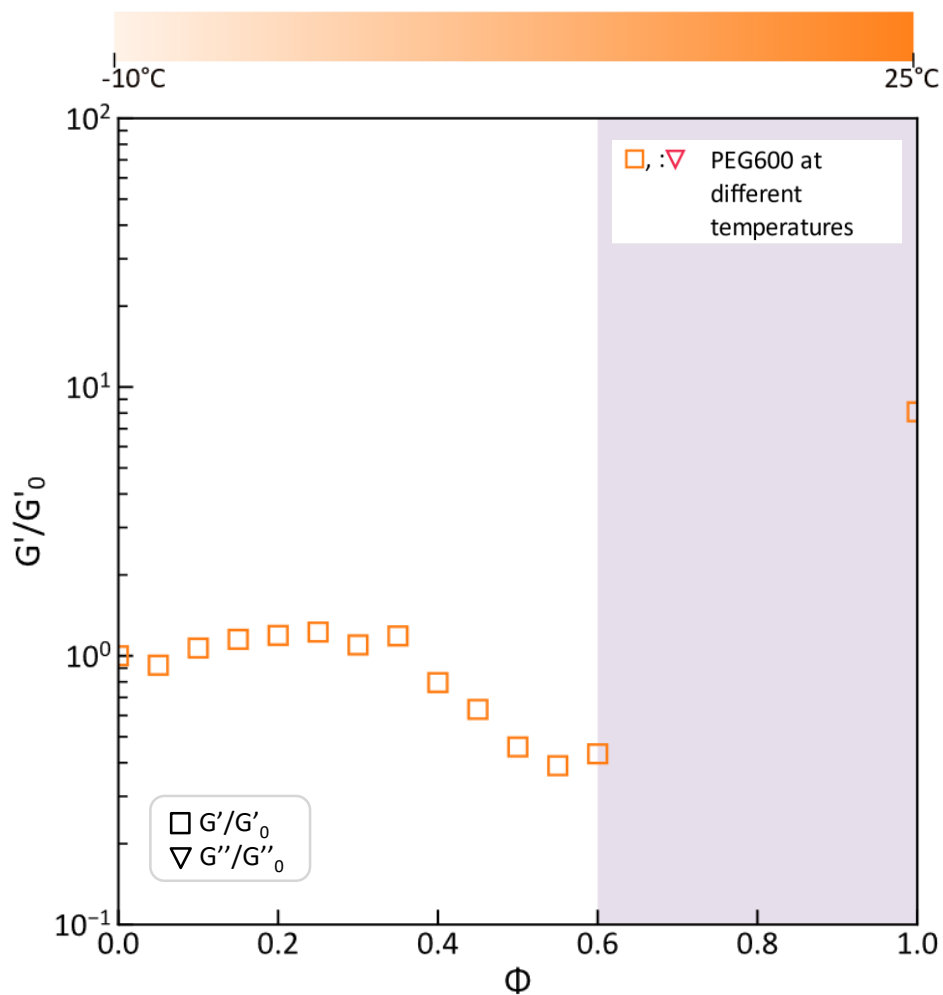
Typical curves for liquid inclusions (T=25°C)



G' almost constant, decreasing with Φ
 G'' increases strongly with Φ at low frequency, up to 10Hz

