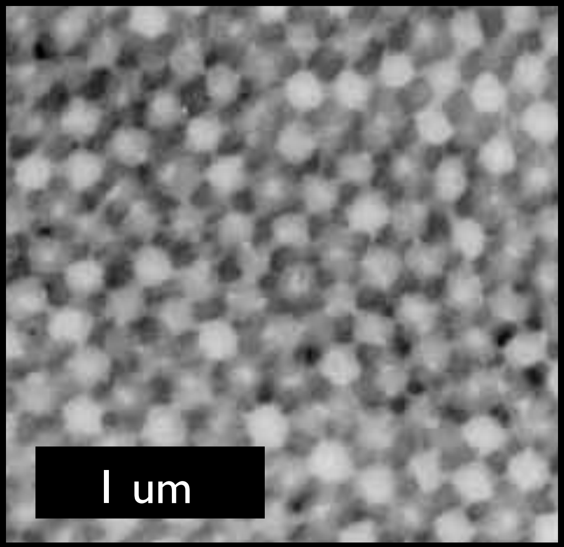
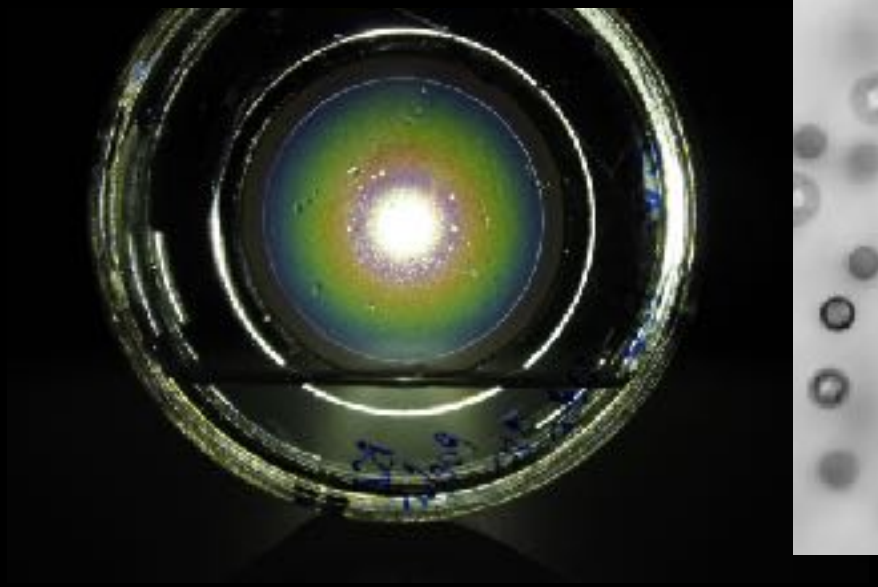
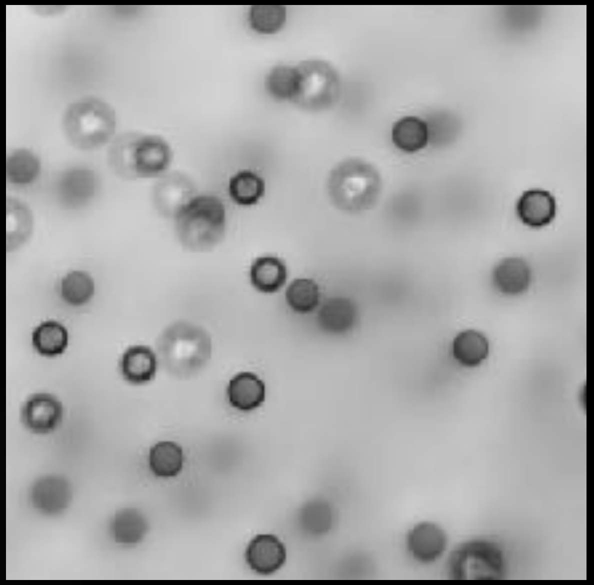
Using phase separation in soft materials to create structural colour

Rob Style
ETH
6 Sep 2018







With:

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Nicolo Fanelli

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Mahdiye Ijavi

Qin Xu

Eric Dufresne

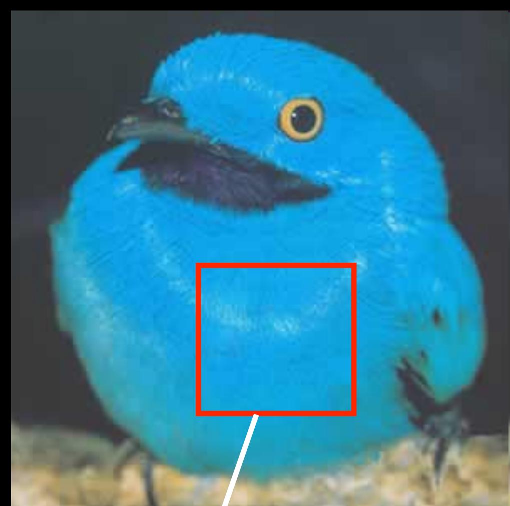
Larry Wilen

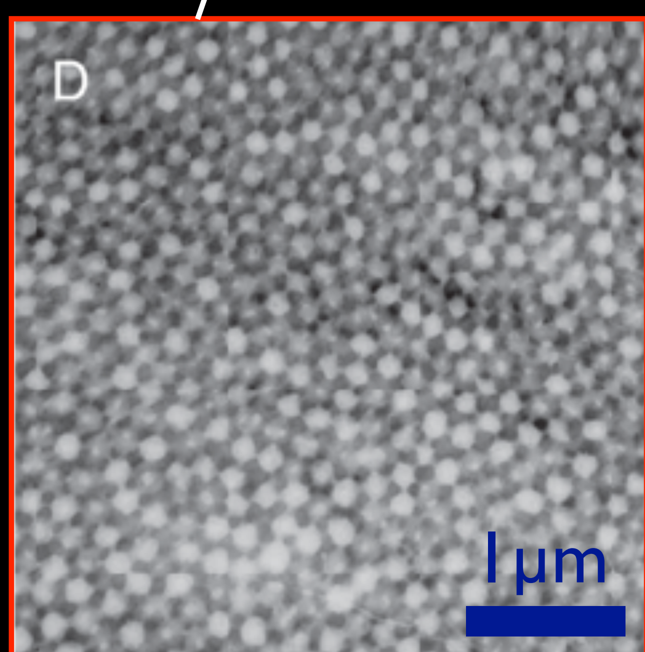
Colours typically fade/change over time

museumshopllc.com

‘Crap taxidermy’, Kat Su

However some animals have vibrant, non-fading colours

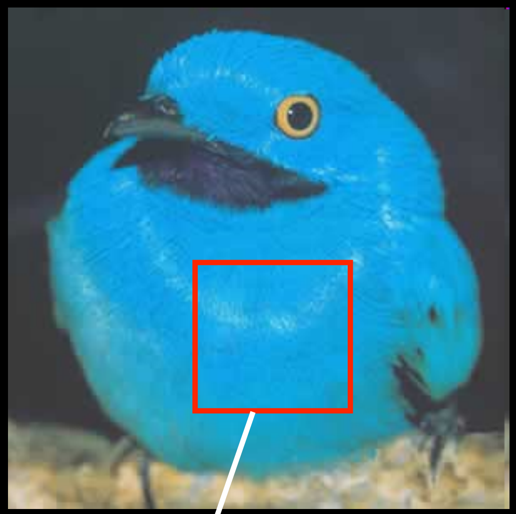


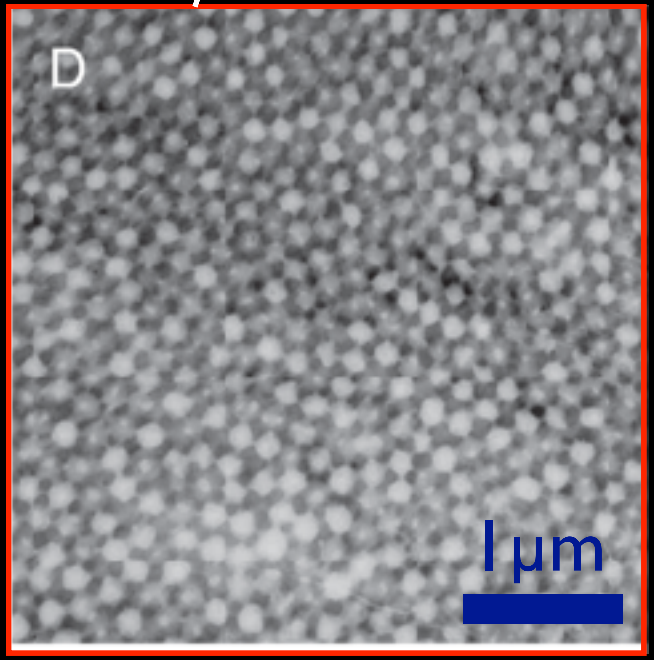


Dufresne et al.
Soft Matter (2009)

Structural colour requires making materials with a very regular microstructure that is close to the wavelength of light

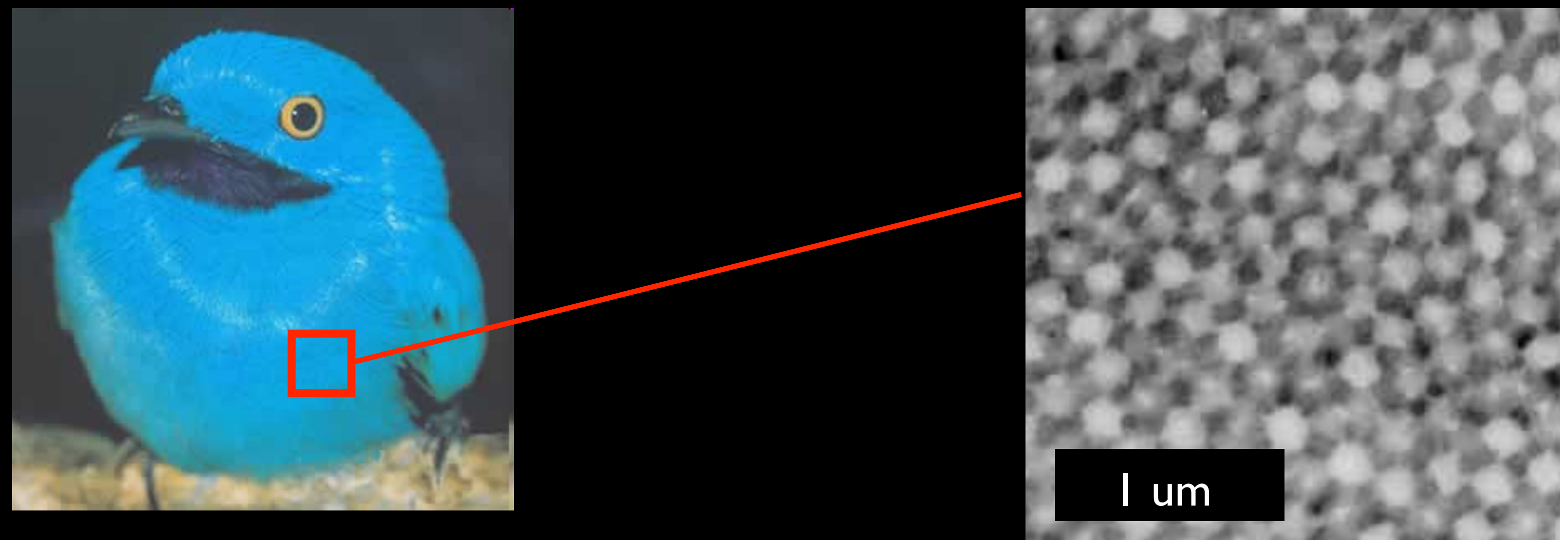
Motivation: can we make similar materials?

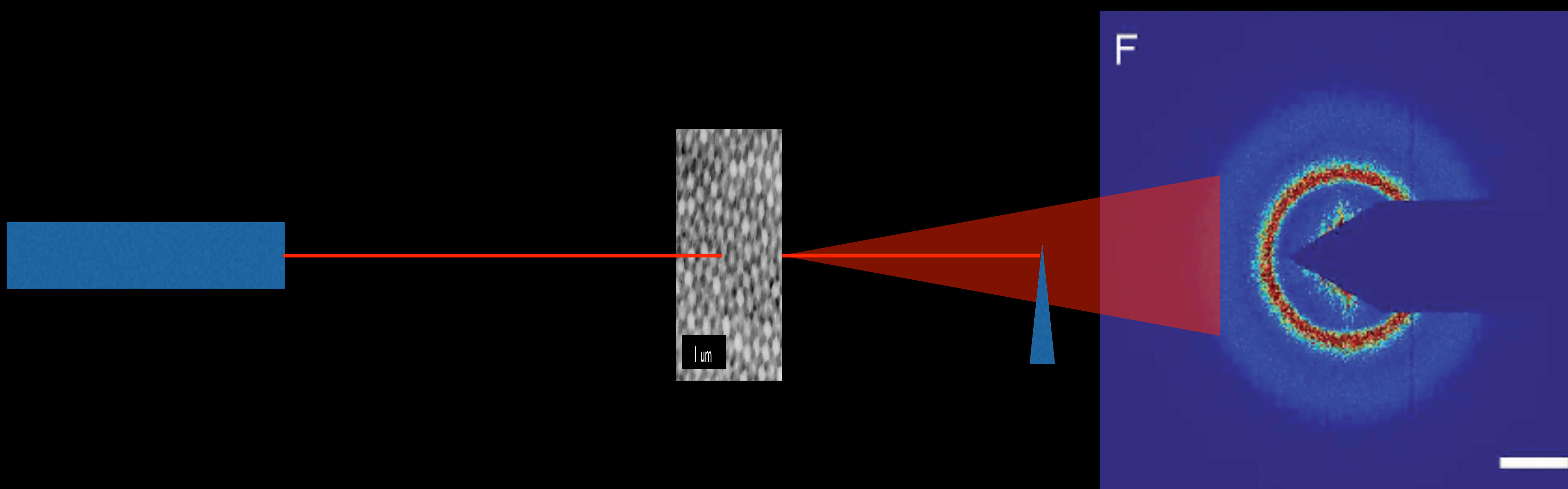




- Can we make similarly monodisperse materials?
- Can we do this over large areas?

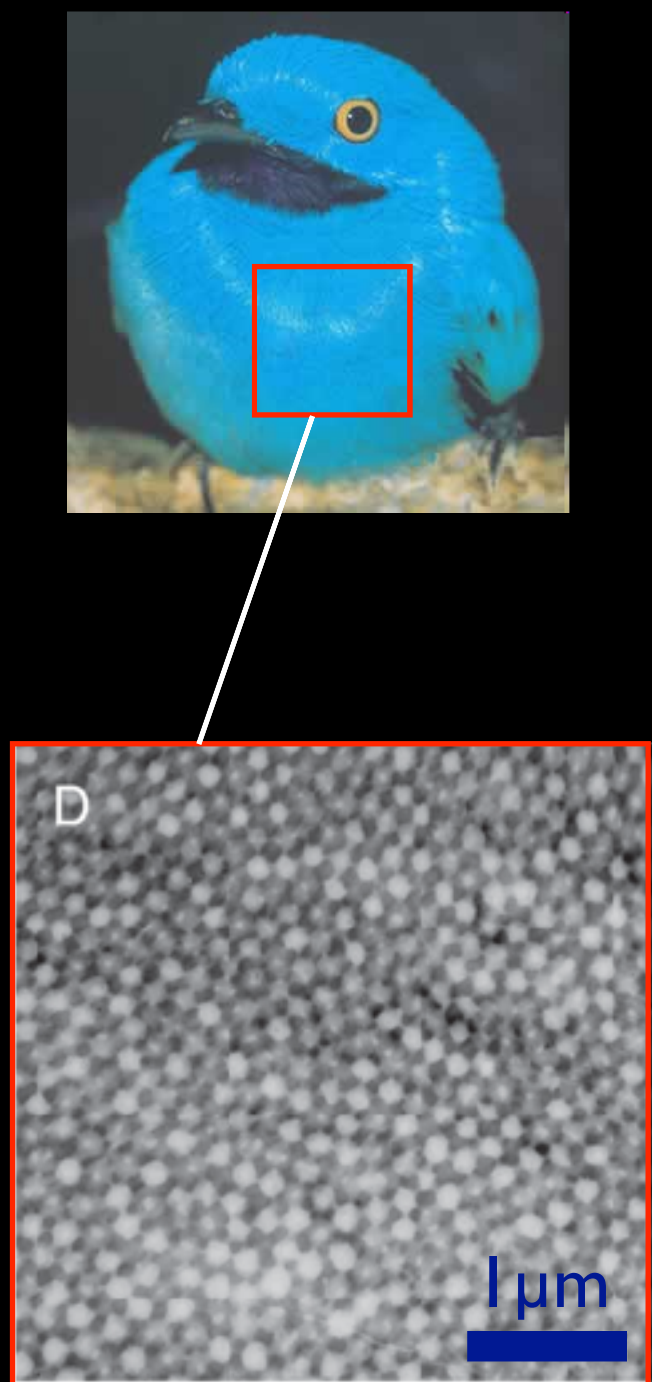
Scattering experiments





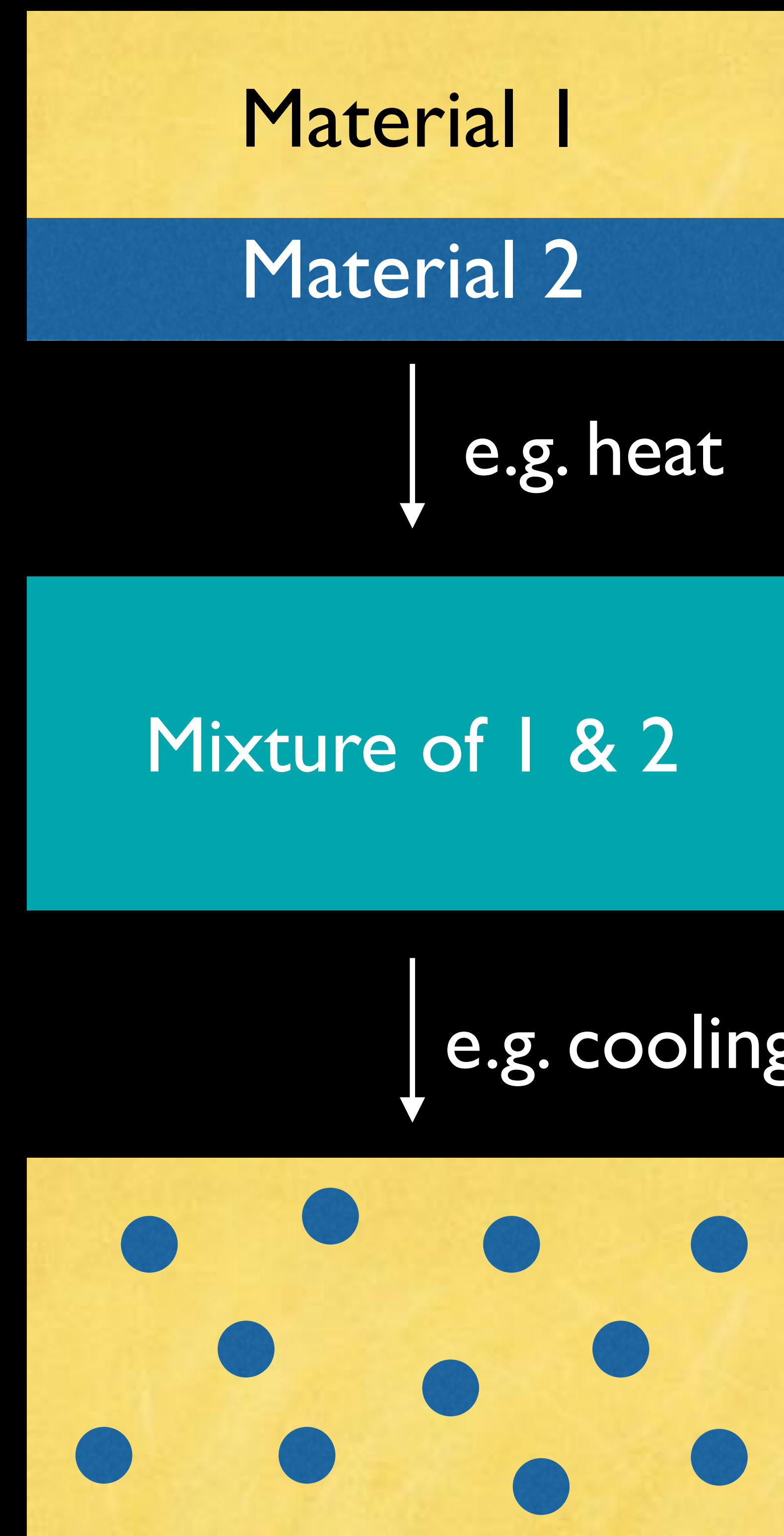
Dufresne et al.
Soft Matter (2009)

How do birds make structures like this?



