

Elastic stresses reverse Ostwald Ripening

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Elastic stresses reverse Ostwald ripening

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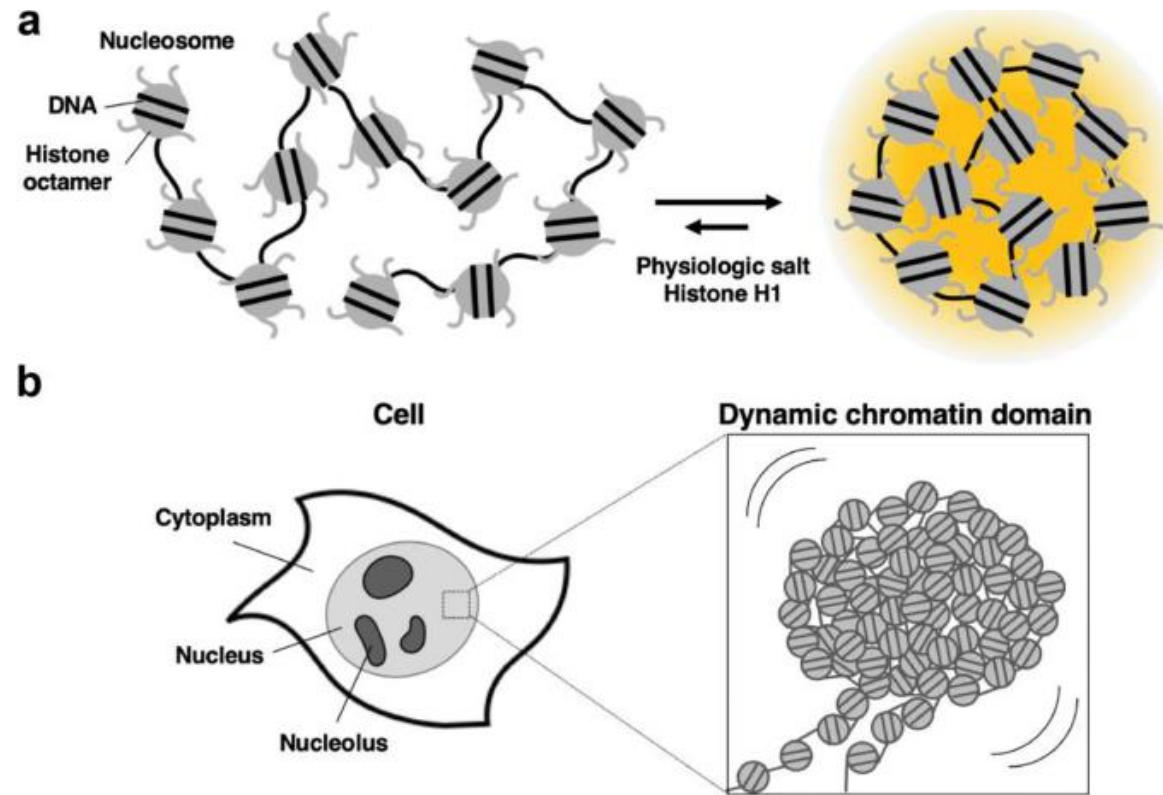
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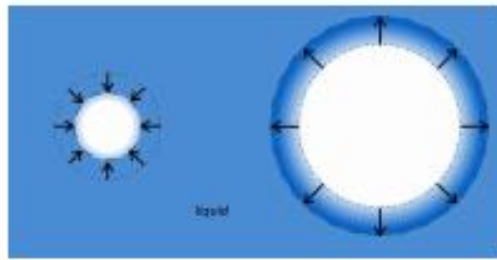
Motivation

The main motivation is the phase separation in living cells.



Ostwald Ripening

➤ Young-Laplace equation: $\Delta P = P_{in} - P_{out} = \frac{2\gamma}{R}$



Two gas bubbles with different radii in a liquid fluid.

Bigger: $\Delta P_R = \frac{2\gamma}{R}$
Smaller: $\Delta P_r = \frac{2\gamma}{r}$

$r < R$
 $P_r > P_R$

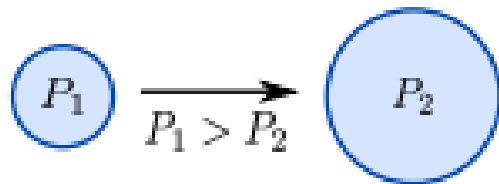
Elastic Ripening

There is an additional term in the Young Laplace equation.