Evolution with volume fraction at 1Hz

$$Ca_{el} = \frac{G'_0 R}{\gamma} \in [5; 20]$$

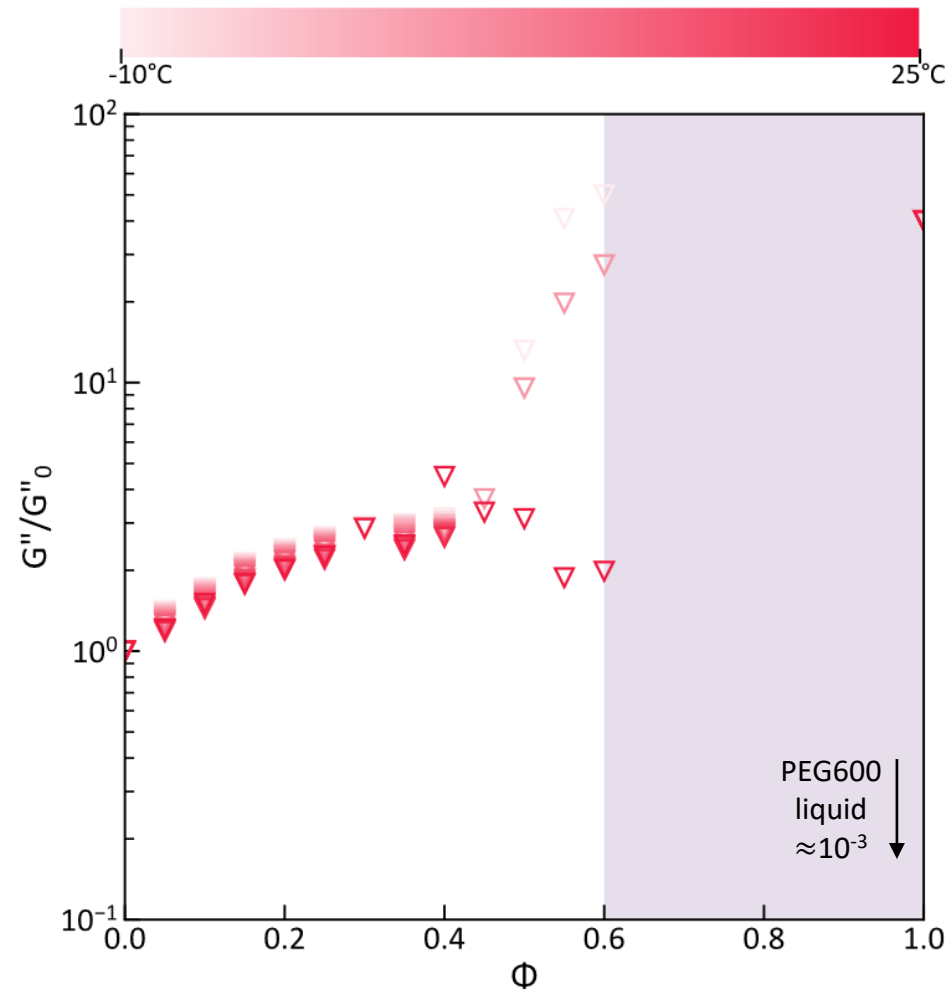
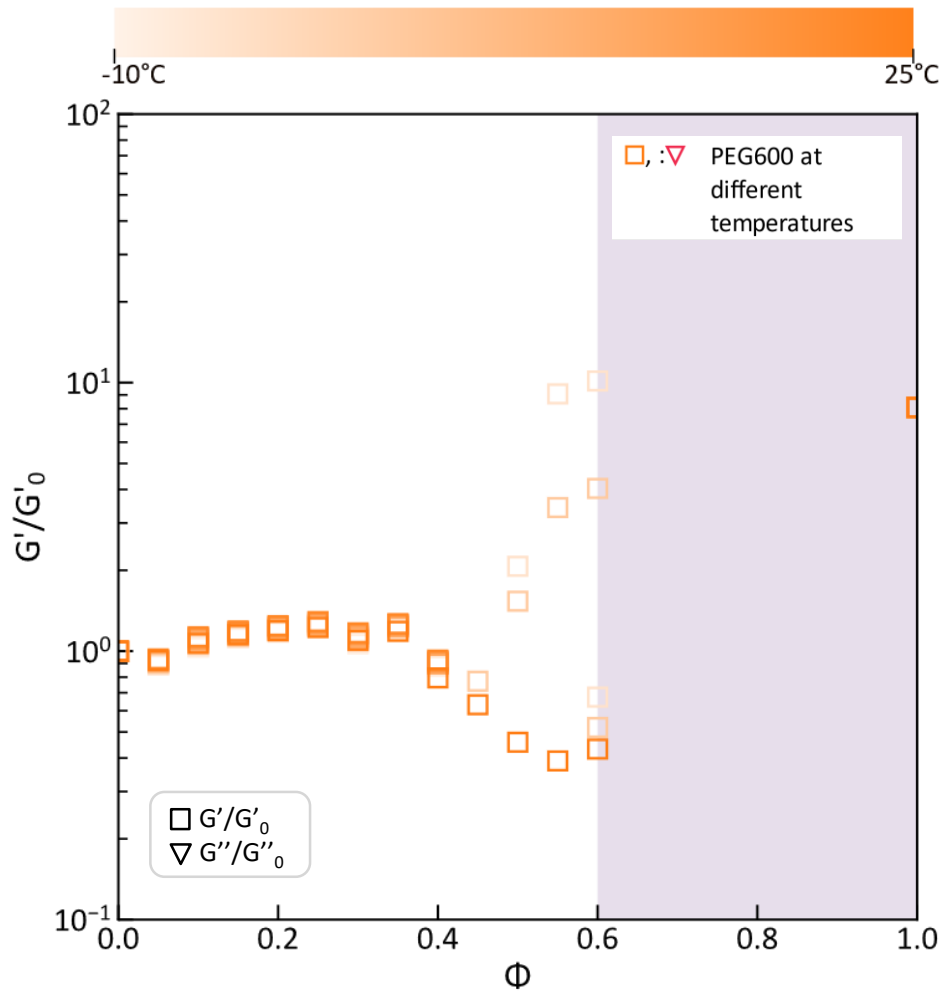


- Non-monotonous moduli
- Up to $\Phi = 0.4$:
 - Almost constant G'
 - Increasing G''
- Decrease for both moduli when $\Phi > 0.4$