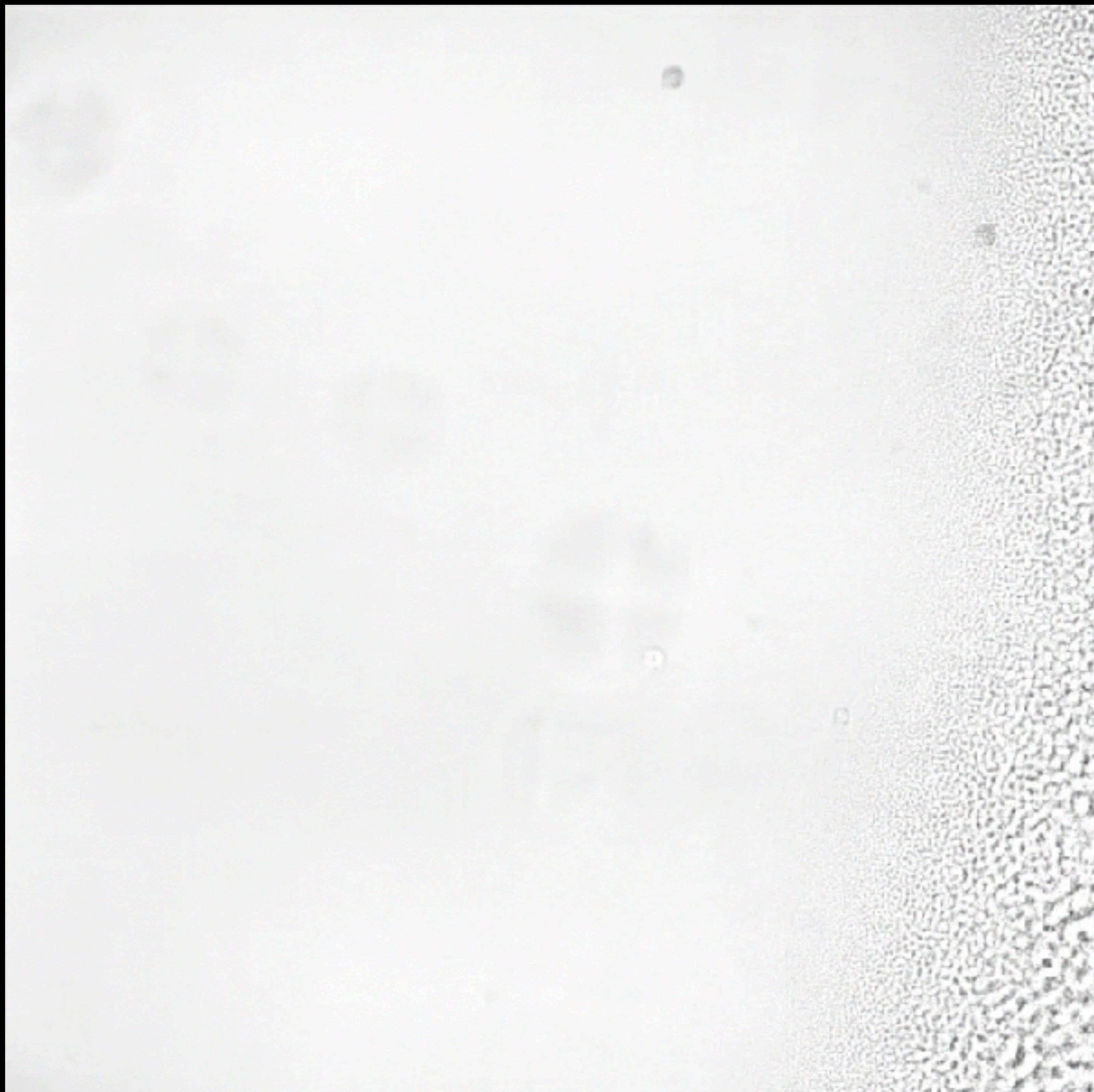
Dufresne et al.
Soft Matter (2009)

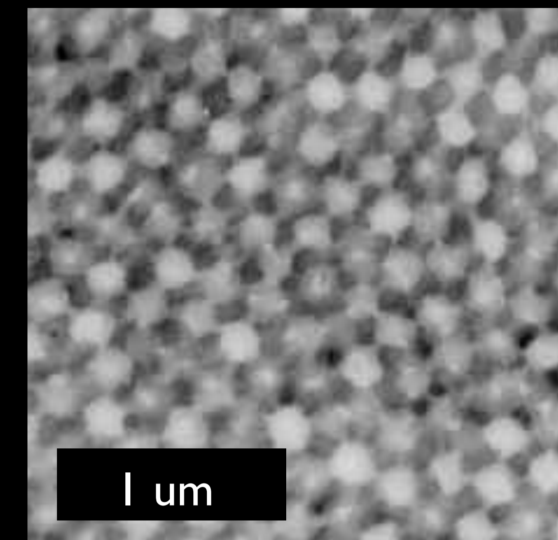
Phase separation



Arrest to preserve the structure

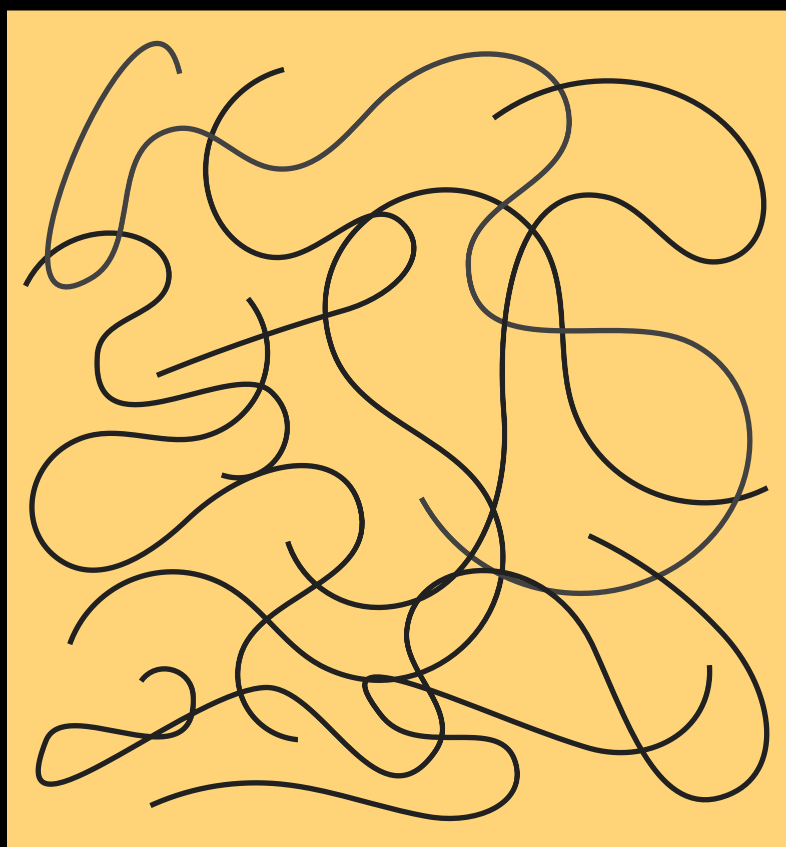
Phase separation is tricky to control!





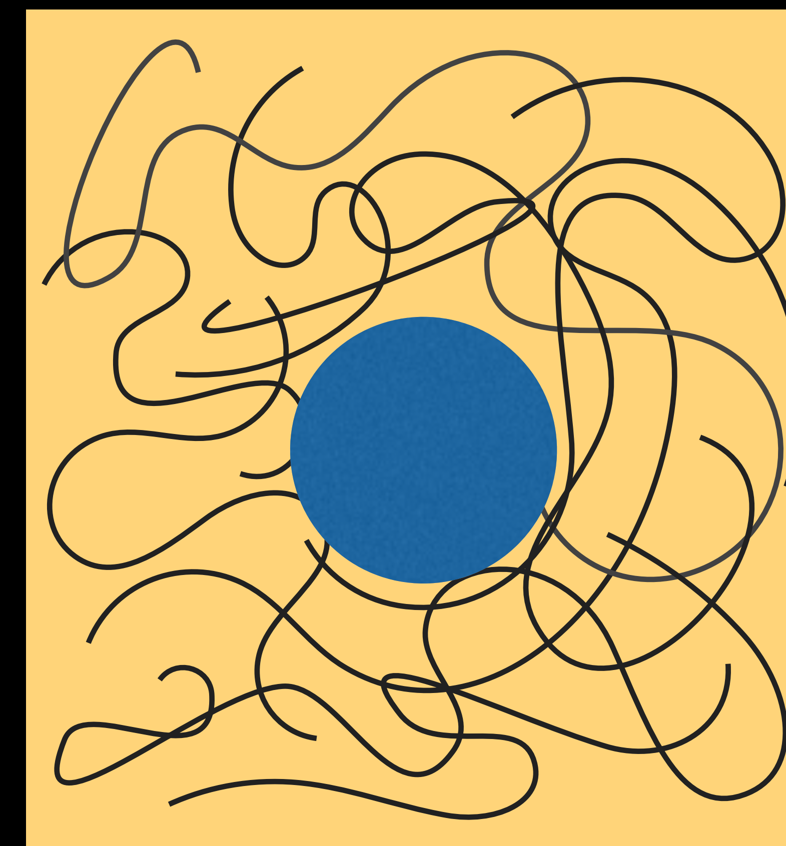
Lutidine 2/6 and water phase separating upon heating

Can we do this with phase separation in a polymer network?



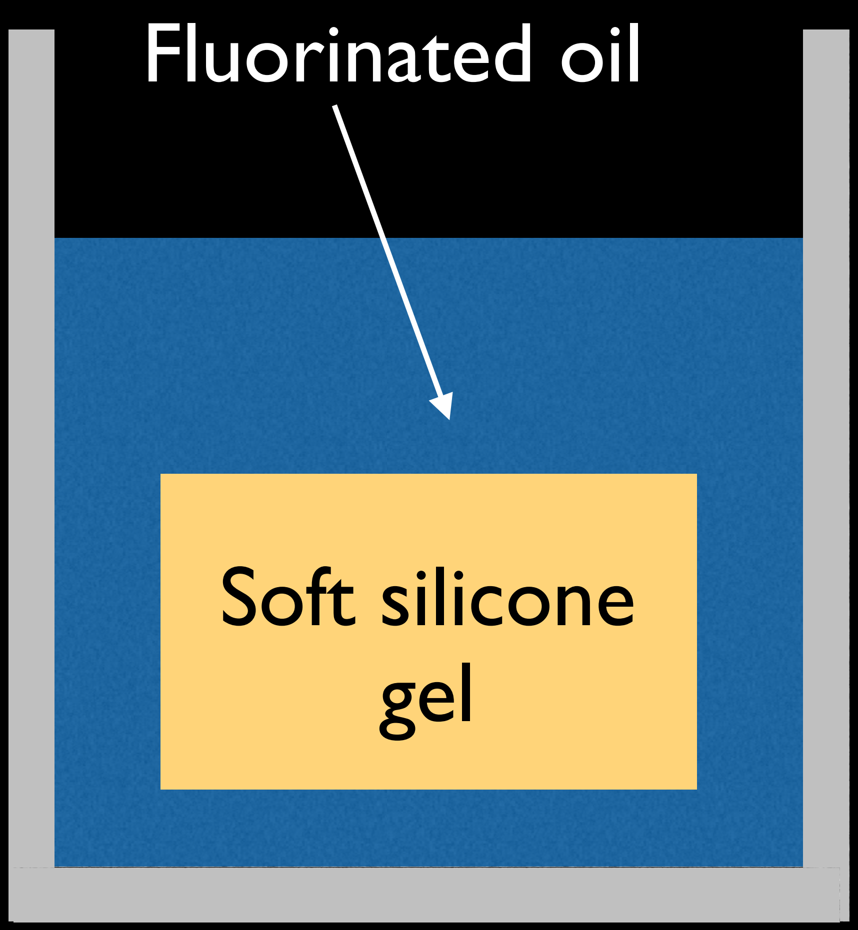
Make soft, crosslinked gel swollen with solvent

Saturate with partially miscible solvent

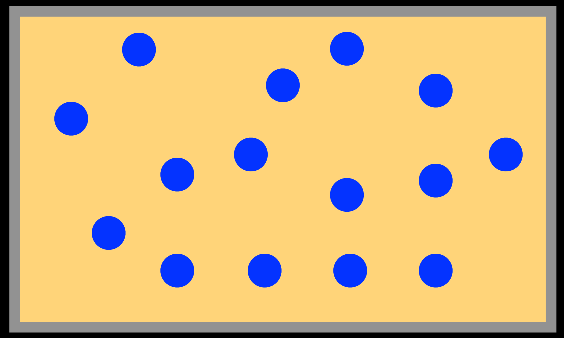


Phase separate

One way of doing it



HEAT at fixed temperature T

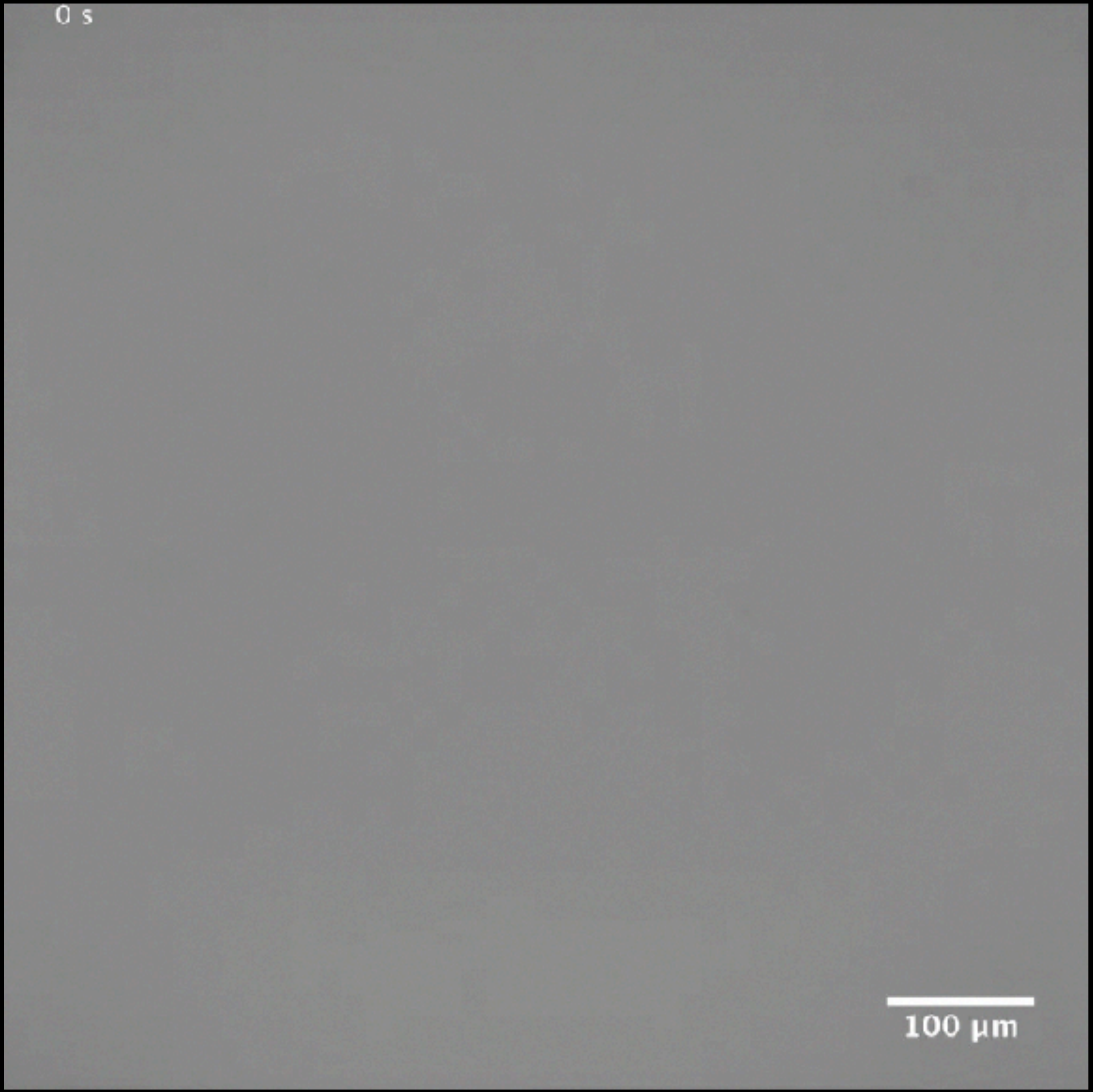


COOL to room temperature

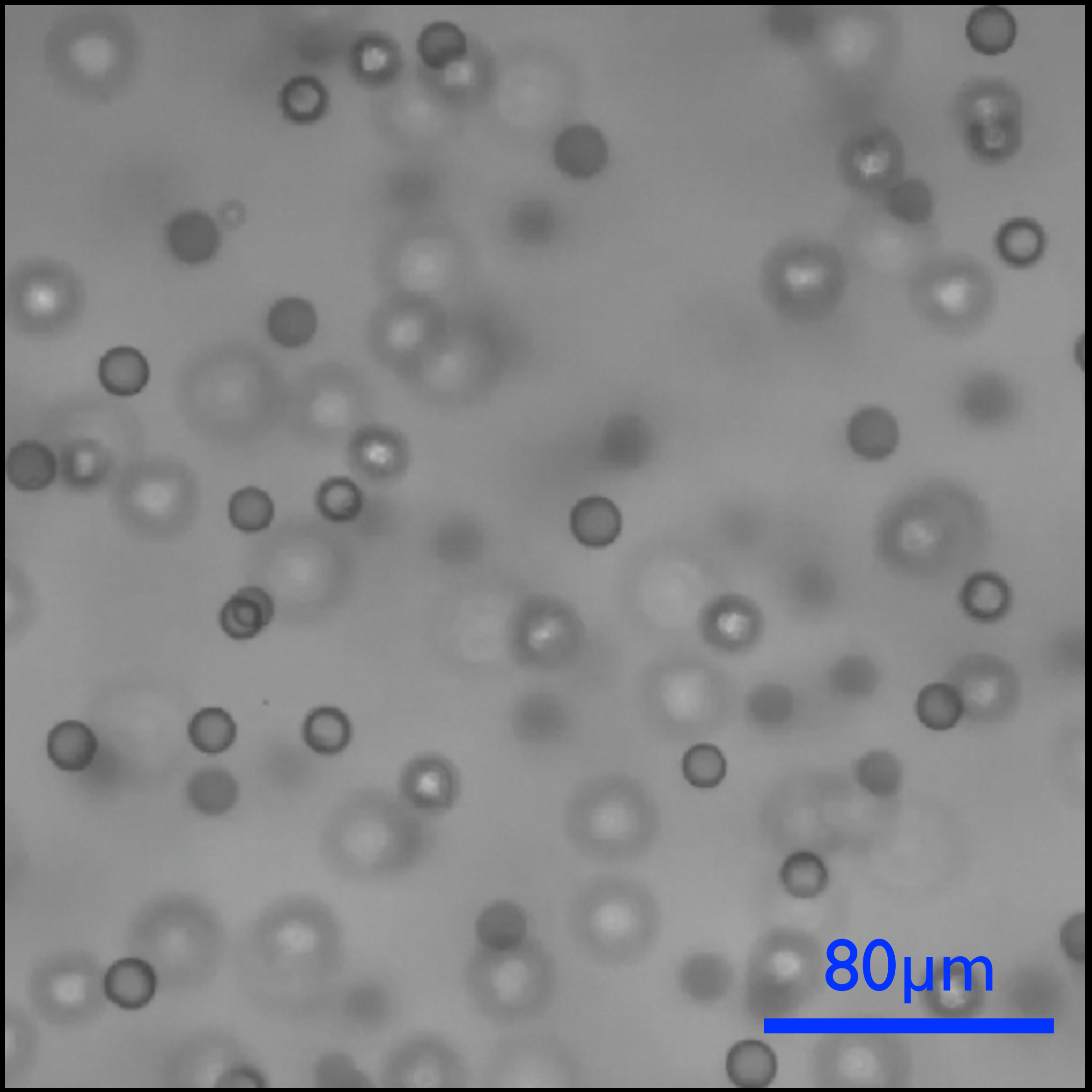
1. Heat submerged sample

2. Seal sample and
cool at a given rate

How it looks under the microscope



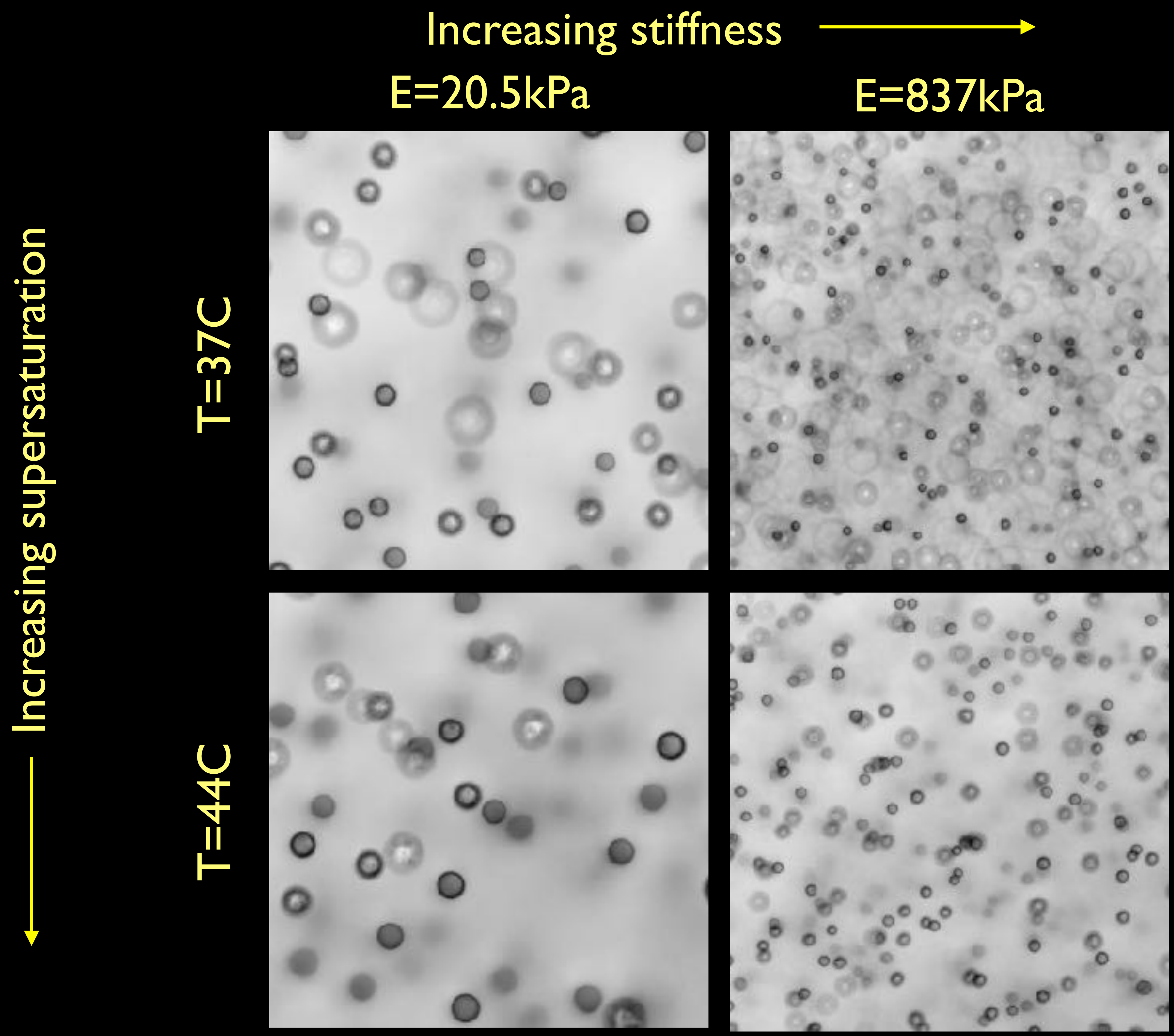
Pretty monodisperse materials!