Existing models don't capture the behavior

Evolution with temperature

$$Ca_{el} = \frac{G'_0 R}{\gamma} \in [5; 20]$$

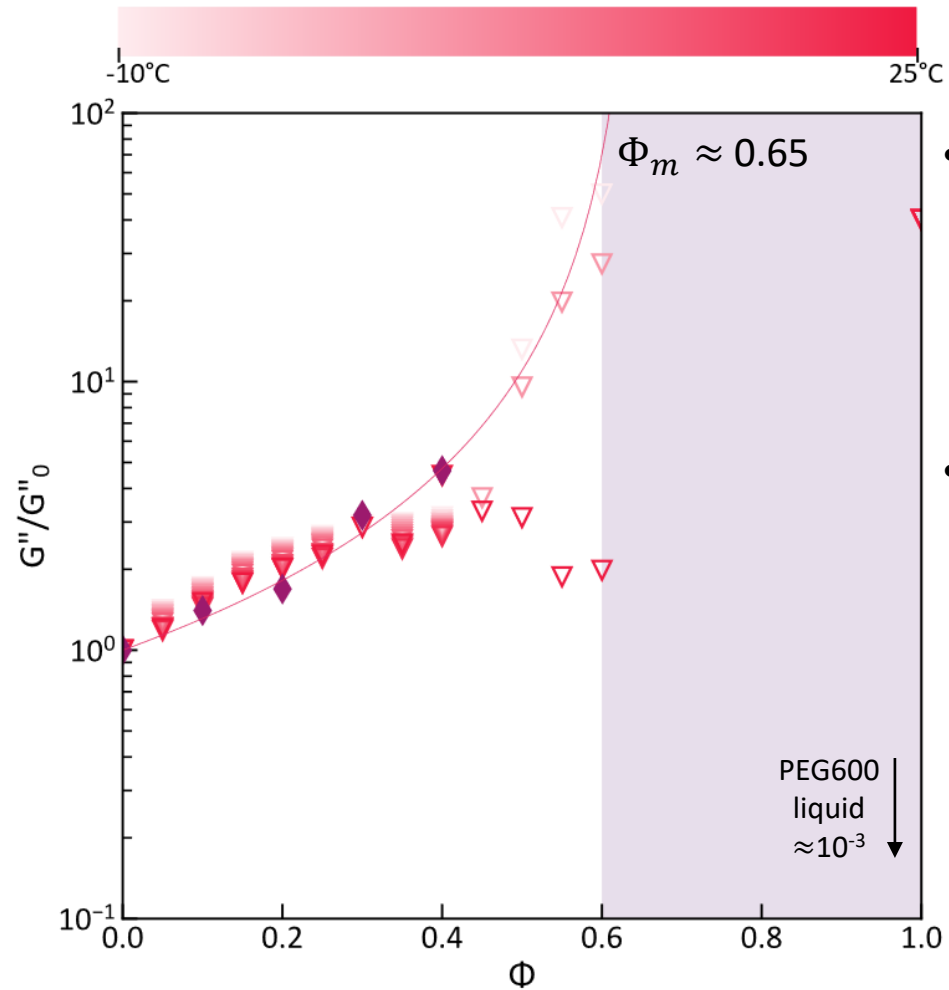
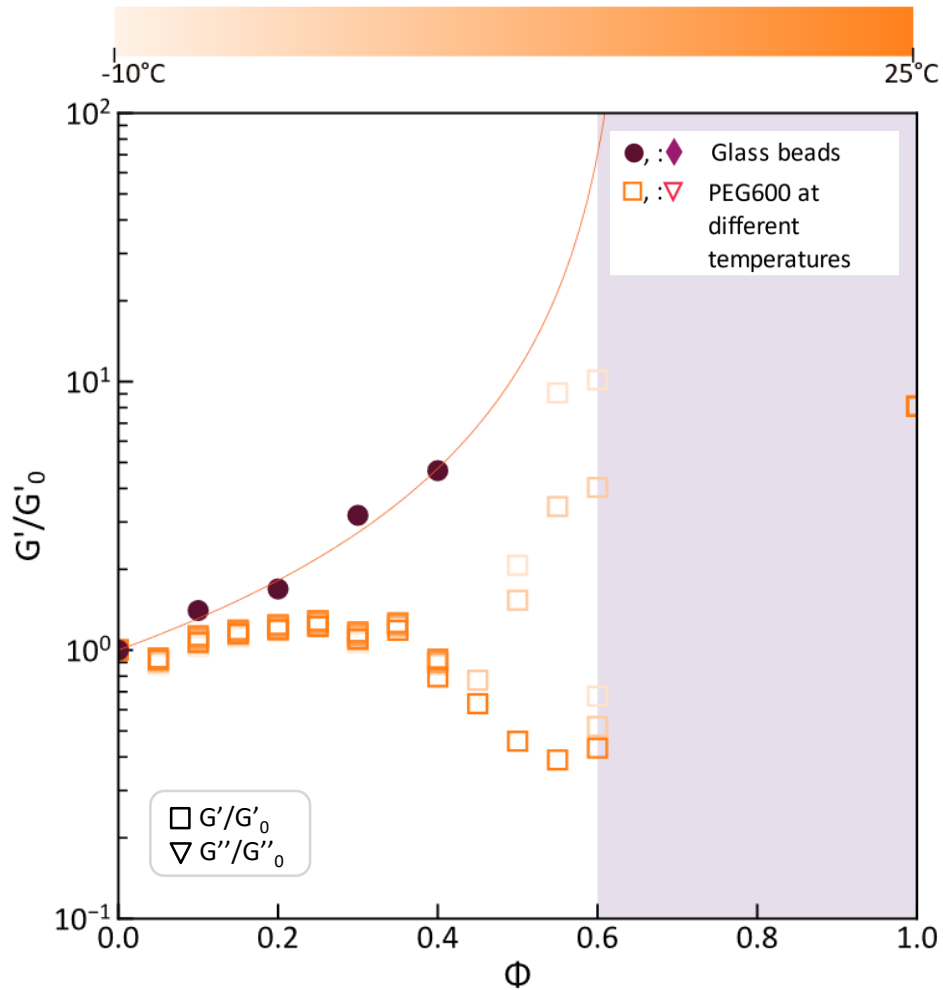


- For $\Phi \geq 0.4$, increase of the moduli at colder temperatures

Recovery of monotonous behavior at low temperature

Comparison with models

$$Ca_{el} = \frac{G'_0 R}{\gamma} \in [5; 20]$$



- Krieger-Dougherty law:

$$\frac{G''}{G''_0} = \left(1 - \frac{\Phi}{\Phi_m}\right)^{-2.5\Phi_m}$$
 fits G'' well
- G' of emulsions with solidified inclusions is not fitted by KD law