Fluorinated oil
droplets in soft silicone

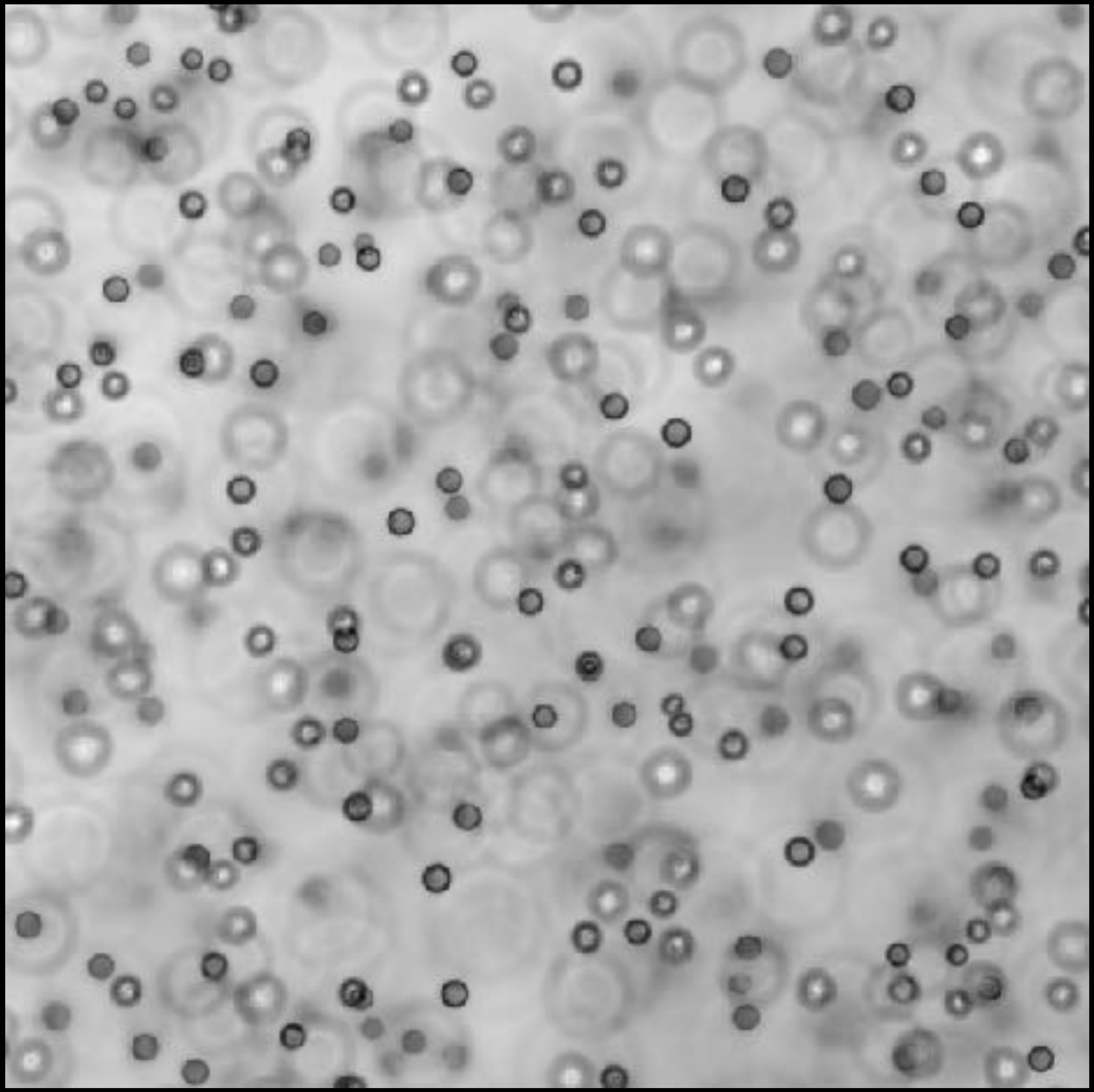
(cooled from 50C)

Supersaturation and stiffness both control hole size

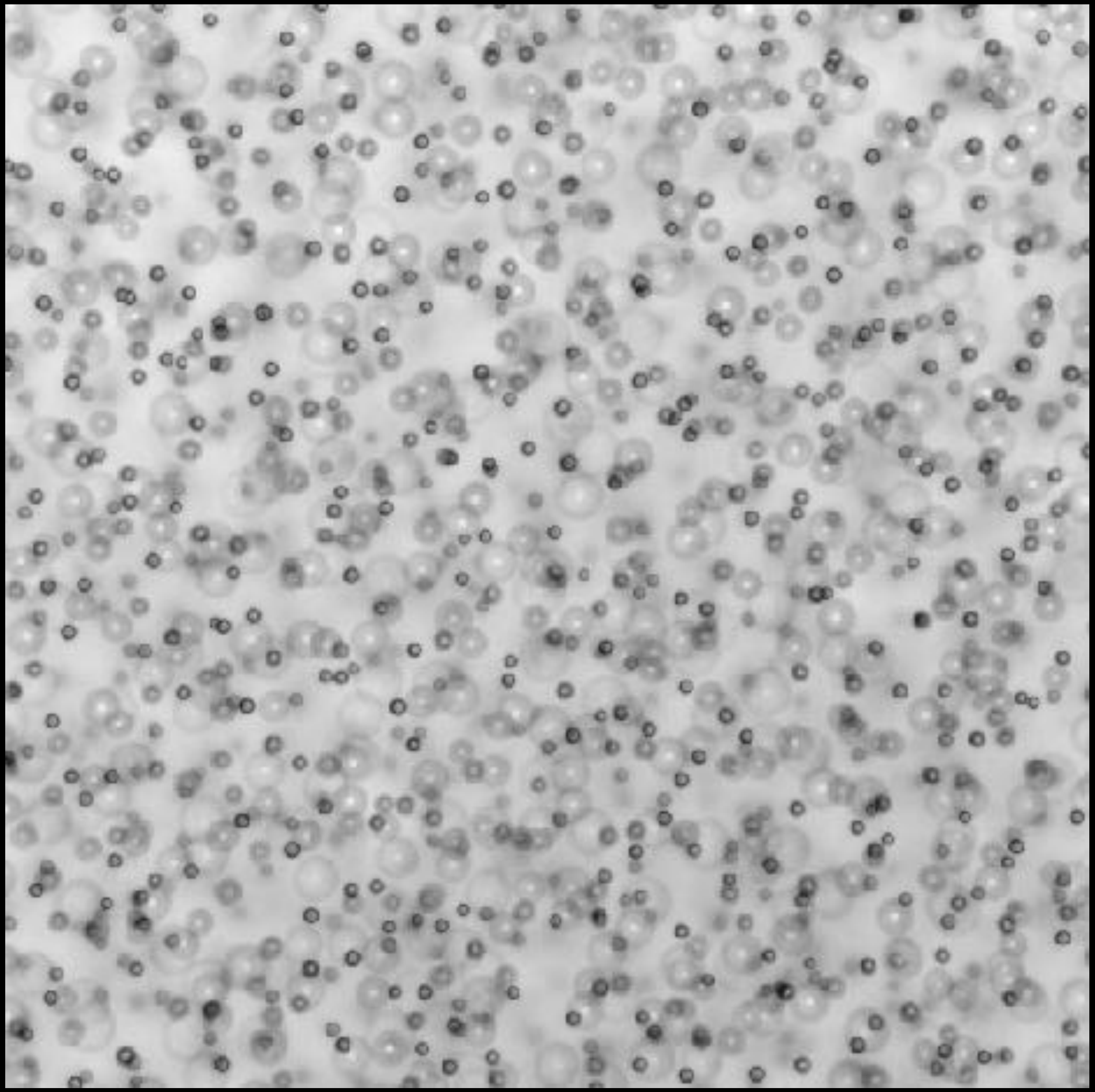


Increasing cooling rate decreases droplet size

1 degree per minute

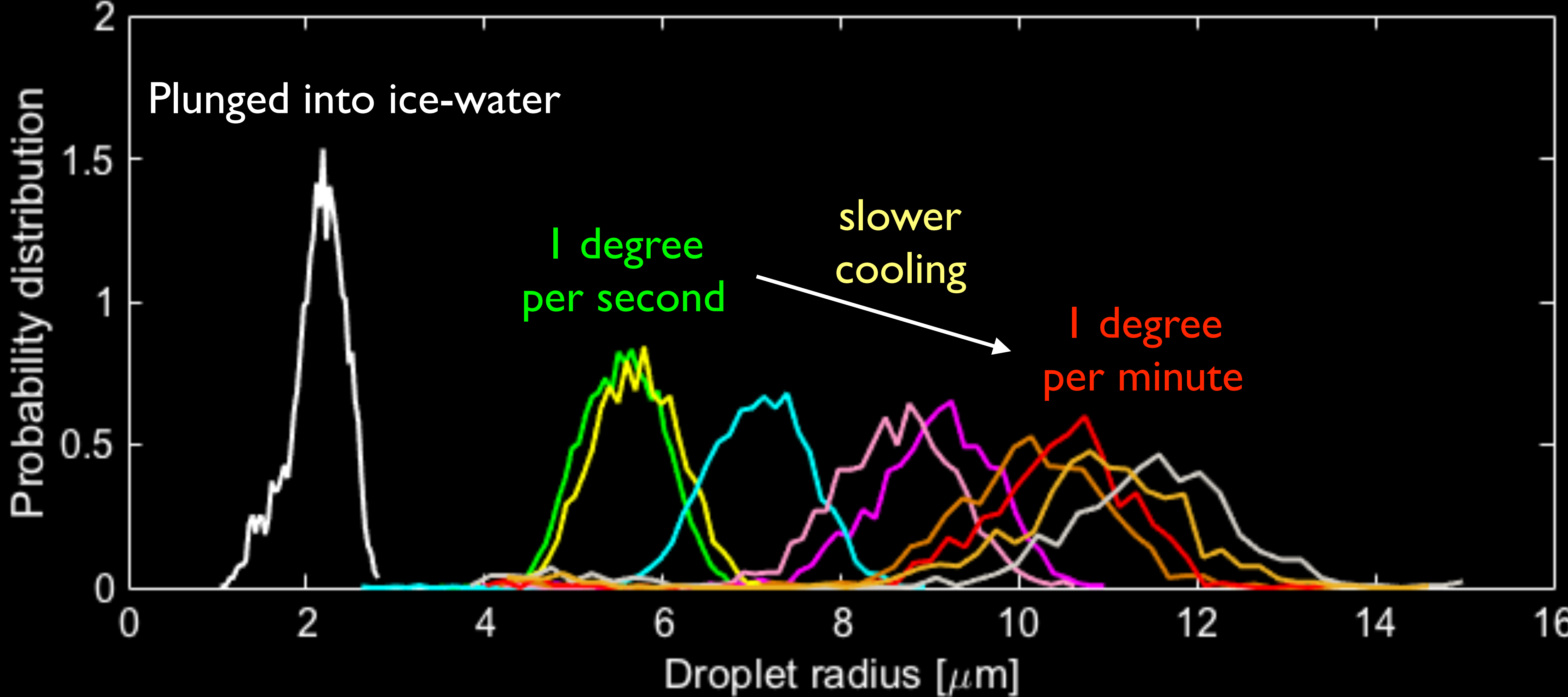


1 degree per second

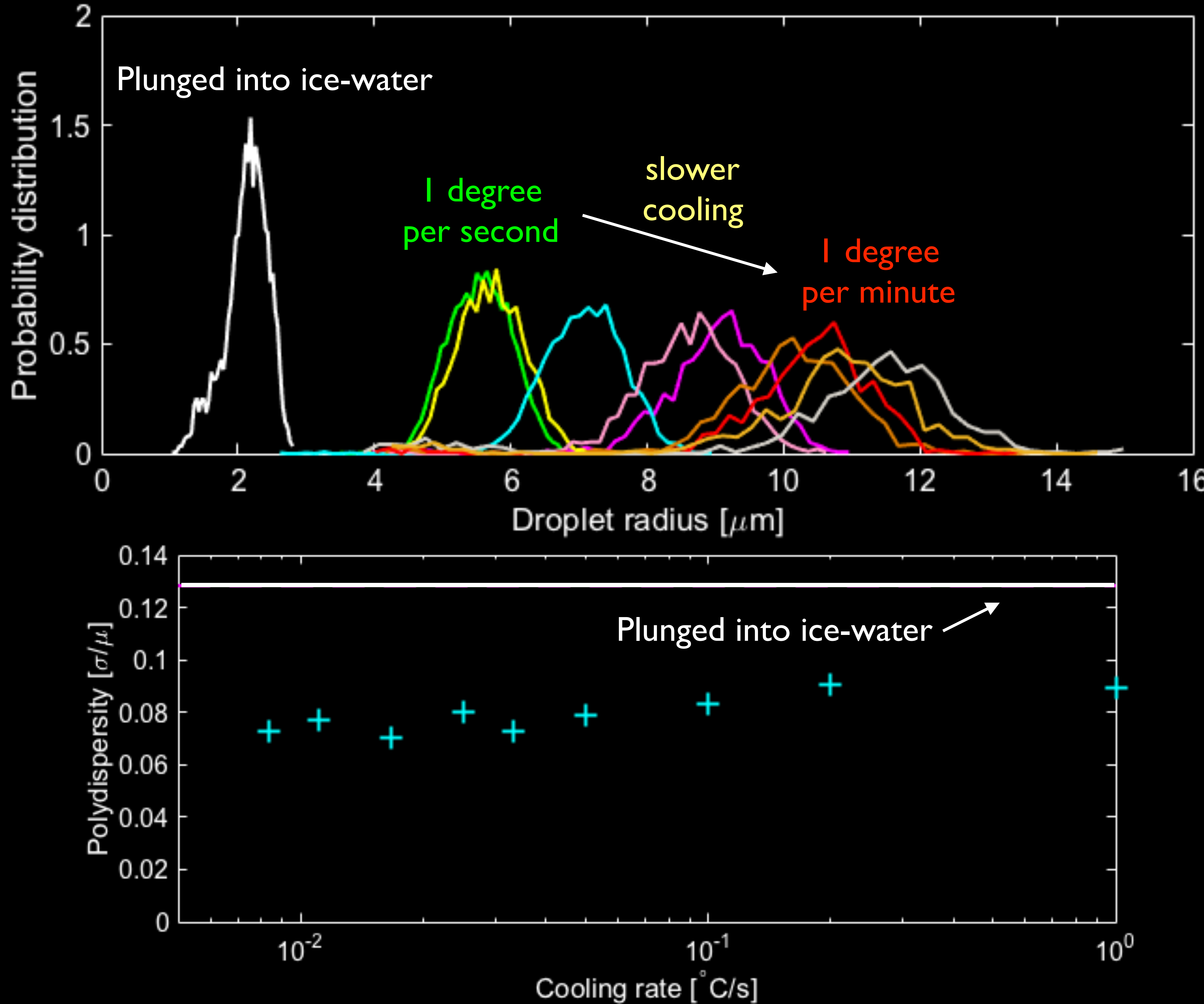


E=185kPa, T=40C

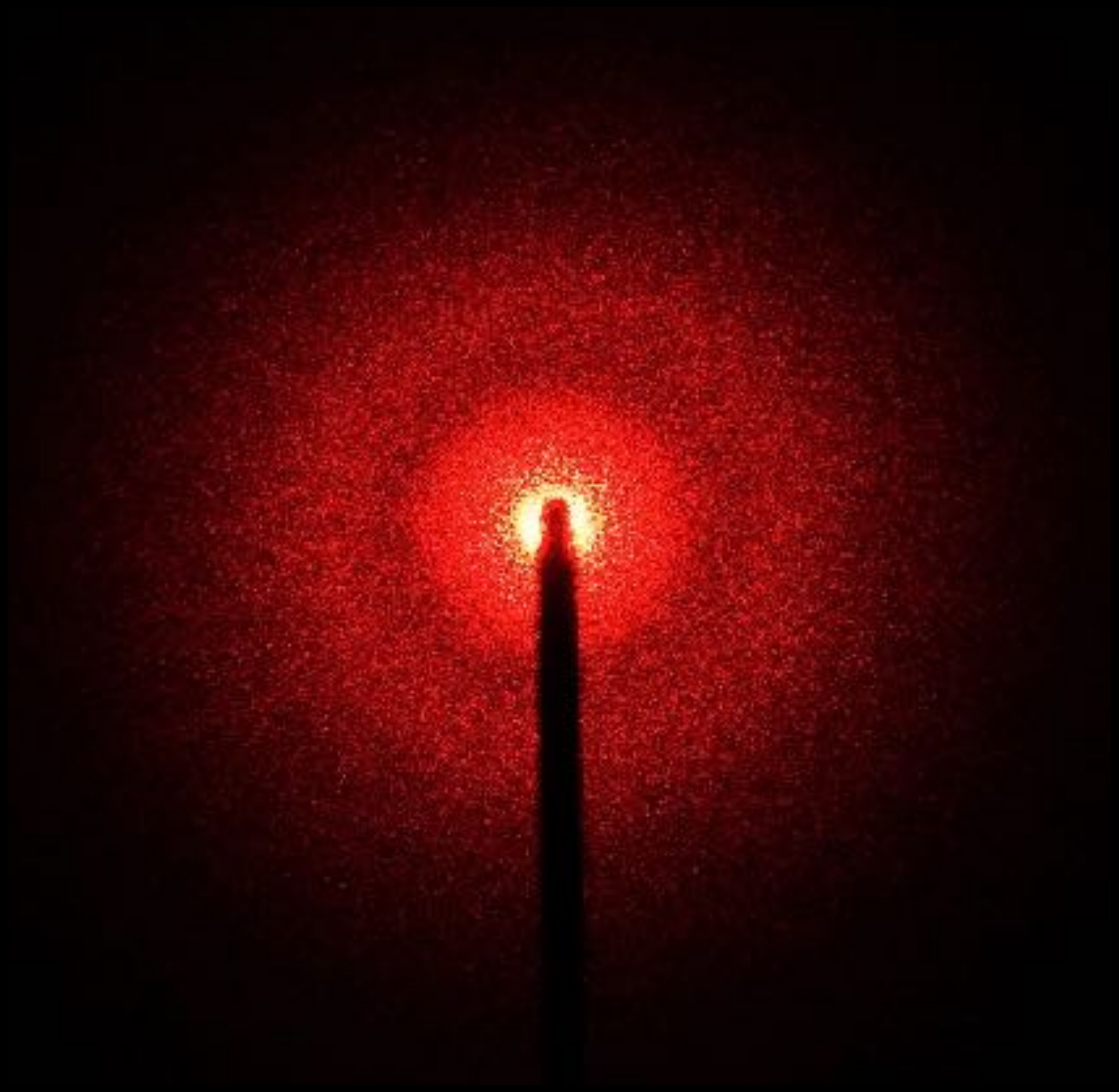
How monodisperse are the samples?



How monodisperse are the samples?