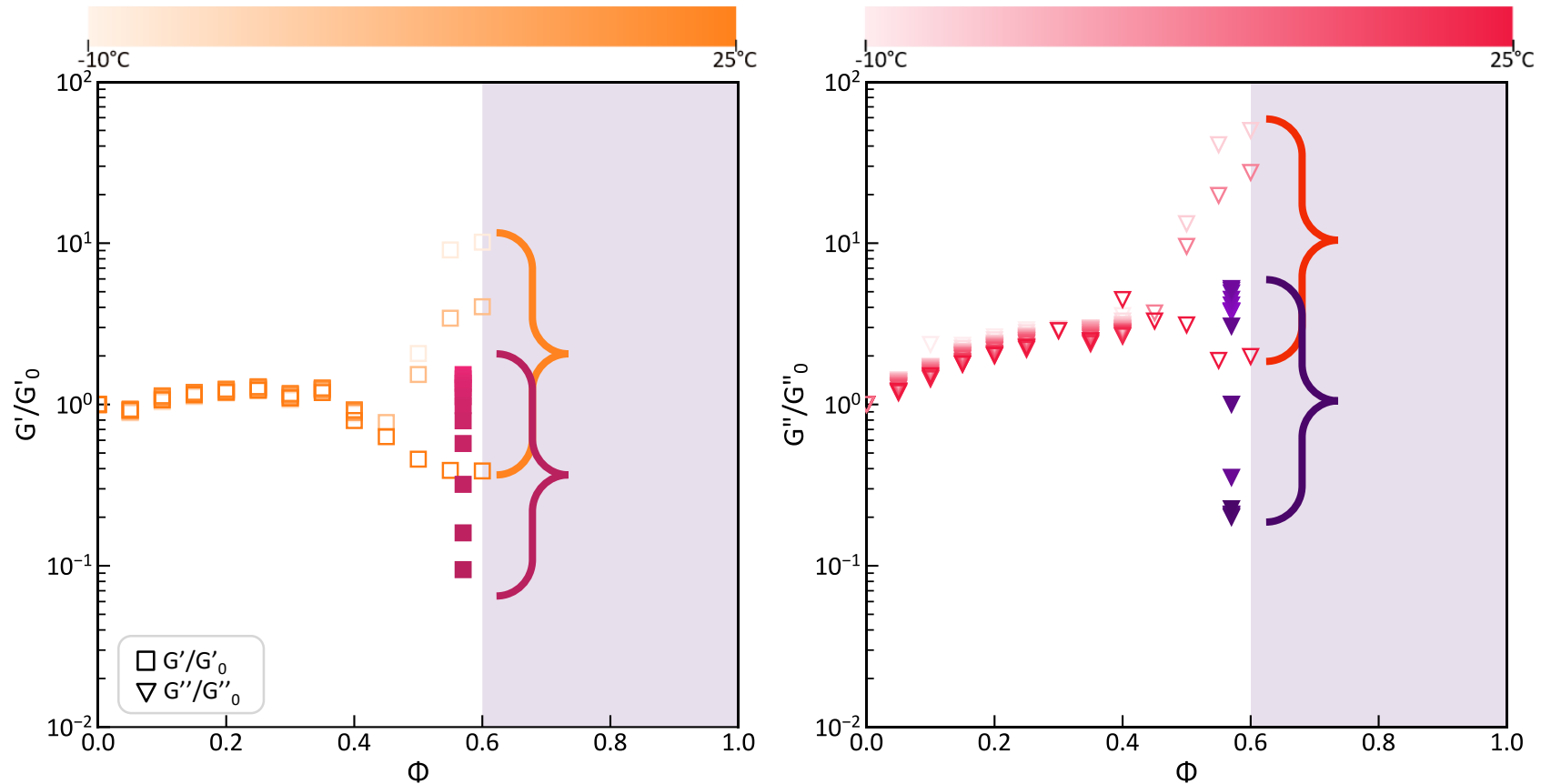
First hypothesis: discrepancy caused by polydispersity

Krieger & Dougherty, 1959, Transactions of the Society of Rheology, 3, 1
 Mahaut et al., 2008, Journal of Rheology, 52, 1

Comparison with microfluidic-generated emulsions

Breakup-under-shear-generated emulsions: $Ca_{el} \in [5; 20]$

Microfluidics-generated emulsions: $Ca_{el} \approx 4000$



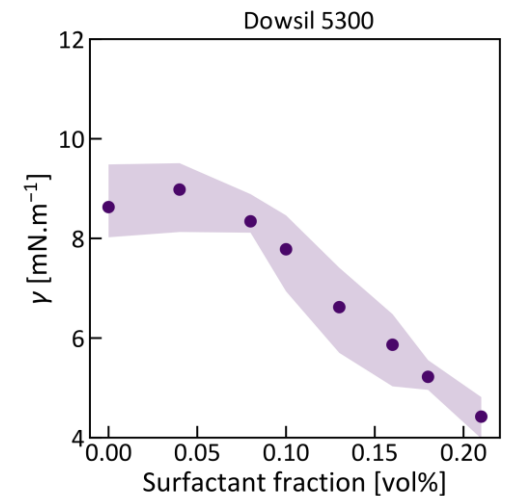
Influence of Ca_{el} on the moduli
Reinforcing behavior at cold temperatures