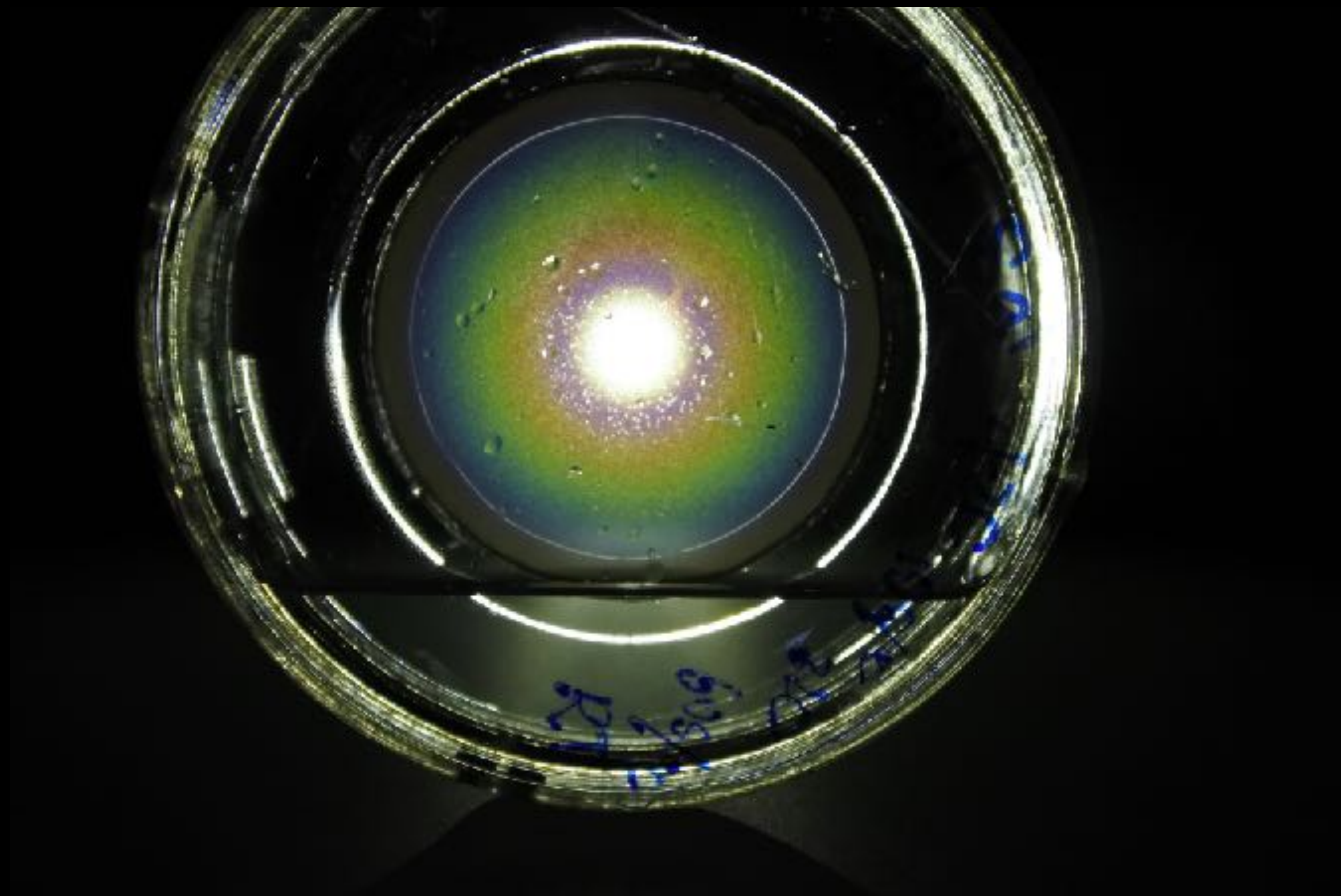


Evidence of monodispersity from light scattering



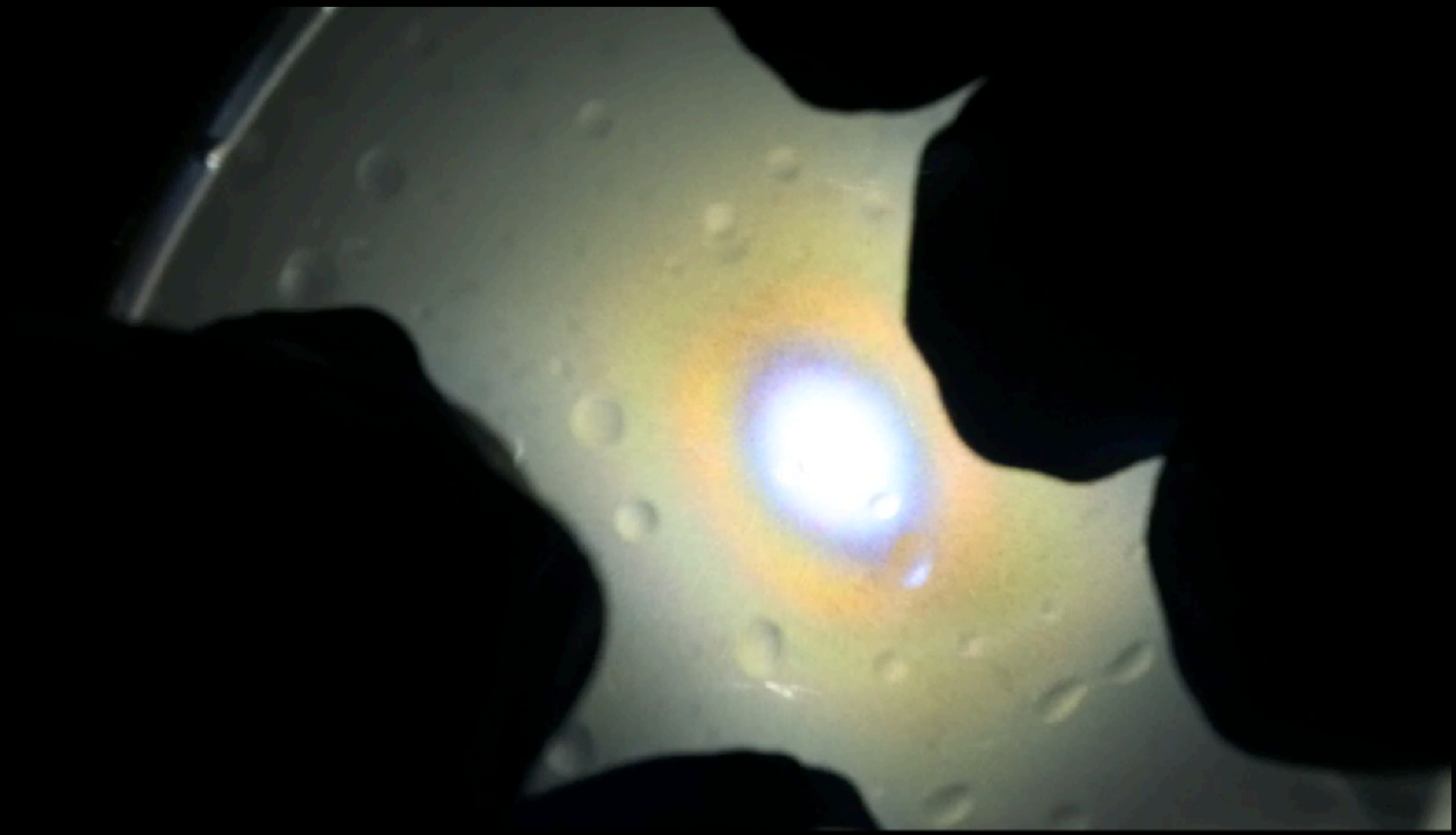
Sample containing 5-6μm radius droplets
in front of a red, HeNe laser

Monodispersity causes colour to appear



Sample containing 5-6μm radius droplets
in front of a white light LED

Colour changes upon stretching

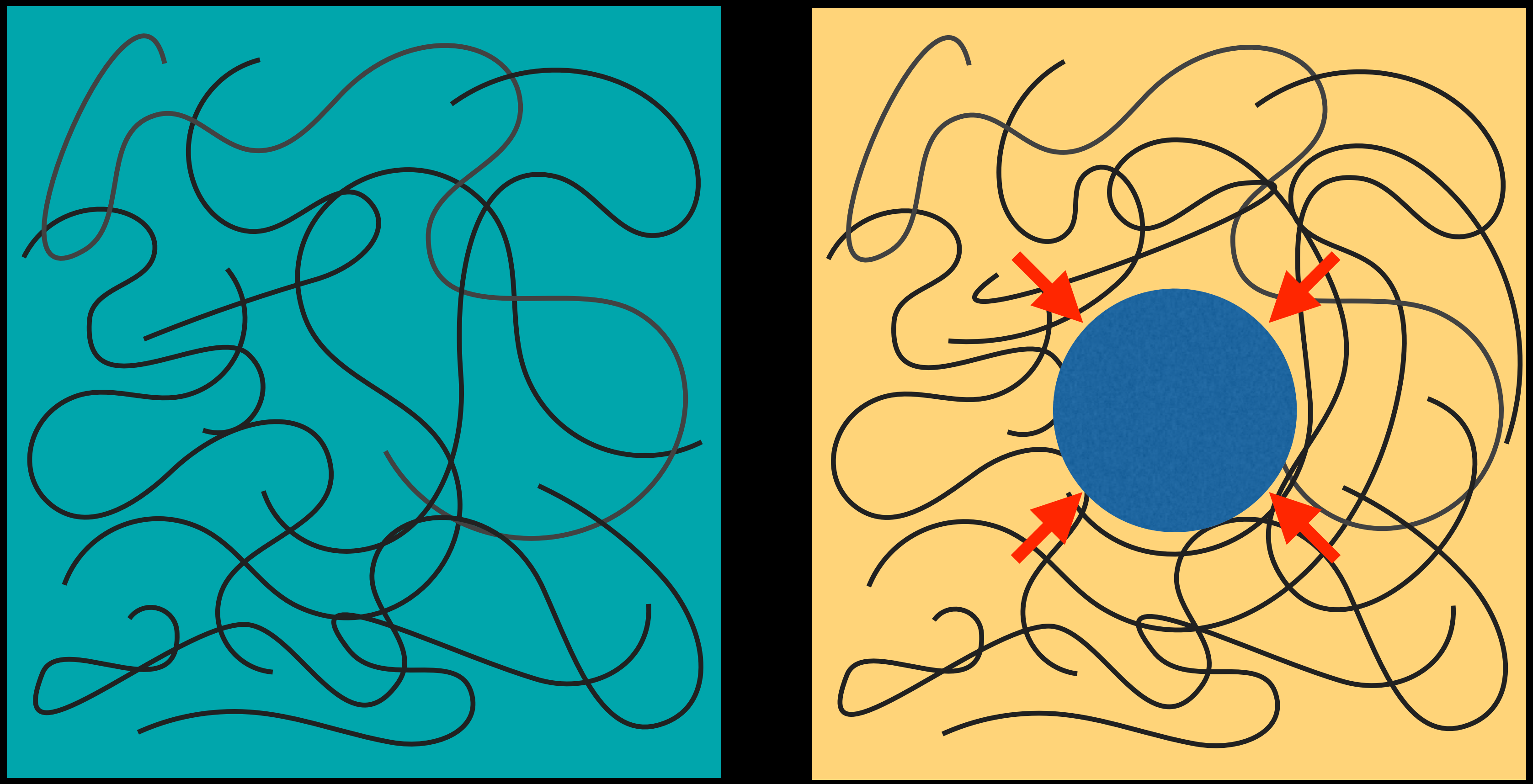


Sample in front of a white light LED

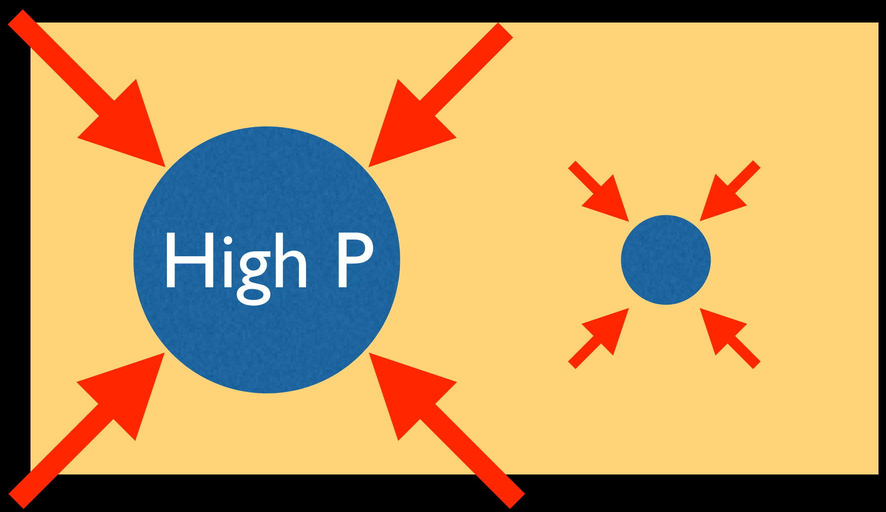
We would like to understand the mechanism so we can work towards better colour

- What role does the surrounding material play?
- Why are the droplets so uniform?
- Can we say anything about appropriate materials?

What is the role of the polymer network?

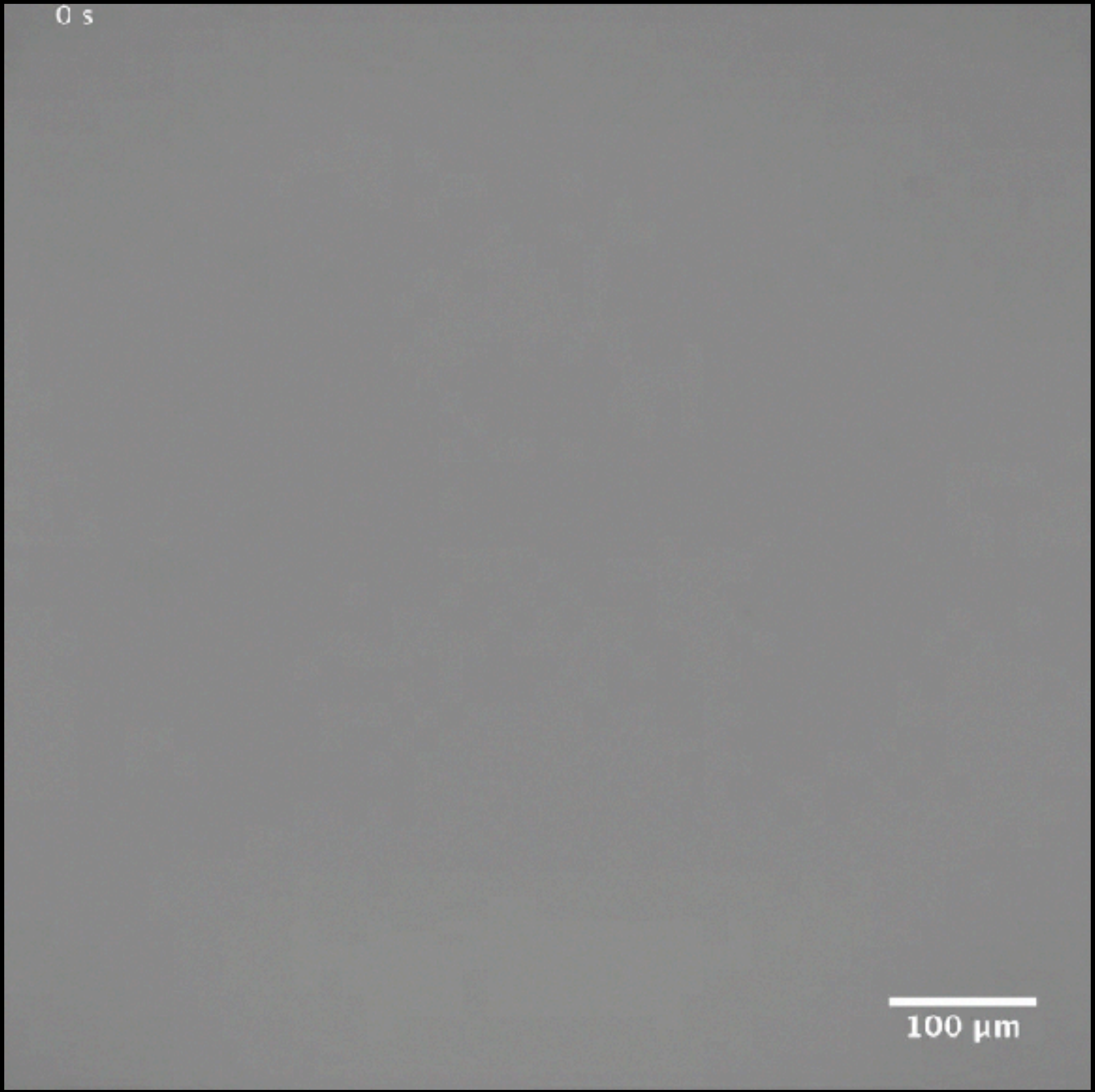


If growth was an elastic process, we might expect to see a unique droplet size and ripening of droplets towards this size



We don't see any evidence of ripening…

Strains in the network around a growing droplet are gigantic



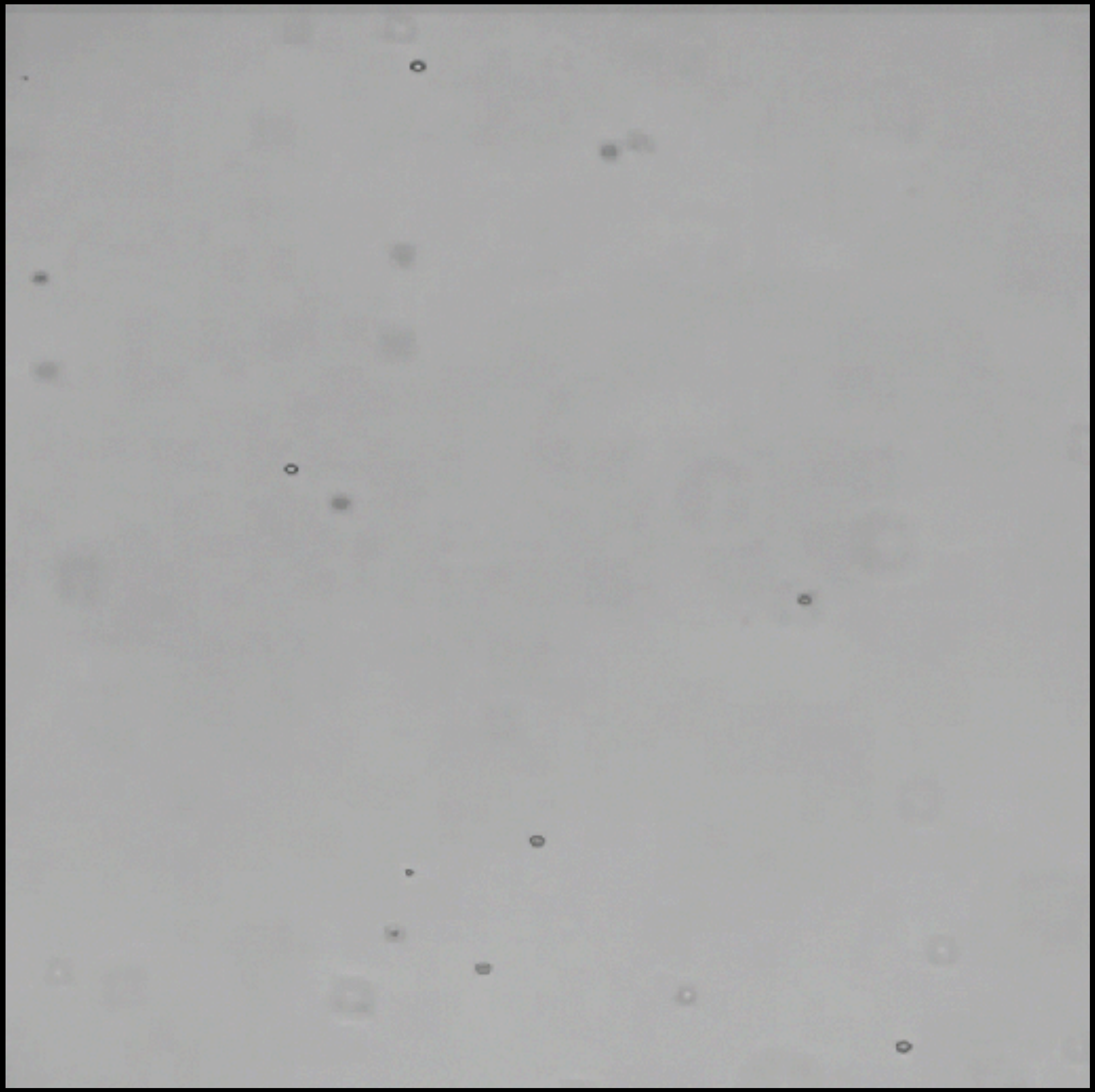
$$r_0 \lesssim 100nm$$

$$r_f \sim 10\mu m$$

$$\epsilon \gtrsim 10{,}000\,\%$$

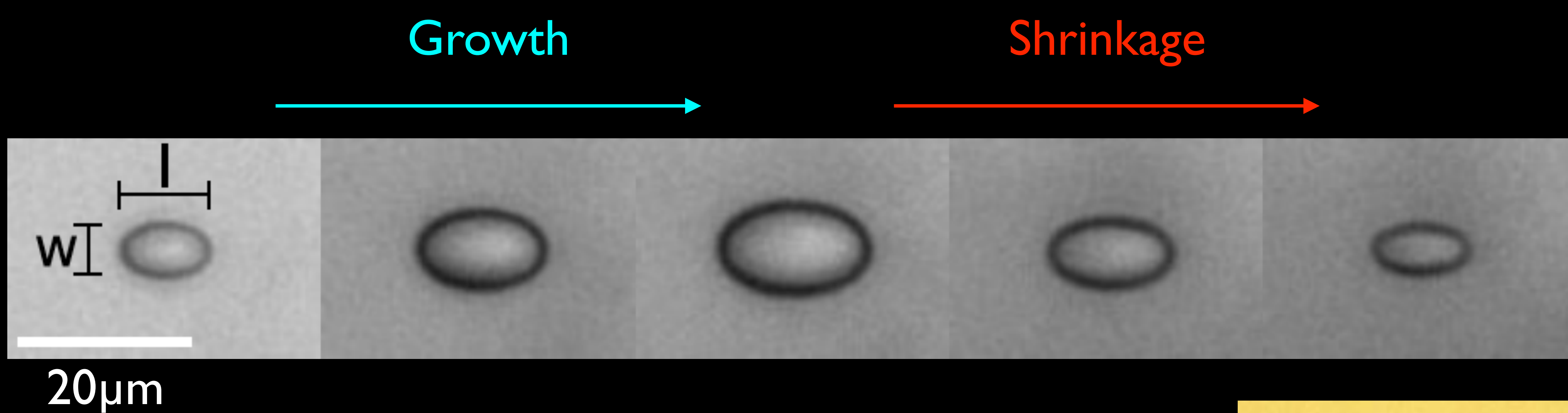
This suggests that the network is yielding around growing droplets

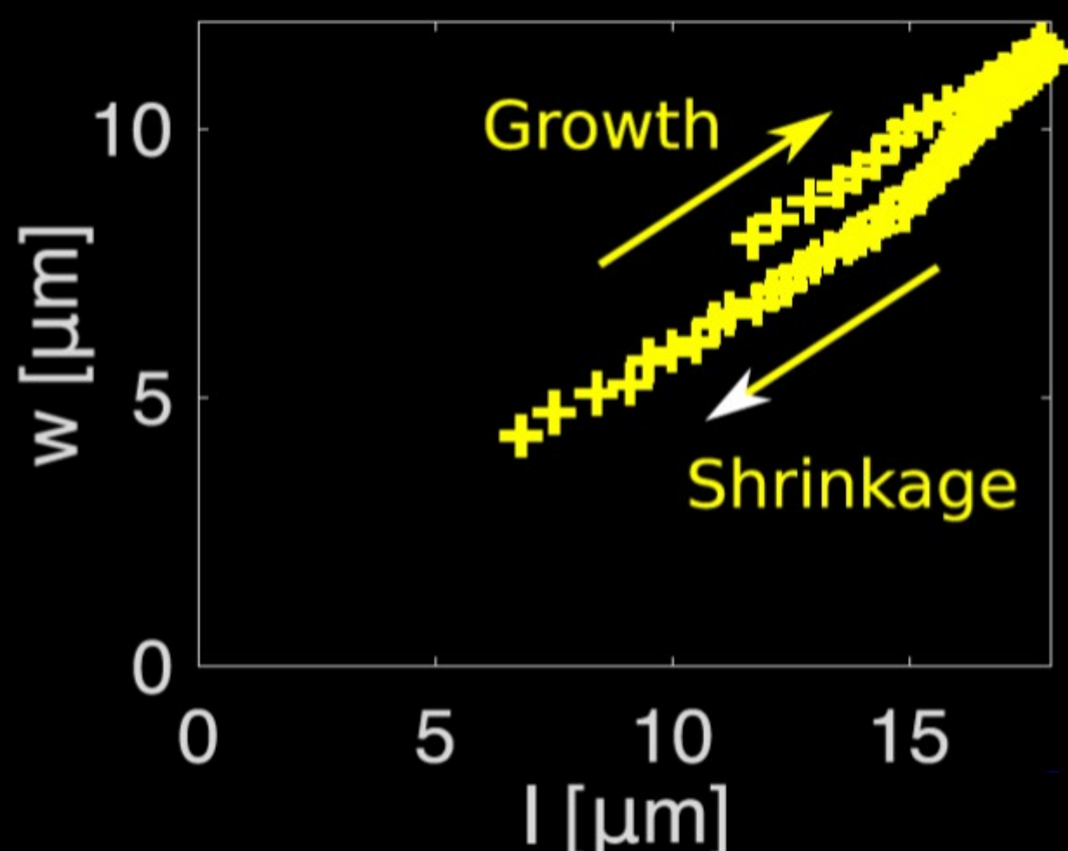
We can look for yielding by breaking symmetry



E=175kPa

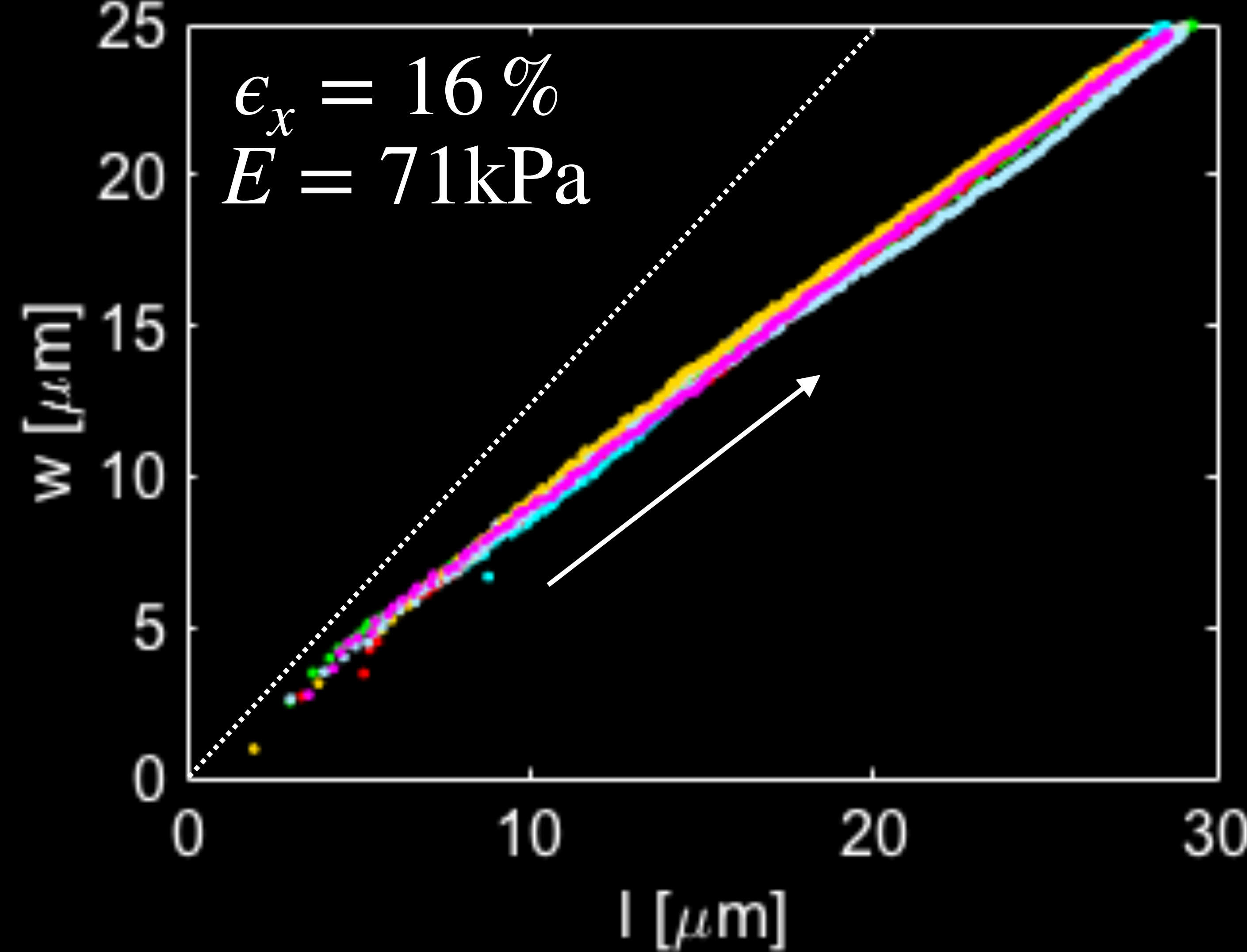
Shape hysteresis indicates bond breakage

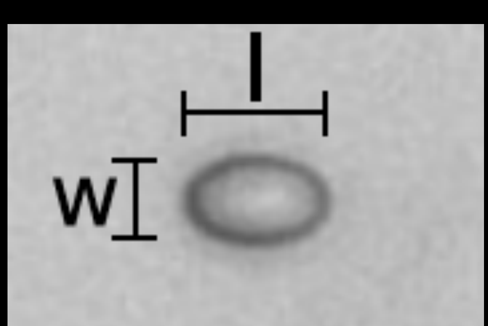


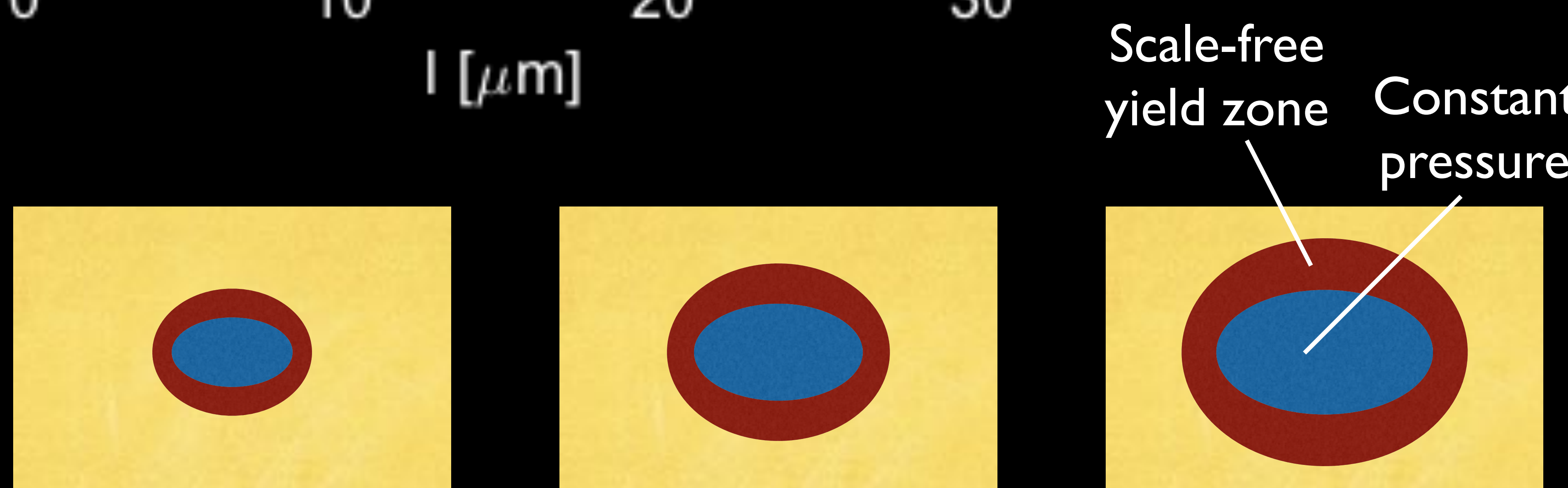


Scale free growth suggests that the pressure inside droplets is also scale free

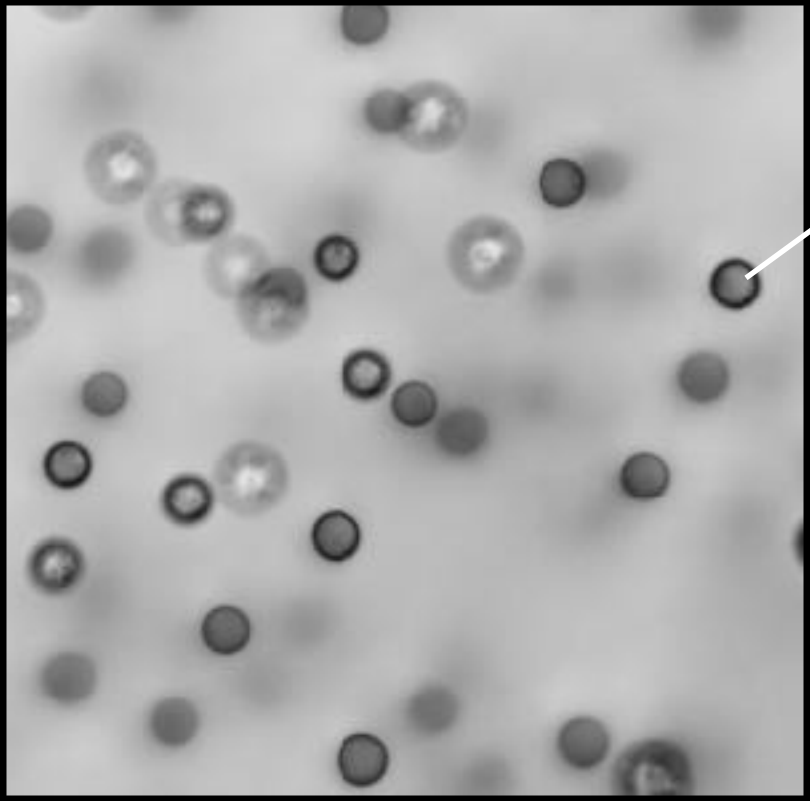
Growth of 10 different droplets under identical conditions







The role of the polymer network



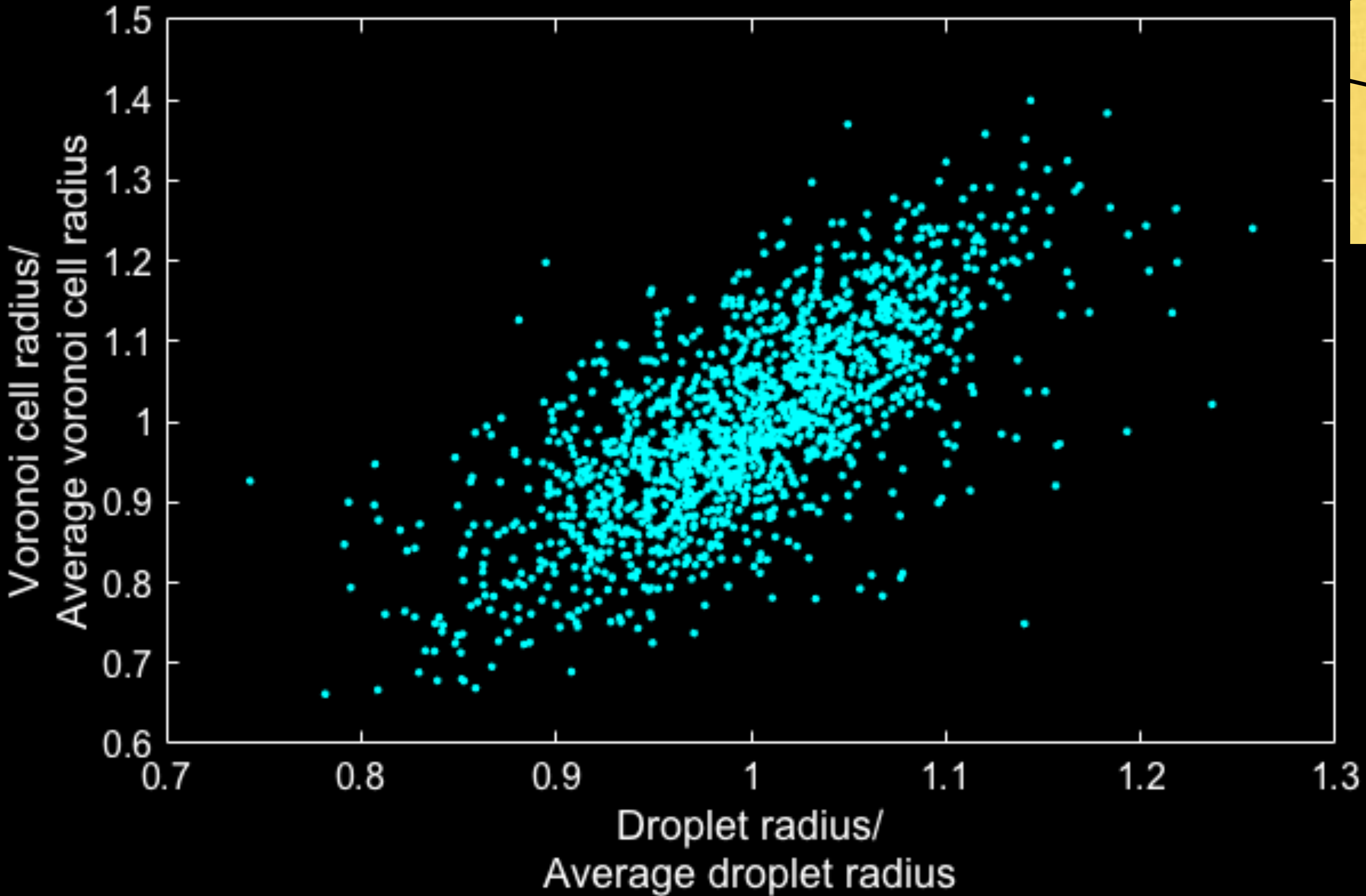
All droplets have the same pressure (no ripening)

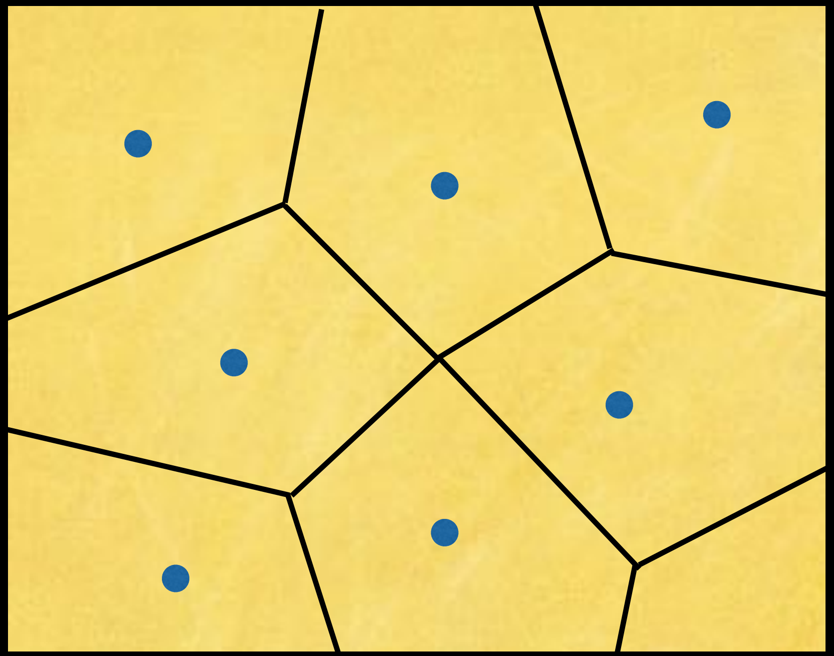
No movement (no coalescence)

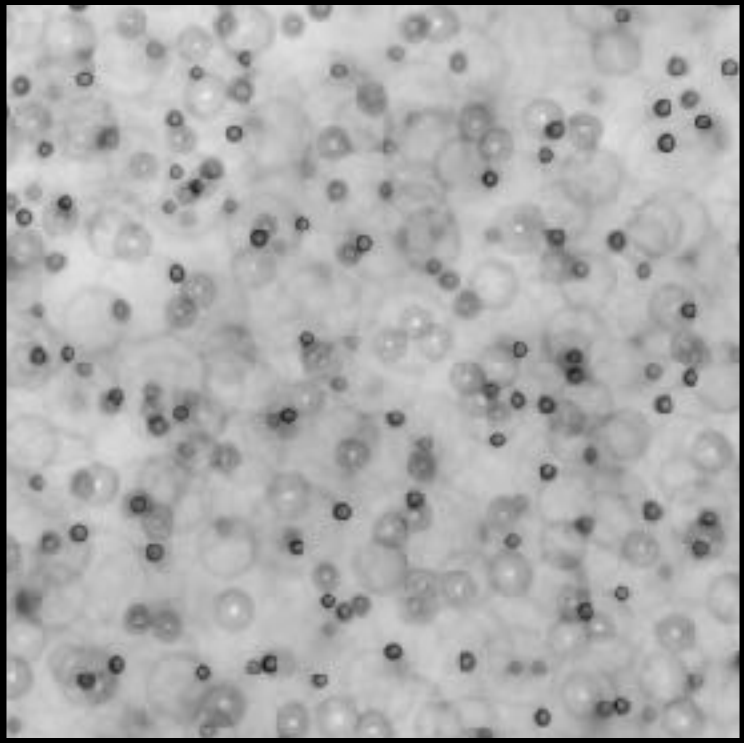
We would like to understand the mechanism so we can work towards good colour

- What role does the surrounding material play?
- <u>Why are the droplets so uniform?</u>
- Can we say anything about appropriate materials?