Conclusion and perspectives

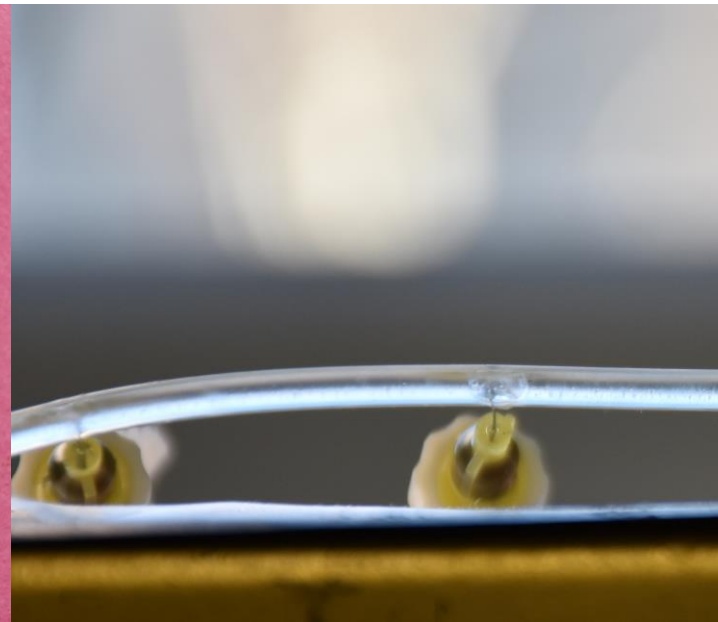
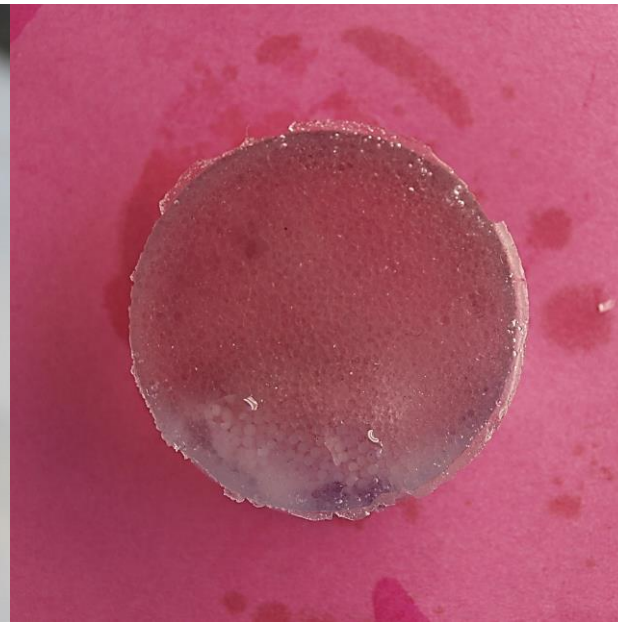
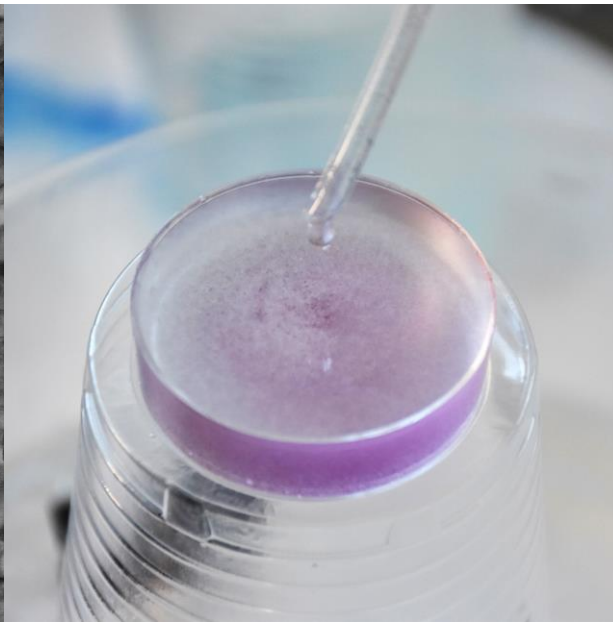
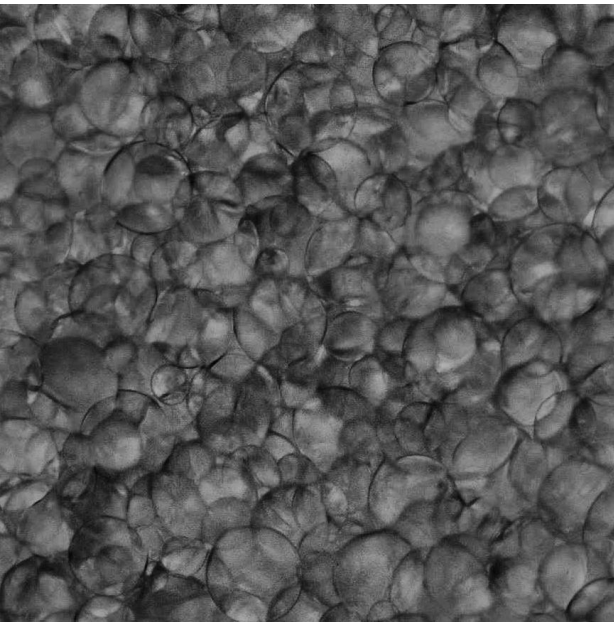
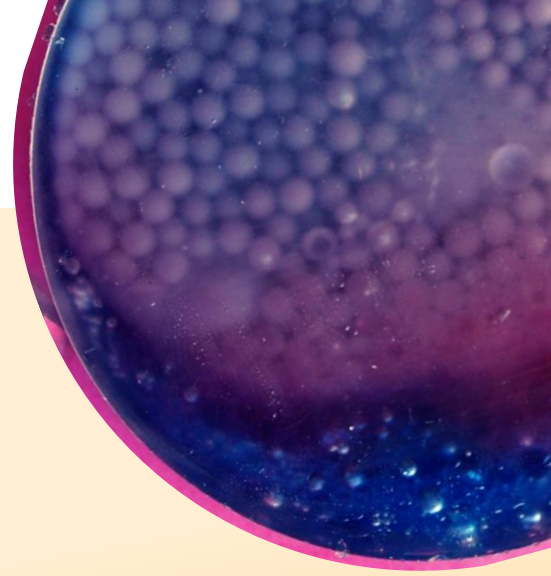
- Test of the rheological parameters G' and G'' for inclusion in a solid matrix versus volume fraction and temperature:
 - High temperature (liquid inclusions): plateau in G' for $\Phi < 0.4$
 G'' well described by a Krieger-Dougherty model
 - For $\Phi \geq 0.4$: decrease of the moduli compatible with Palierne model
 - Low temperature: increase of the moduli compatible with literature
- Hypothesis for discrepancy with theory: polydispersity, preliminary tests with microfluidics-generated samples

- Generation of more monodisperse samples with different droplet sizes
- Variation of key parameter elastocapillary number Ca_{el}
 - Changing the surface free energy γ with different surfactants
 - Controlling the droplet radius and the polydispersity

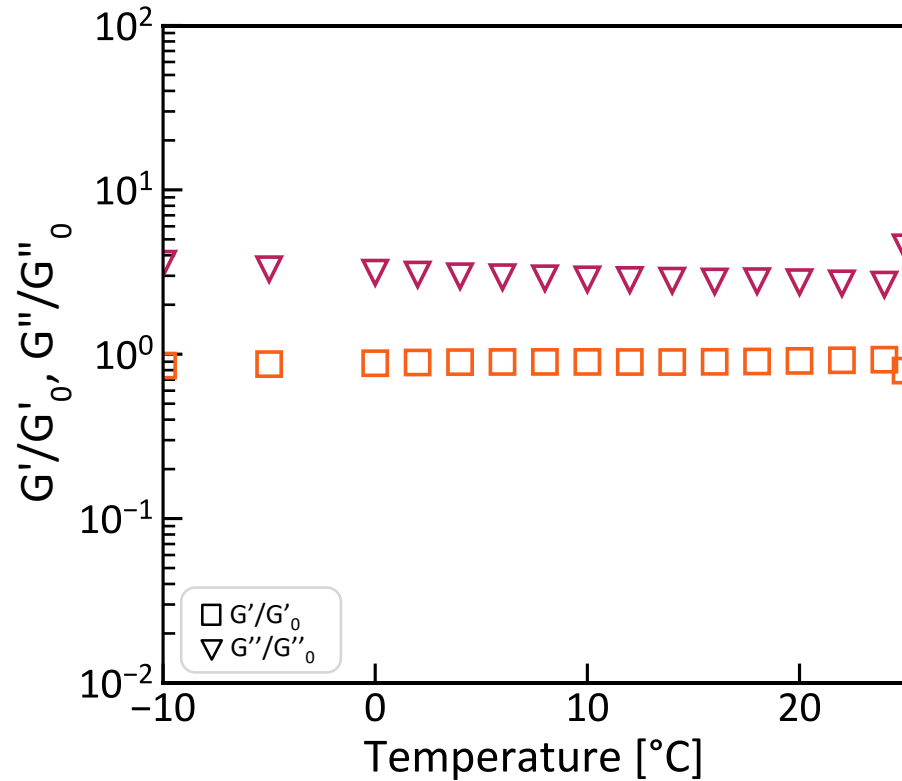
Ghosh, Lopez-Pamies, 2022, Elastomers filled with liquid inclusions: Theory, numerical implementation, and some basic results, preprint



Thank you for your attention !