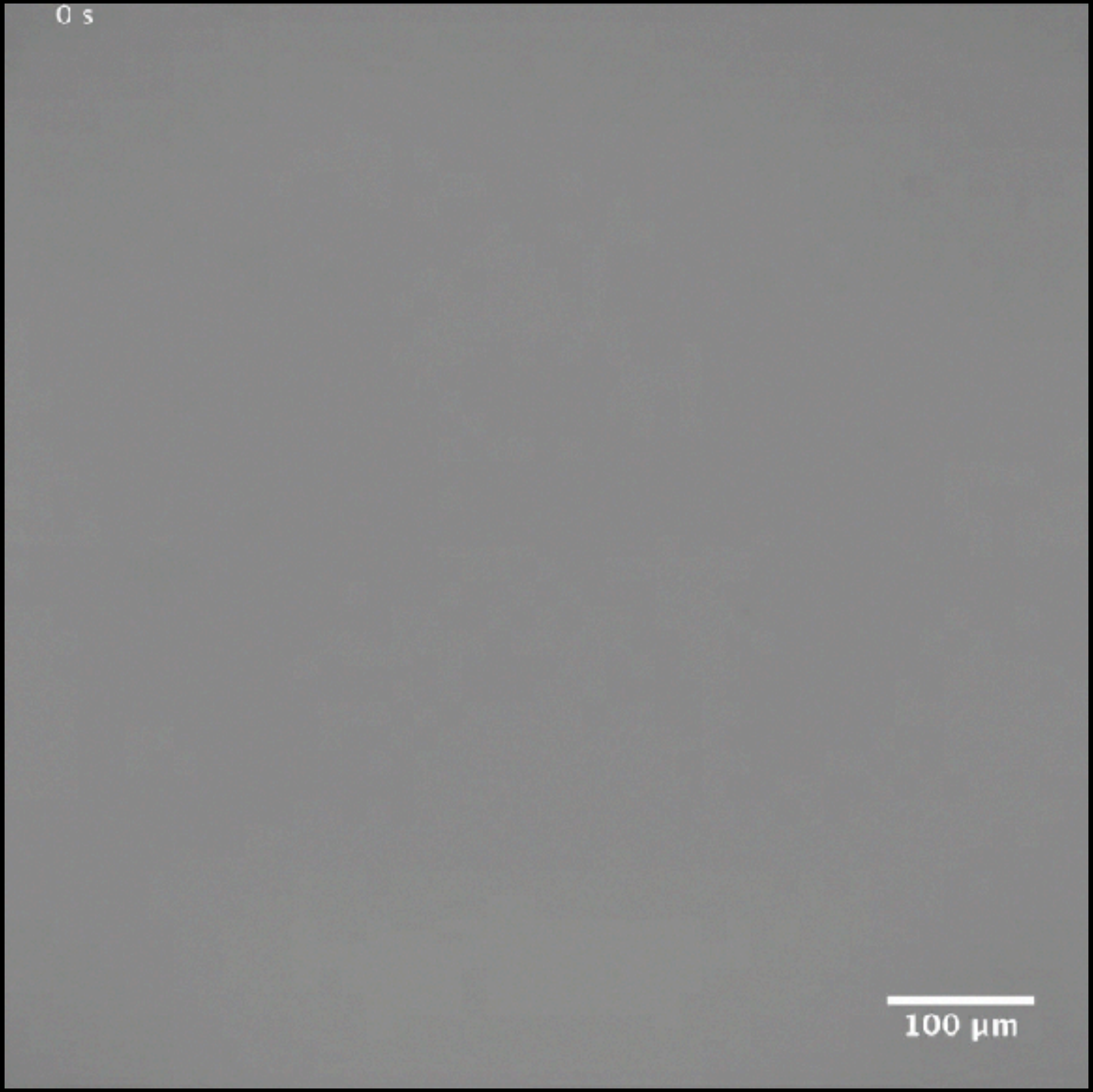
A droplet's size is correlated with its Voronoi volume



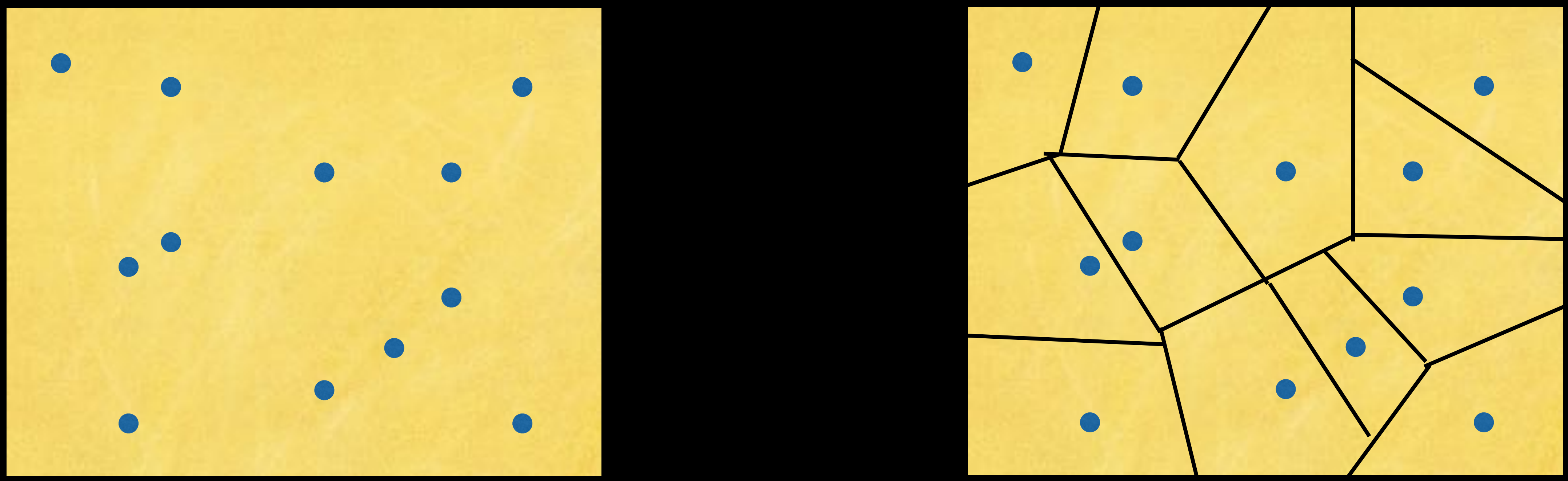




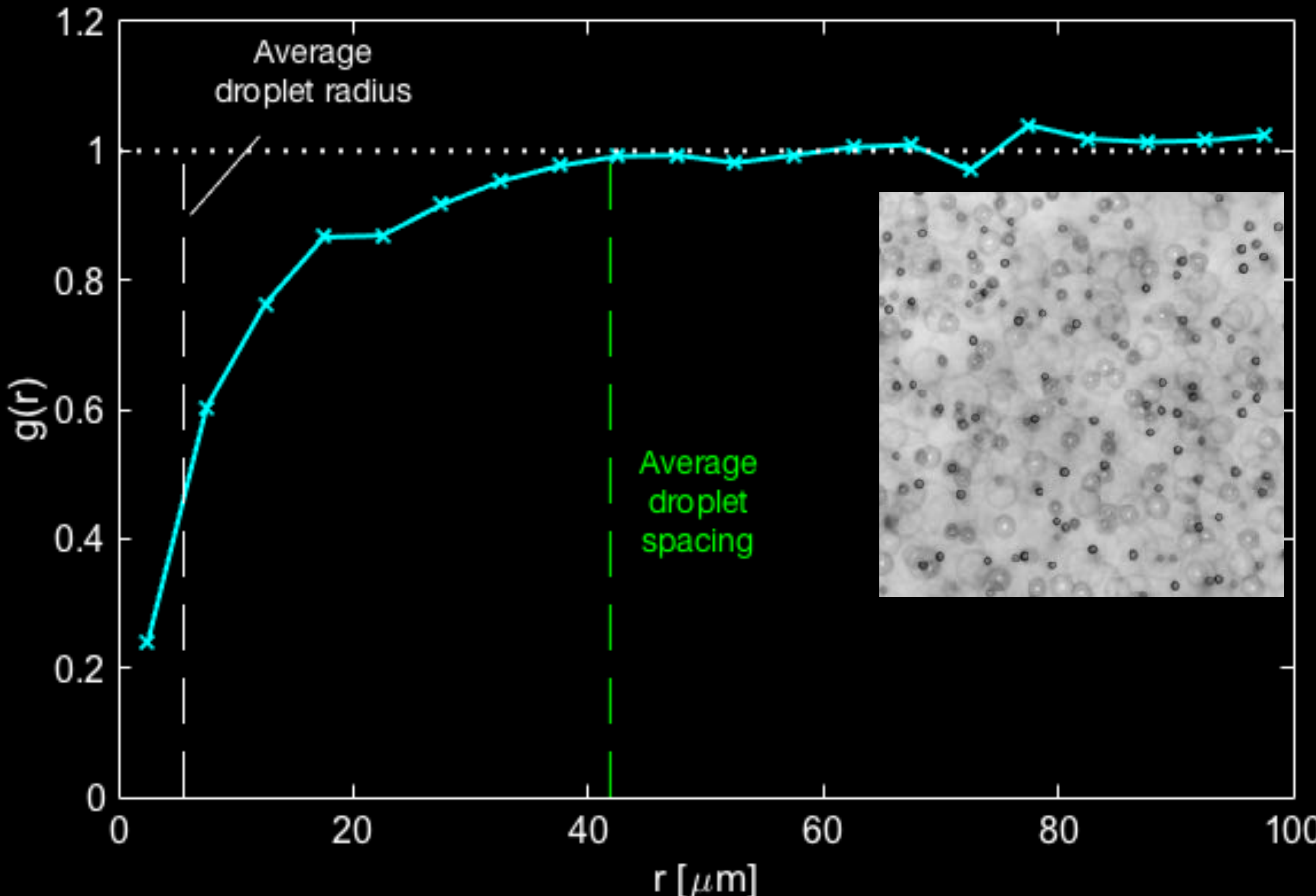
Nucleation is confined to the initial stages of growth



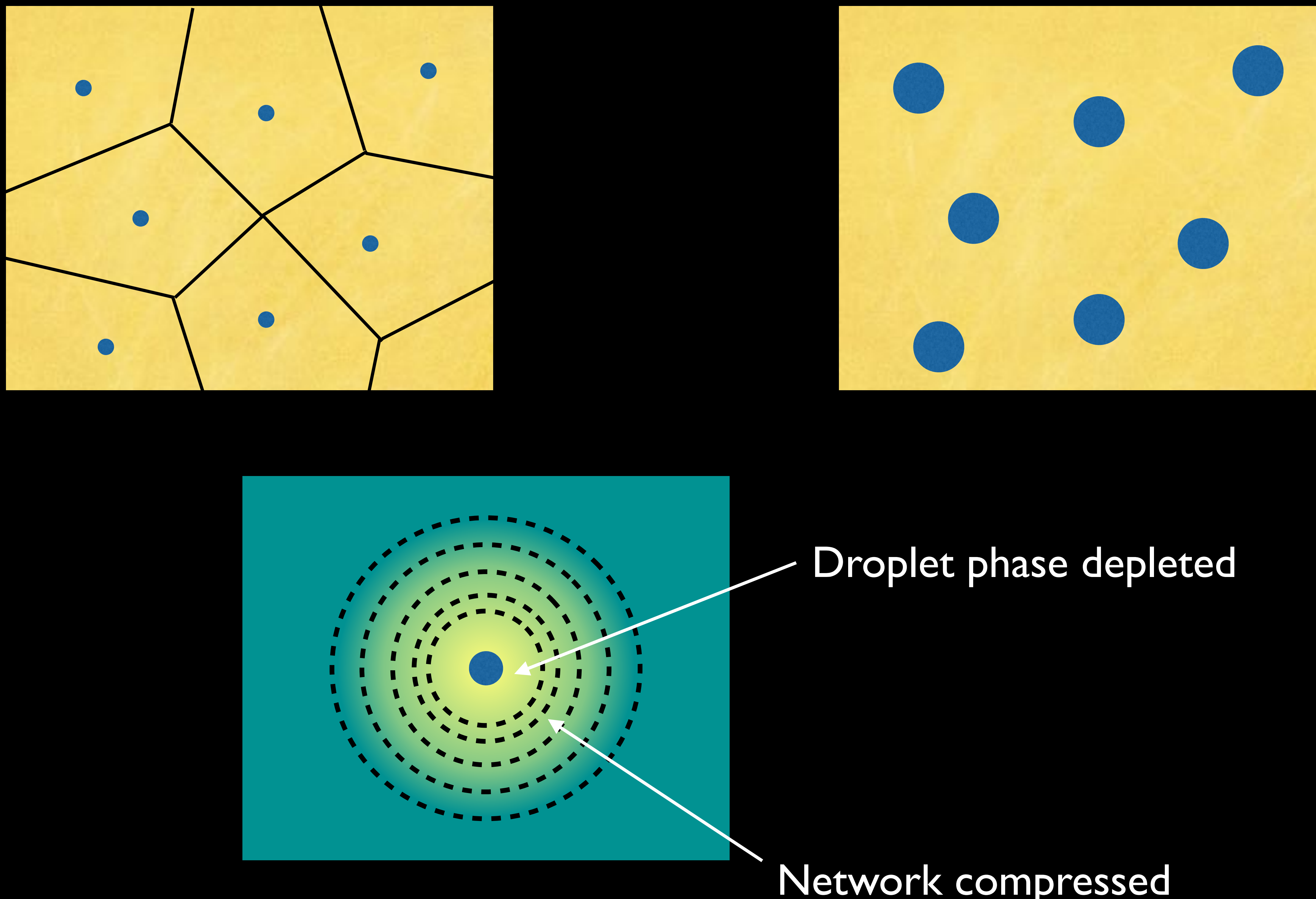
Randomly nucleating droplets doesn't quite explain the uniformity that we see



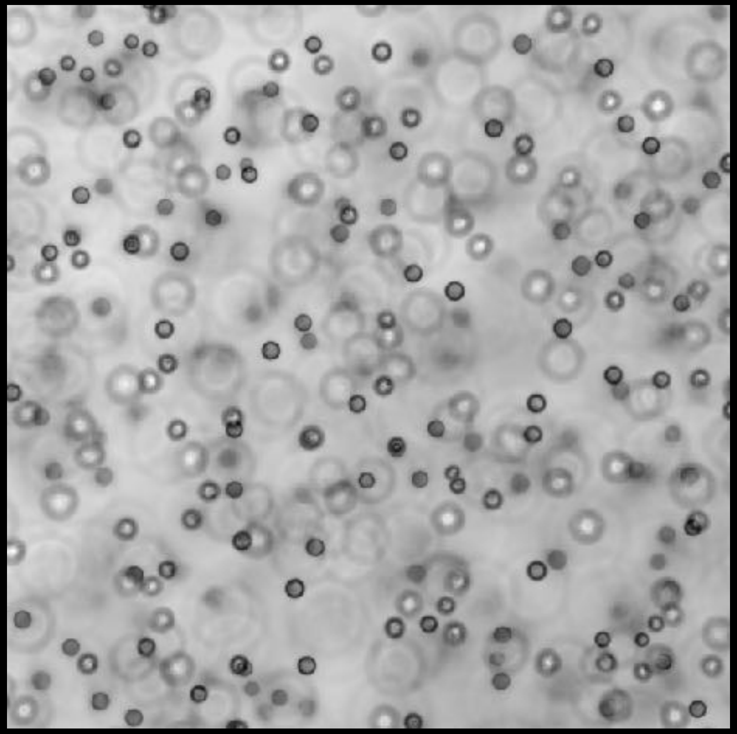
Droplets do not nucleate near each other



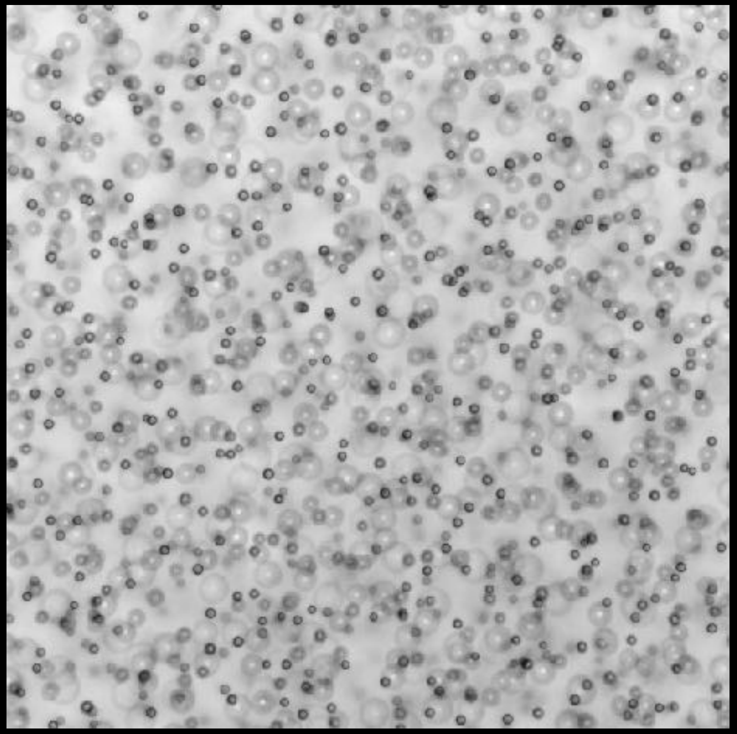
Nucleating droplets prevent other droplets from growing nearby



This mechanism explains how cooling rate could affect droplet size



Slow cooling > fewer nuclei

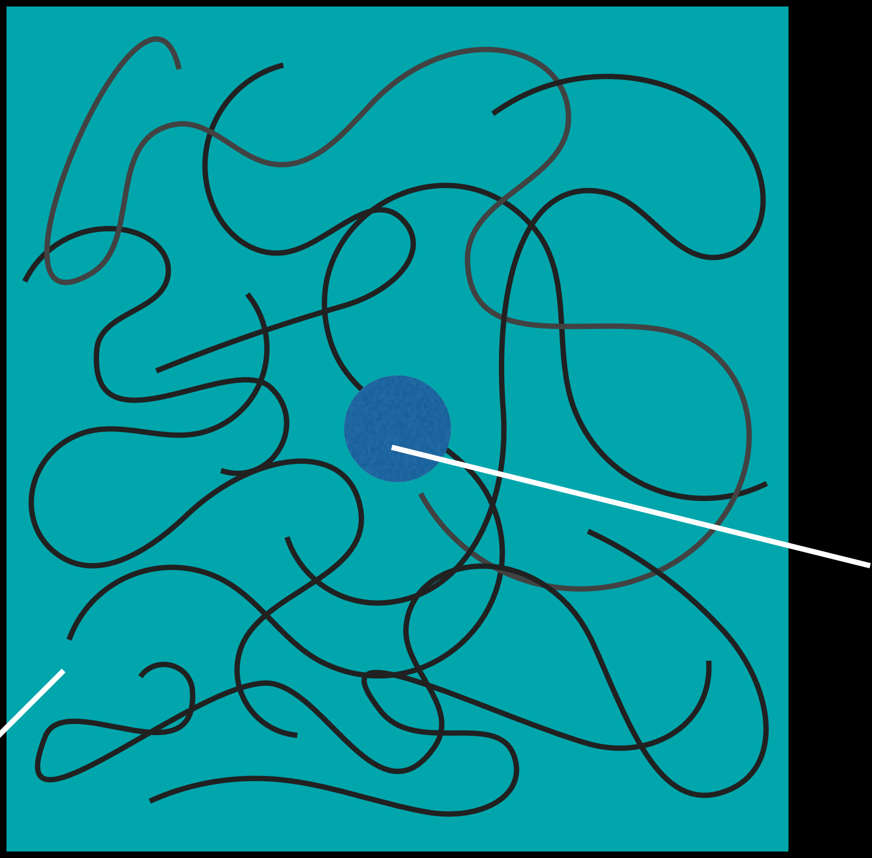


Rapid cooling > lots of nuclei

We would like to understand the mechanism so we can work towards good colour

- What role does the surrounding material play?
- Why are the droplets so uniform?
- Can we say anything about appropriate materials?

Can we say anything about what materials we might expect this to work with?

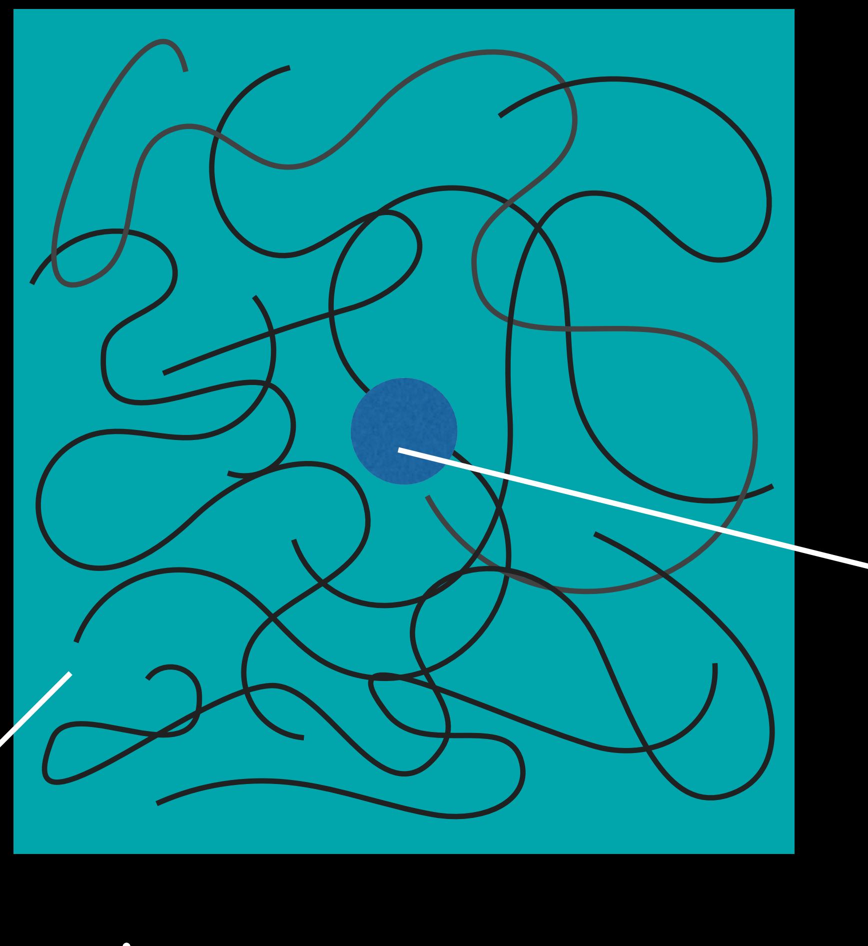


$$\mu = PM/\rho_l \quad \text{(P x molar volume)}$$

$$C > C_{sat}$$

$$\mu = RT \ln(c/c_{sat})$$

Can we say anything about what materials we might expect this to work with?



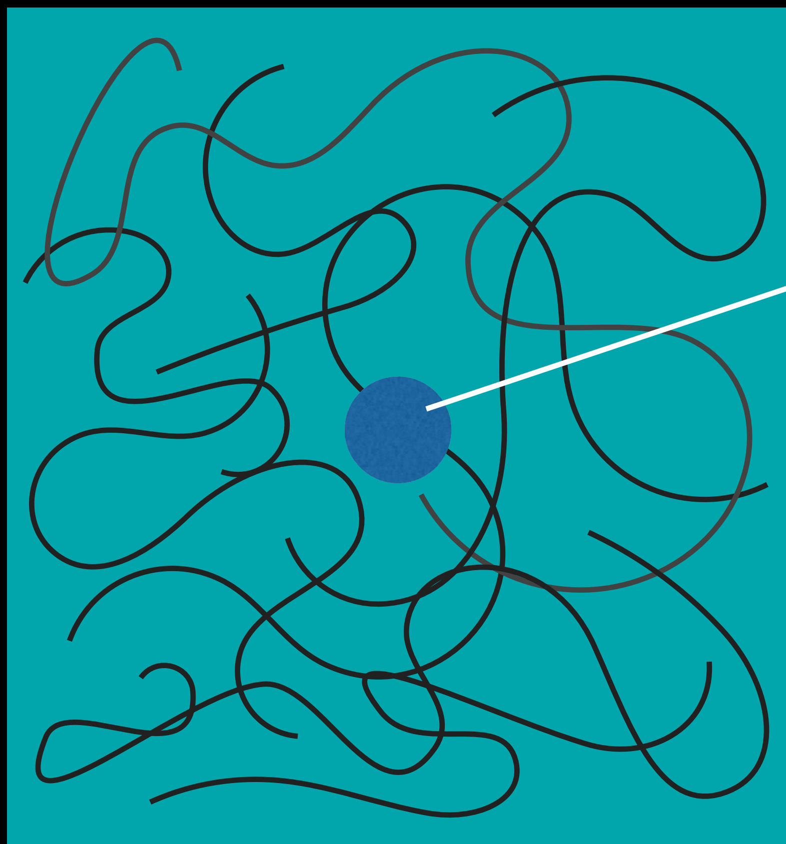
$C > C_{sat}$

$\mu = PM/\rho_l$ (P x molar volume)

$\mu = RT\ln(c/c_{sat})$

$$\boxed{P = \frac{\rho_l RT}{M}\ln\left(\frac{c}{c_{sat}}\right)}$$

Can we say anything about what materials we might expect this to work with?

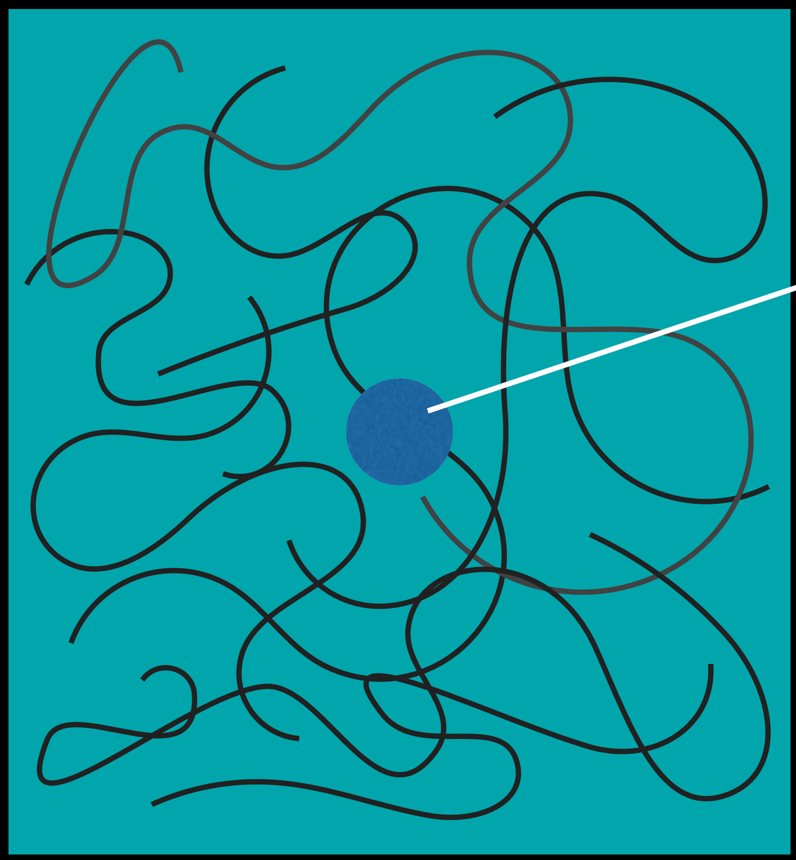


$$P = \frac{\rho_l RT}{M} \ln\left(\frac{c}{c_{sat}}\right)$$

From cavitation theory, in order for a macroscopic hole to appear, $P \gtrsim E$

$$\frac{\rho_l RT}{M} \ln\left(\frac{c}{c_{sat}}\right) \gtrsim E$$

Can we say anything about what materials we might expect this to work with?



$$P = \frac{\rho_l RT}{M} \ln\left(\frac{c}{c_{sat}}\right)$$

From cavitation theory, in order for a macroscopic hole to appear, $P \gtrsim E$

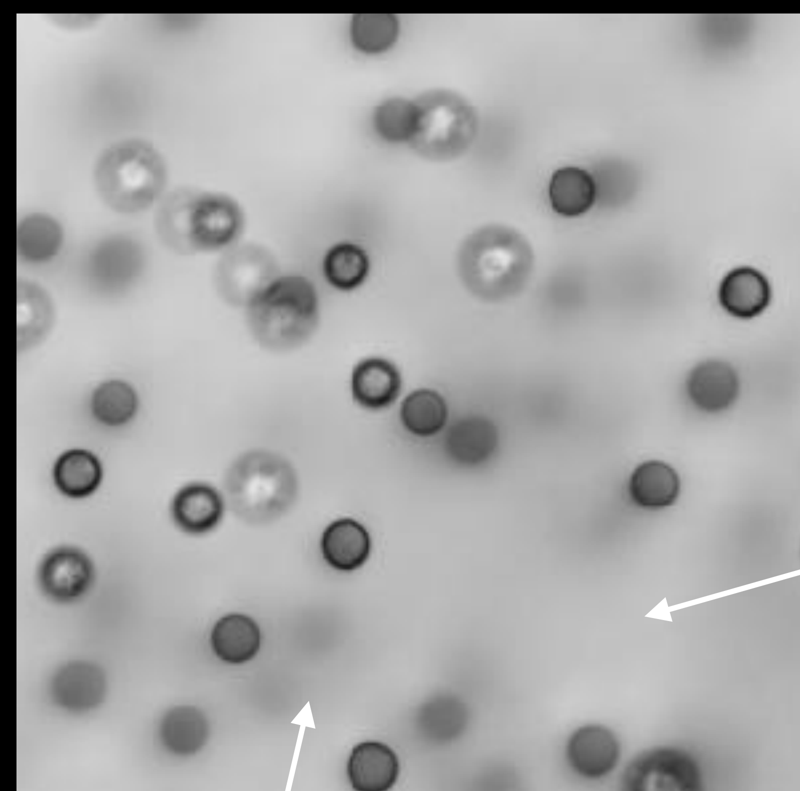
$$\frac{\rho_l RT}{M} \cancel{\ln\left(\frac{c}{c_{sat}}\right)} \gtrsim E$$

Can we say anything about what materials we might expect this to work with?

$$E \lesssim \frac{\rho_l RT}{M}$$

Phase separating liquid	M	E_{crit}	Suitable materials
Small molecule	100 g/mol	24MPa	Elastomers, Gels
Protein	10^5 g/mol	24kPa	Cell cytoskeleton

This should work for general systems where phase separation happens in soft materials



Fluorinated oil

Silicone gel

Phase separation with the ouzo effect

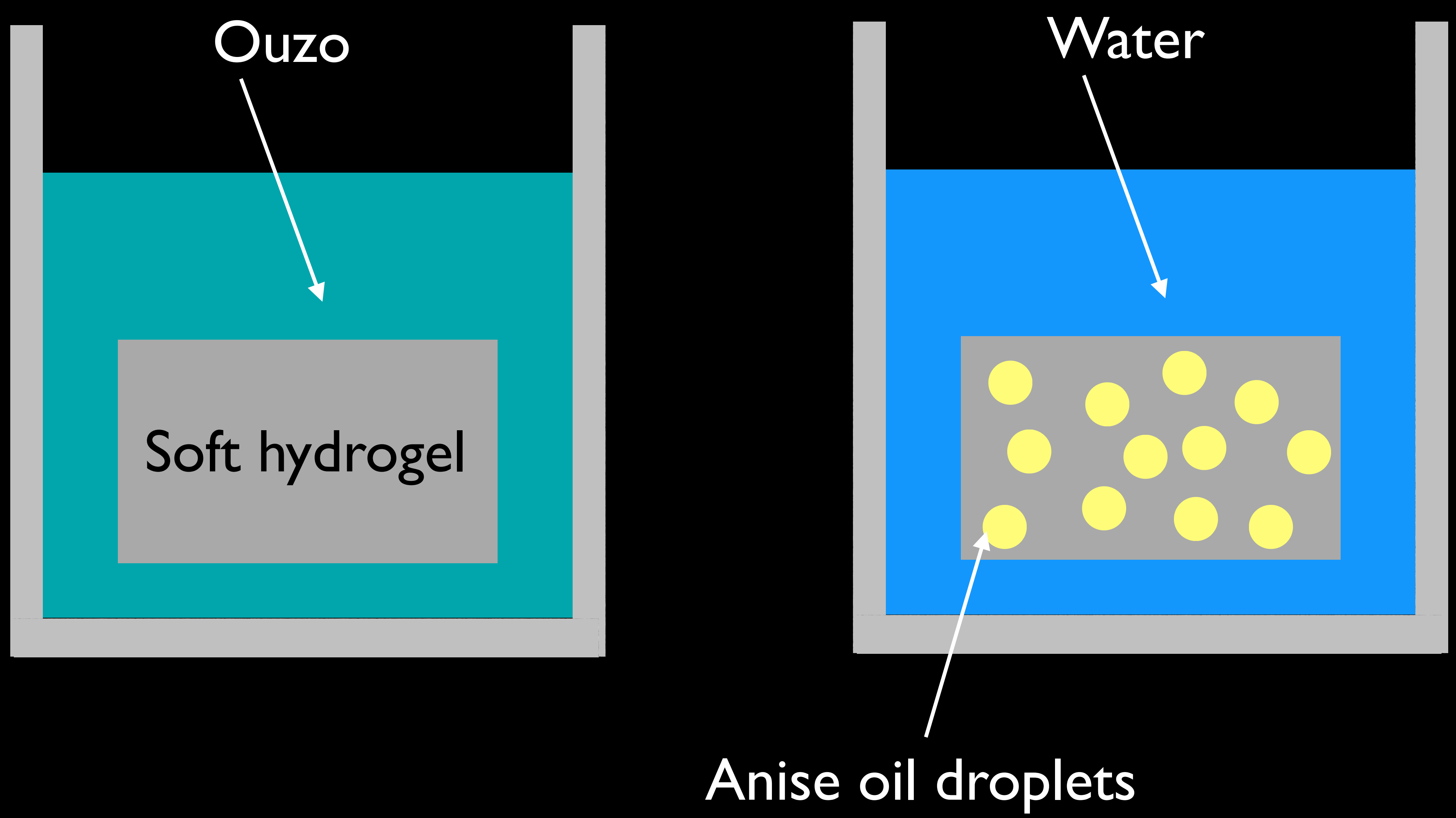
wikipedia

wikipedia

Ouzo contains anise oil, which is soluble in ethanol, but not water

Droplets form when you add water/ice

Ouzo phase separation in hydrogels

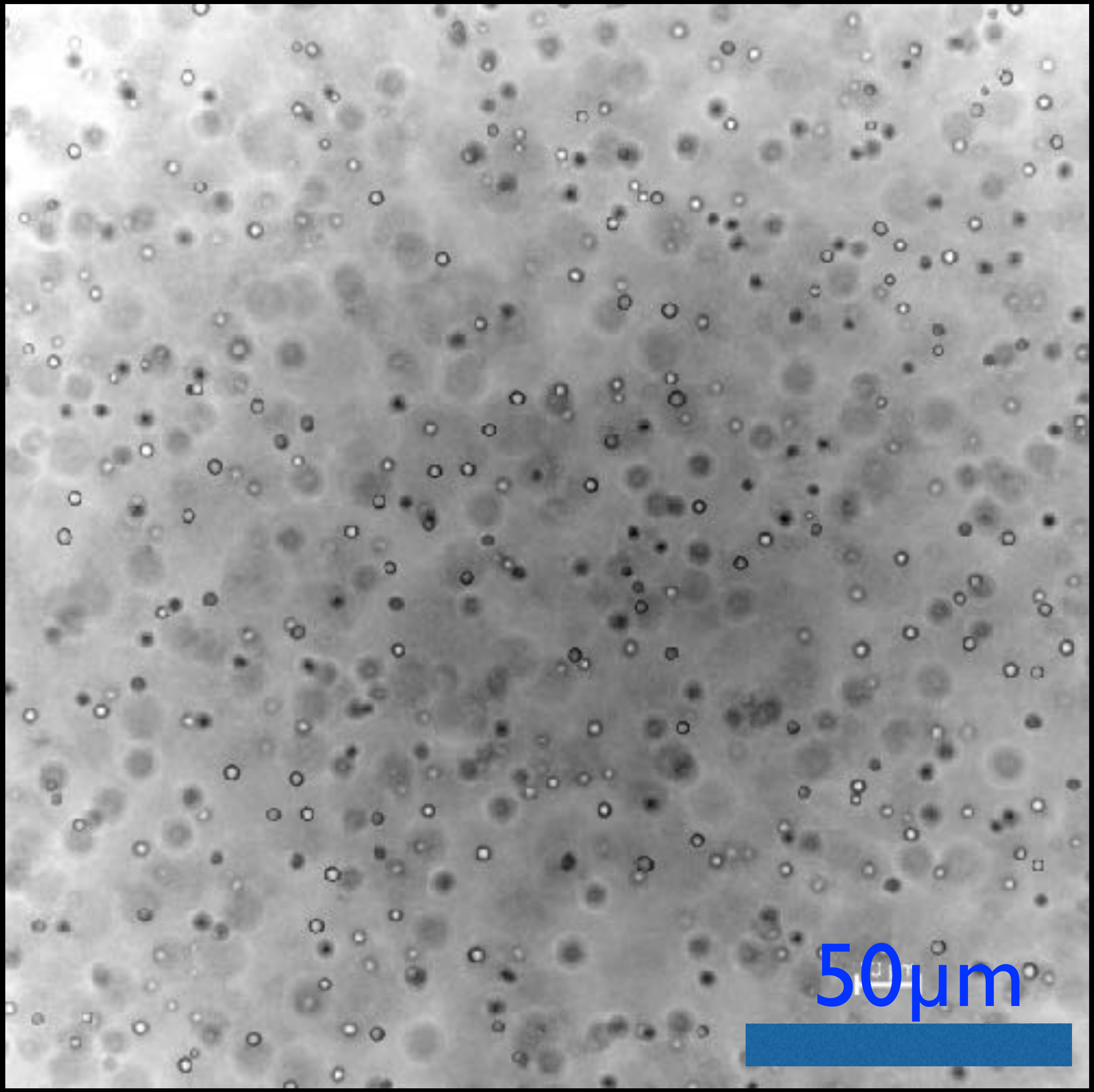


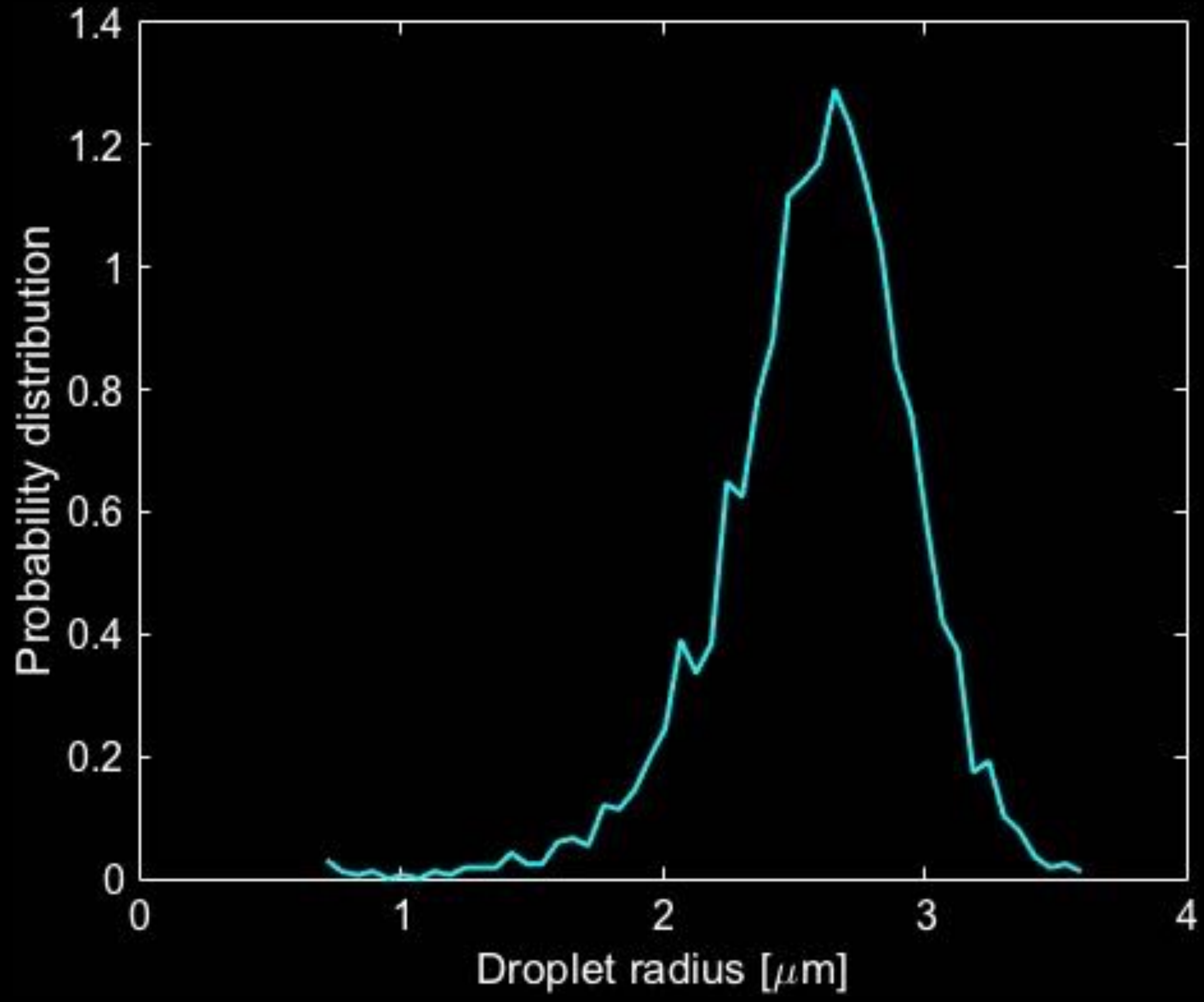
1. Soak hydrogel in ouzo

2. Submerse in water

Phase separation in hydrogels

Anise oil droplets in gellan gum
(physically crosslinked gel)