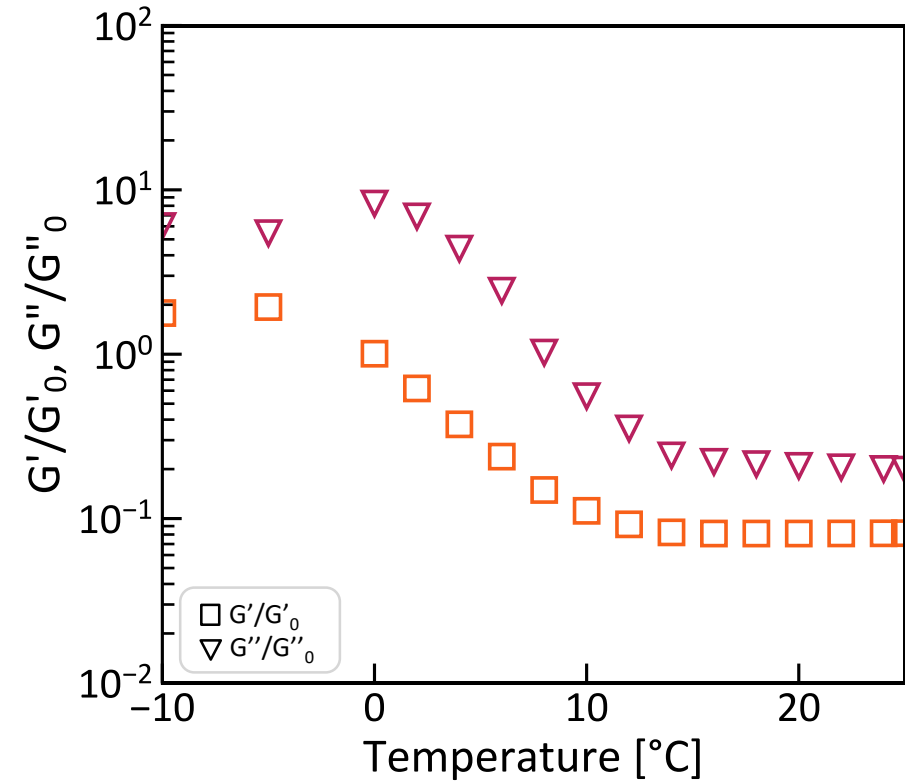


Different behaviors with temperature



UltraTurrax-generated samples (here $\Phi = 0.4$):

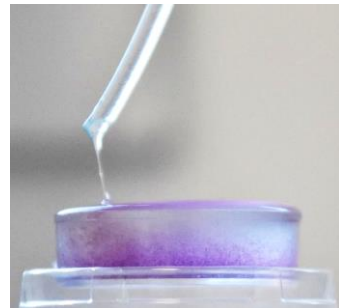
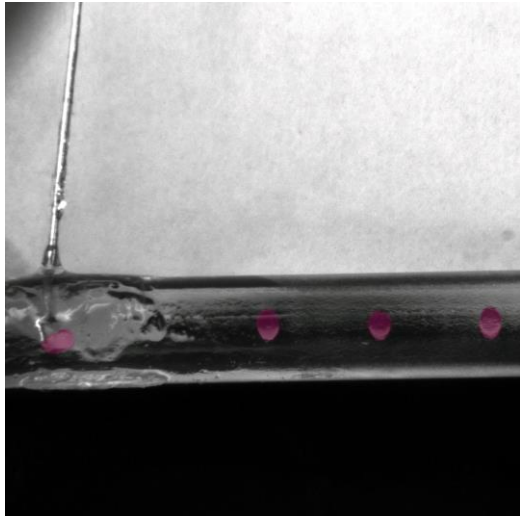
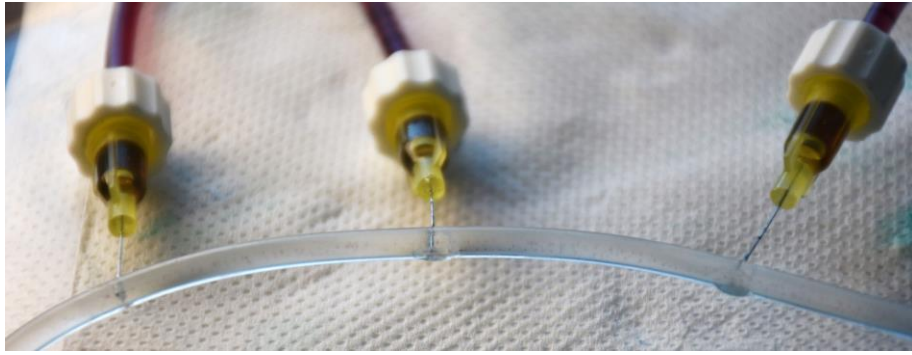
- Very slow decrease of loss modulus as temperature increases
- Constant storage modulus



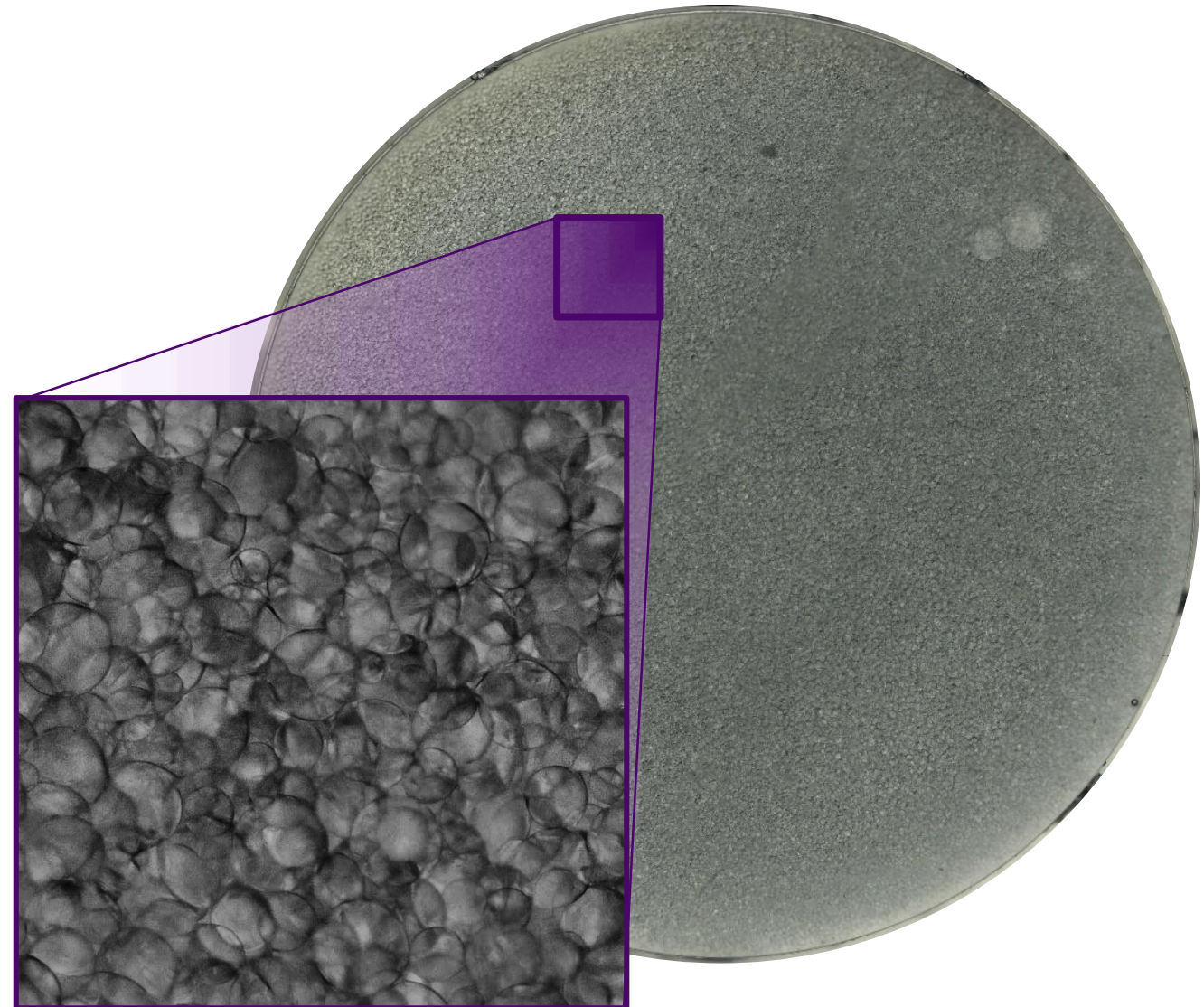
Microfluidic-generated samples:

- Sharper change around the PEG transition

Millifluidics device

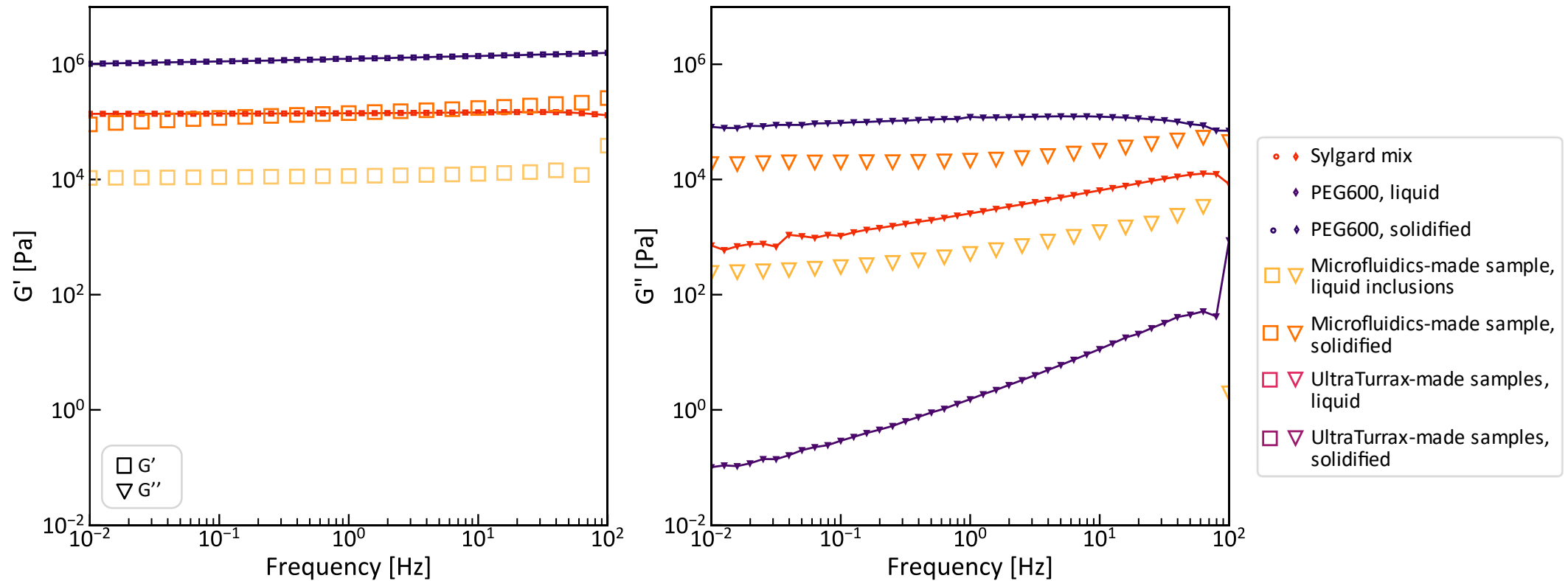


- PDMS mix pushed with a peristaltic pump to reuse surplus at a rate of 2,5 to 10rpm
- PEG600 pushed to 10 syringes in series at rate of 200 μ L/h
- PEG droplets let to sediment in PDMS $\Rightarrow \Phi \approx 0.6$



$R \approx 150 \mu\text{m}$

Typical curves for microfluidics-generated samples



Typical curves for microfluidics-generated samples