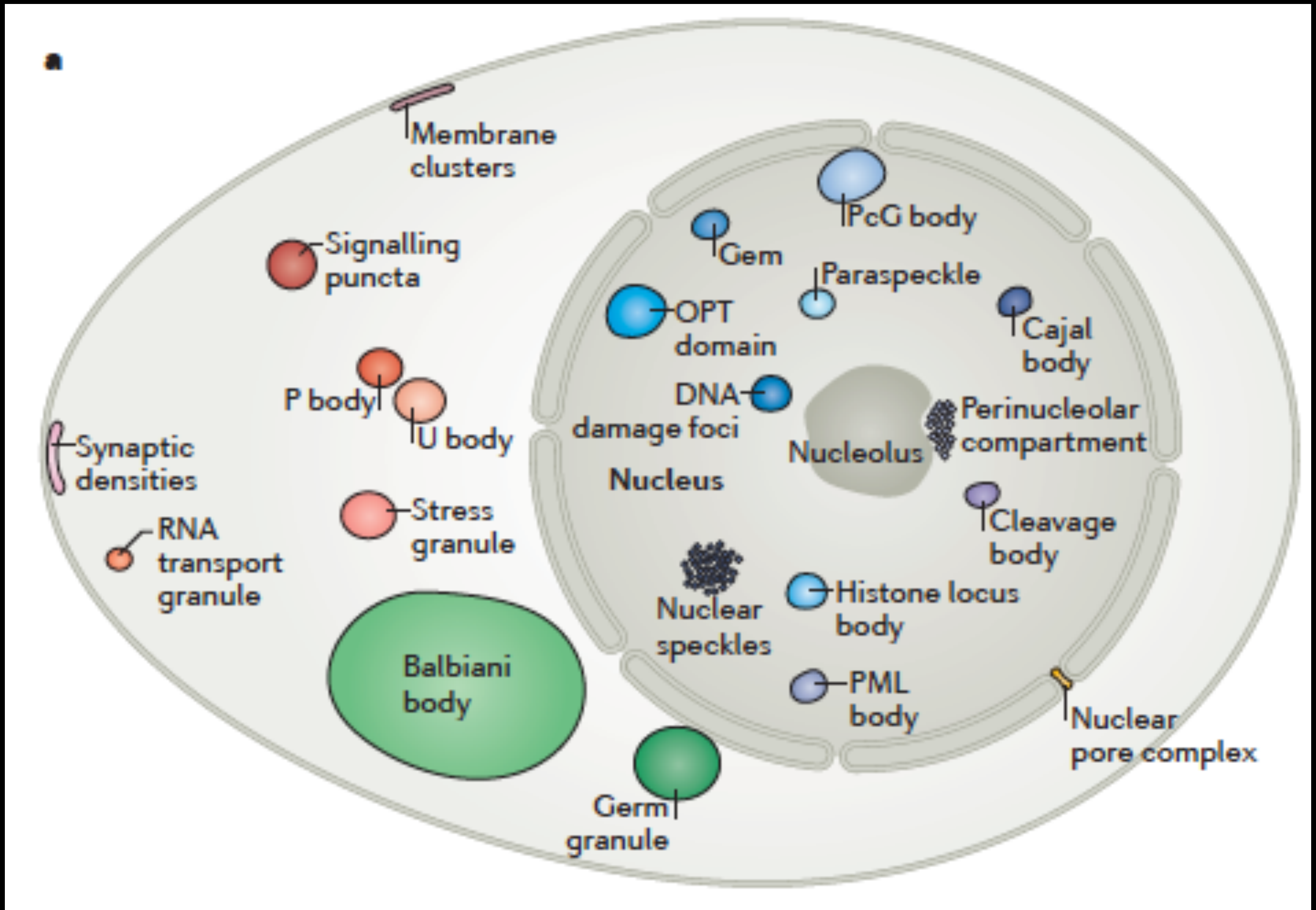


Phase separation of proteins in the cell

$$E \lesssim \frac{\rho_l RT}{M}$$

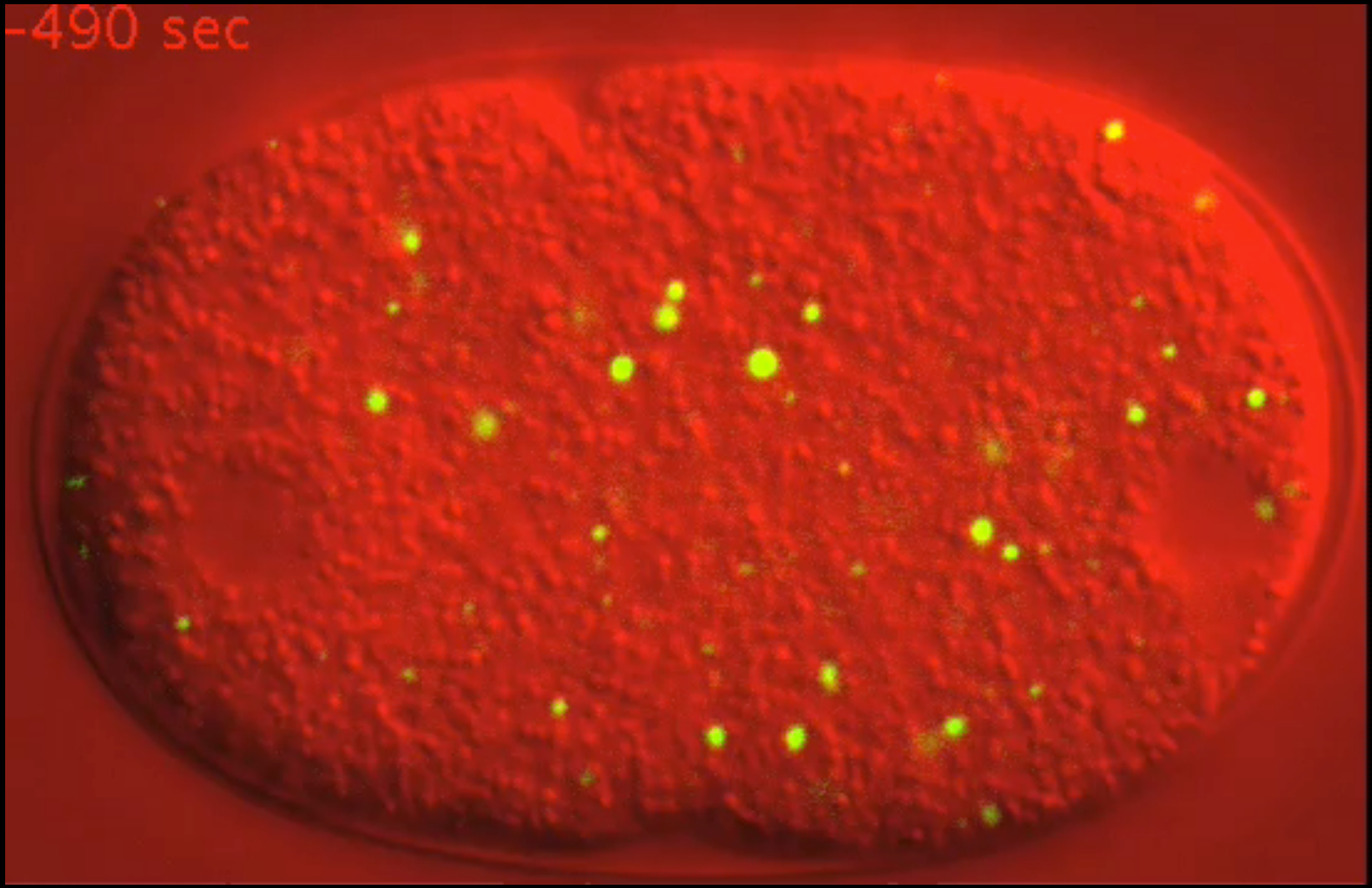
Phase separating liquid	M	E_{crit}	Suitable materials
Small molecule	100 g/mol	24MPa	Elastomers, Gels
Protein	10^5 g/mol	24kPa	Cell cytoskeleton

Phase separation in cells



Banani et al., *Nature Rev. Mol. Cell Biol.* (2017)

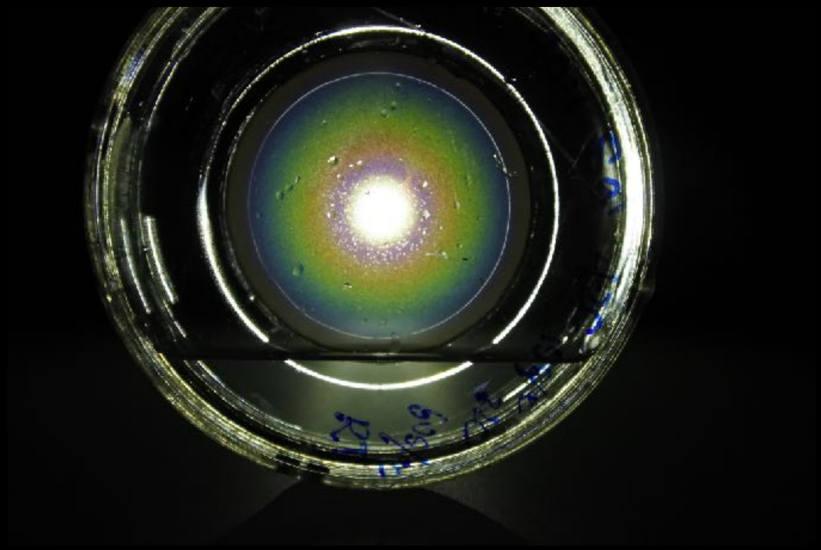
Phase separation in cells

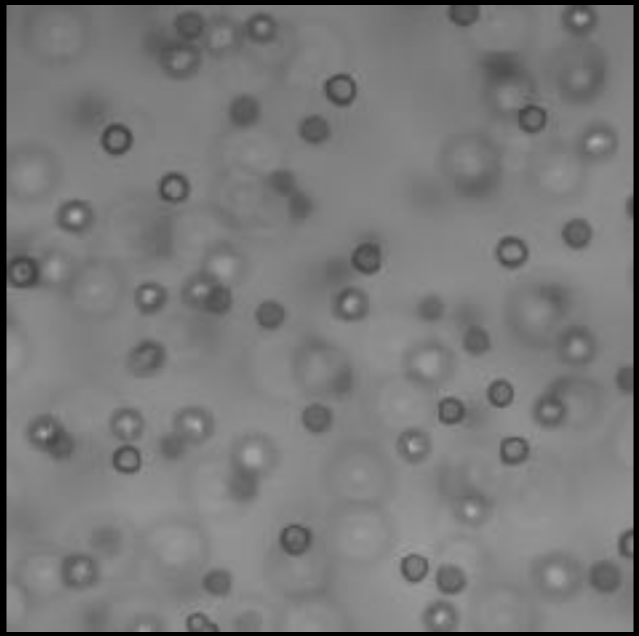


Brangwynne et al., *Science* (2009)

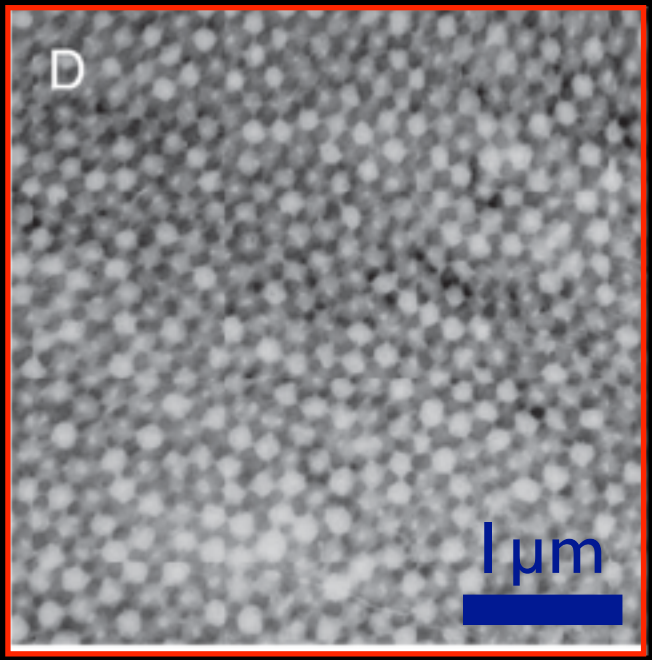
Next steps..

1) Make better colour!



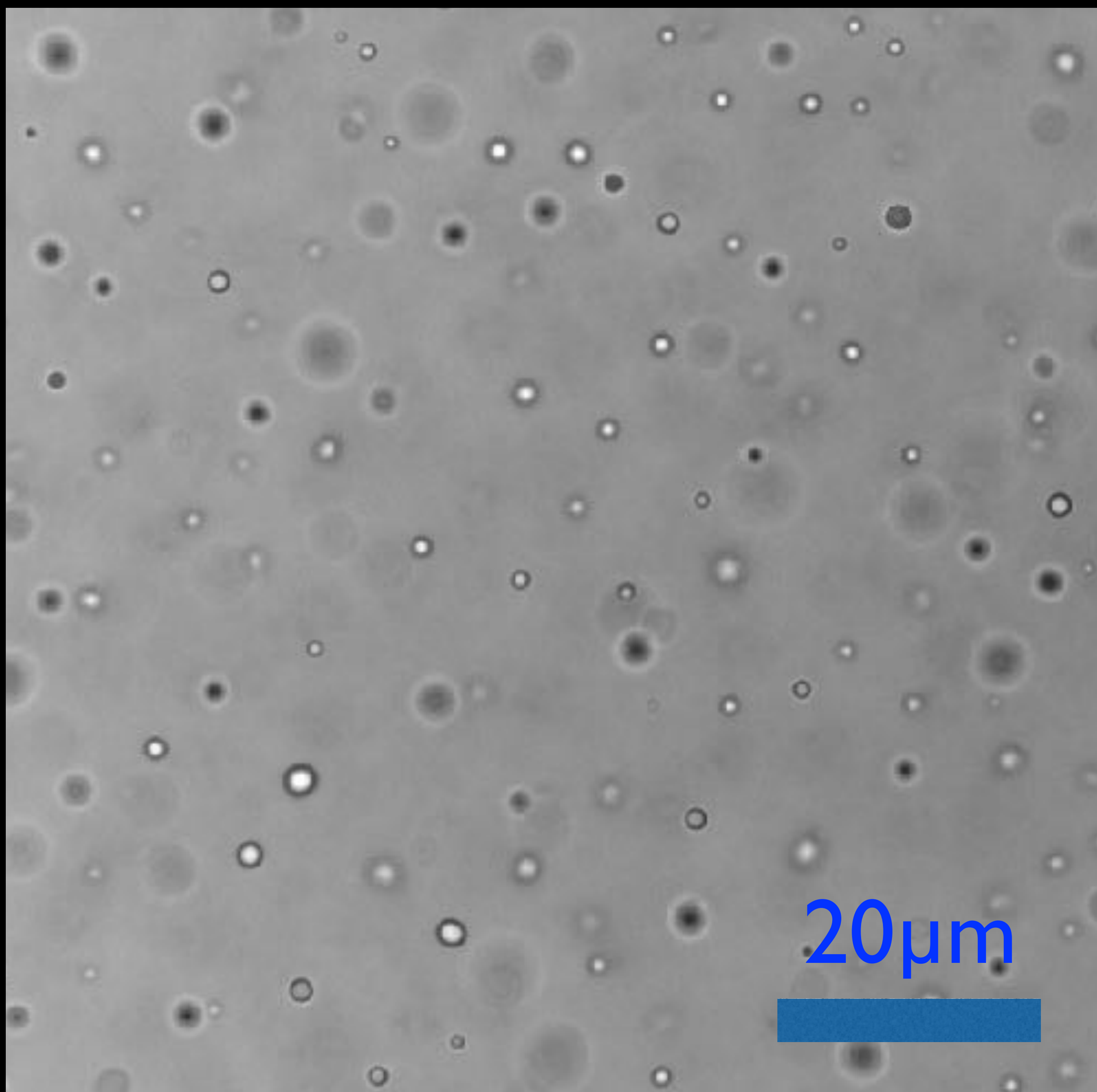


Need much denser materials

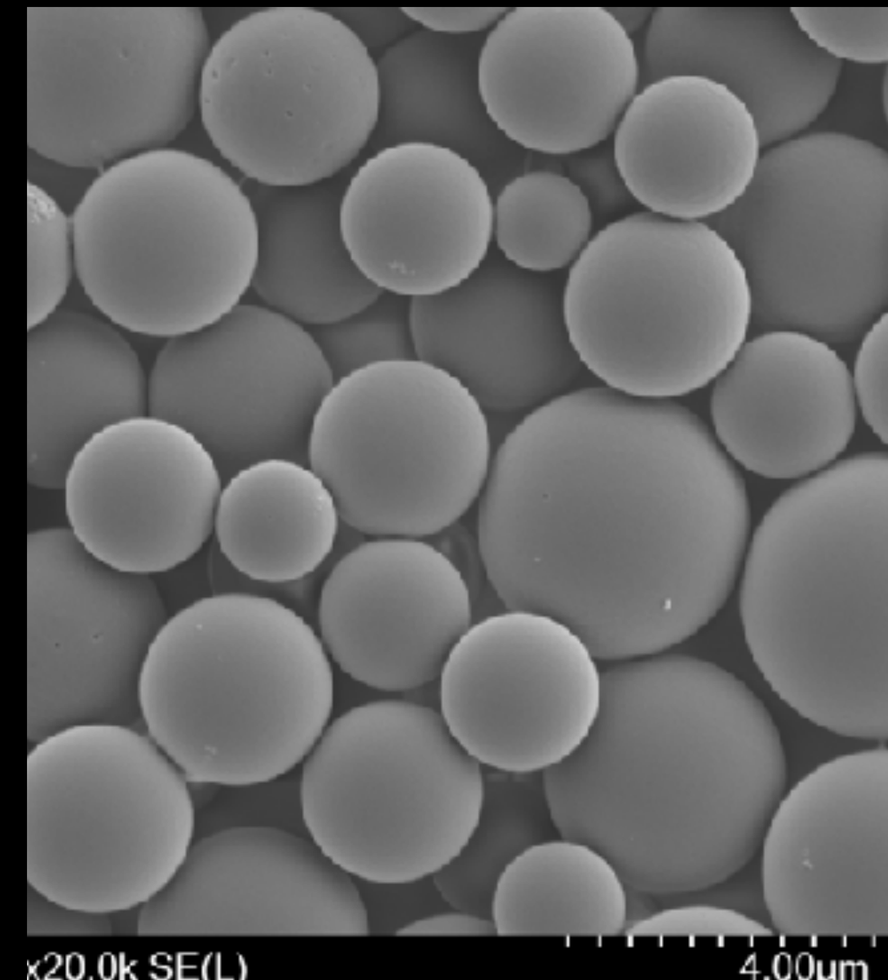


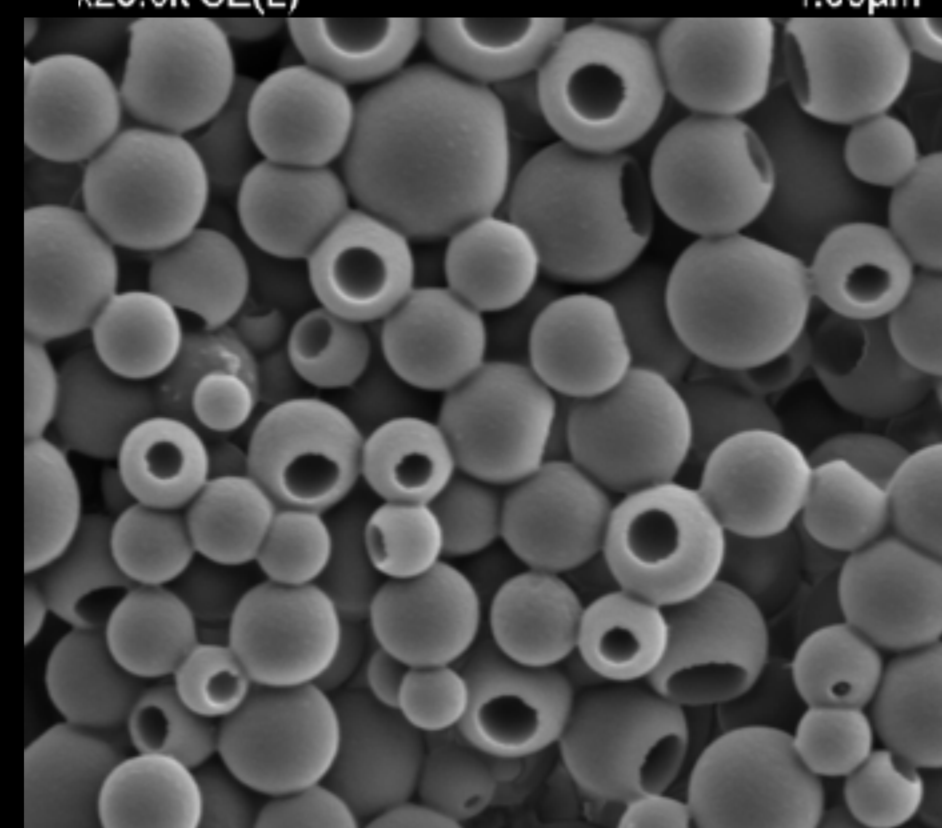
2) Make permanent colour

With a monomer, we can polymerise droplets
to make colloidal particles



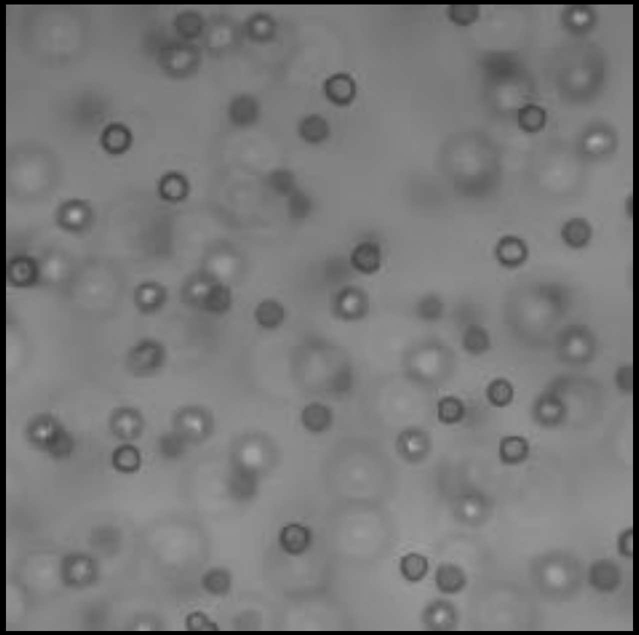
Styrene droplets in gellan gum
(physically cross linked gel)





Conclusions

- We can use nucleation/cavitation in soft solids to produce materials with well-defined/controlled microstructure



- Phase separation inside polymer networks has range of applications from colour, to studying small-scale fracture, making model composites, and cell biophysics, and there seems to be a lot of interesting physics to explore