Ostwald ripening
in liquids

$$P = \frac{2\gamma}{R}$$

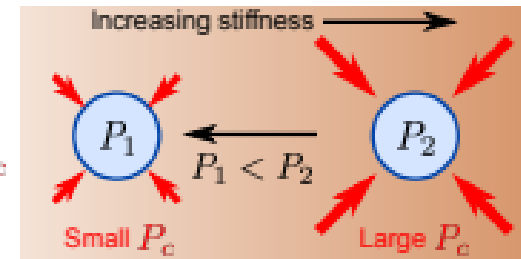
A



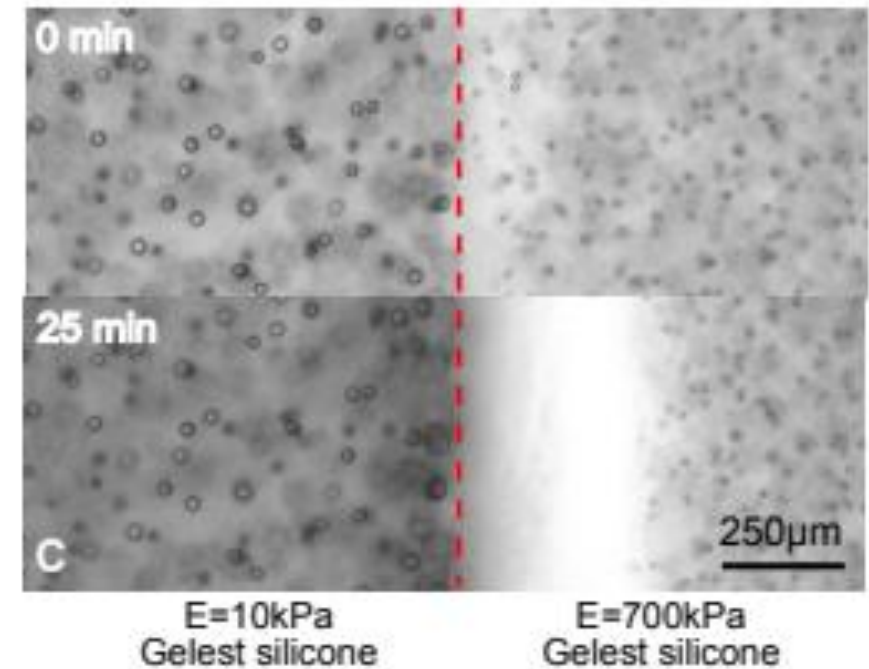
Elastic ripening
in solids

$$P = \frac{2\gamma}{R} + P_c$$

B

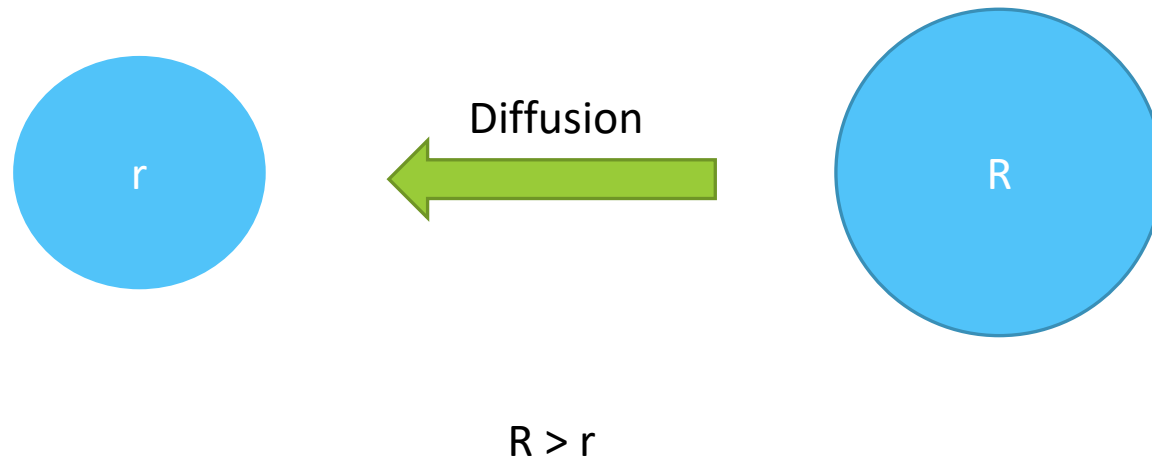


-
- Bubbles monodisperse
 - Growth = more the network squeezes
 - $P_c \sim E$
 - Pressure is heterogeneous.



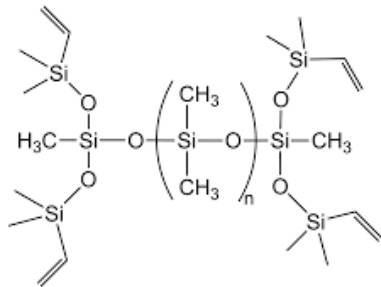
Objective

Elastic ripening phenomena can differ from the Ostwald ripening. In particular if certain conditions we can observe the growth of small droplets fed by the dissolution of large ones.

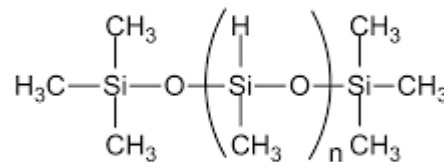


Gelest

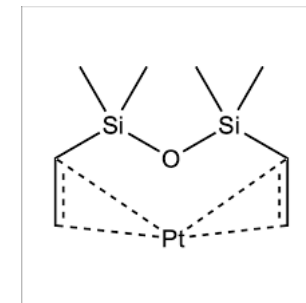
- Degased
- Cured at 60°C for at least one week.



(Divinyl-terminated
polydimethylsiloxane)(chains.)
(DMSV31, Gelest)



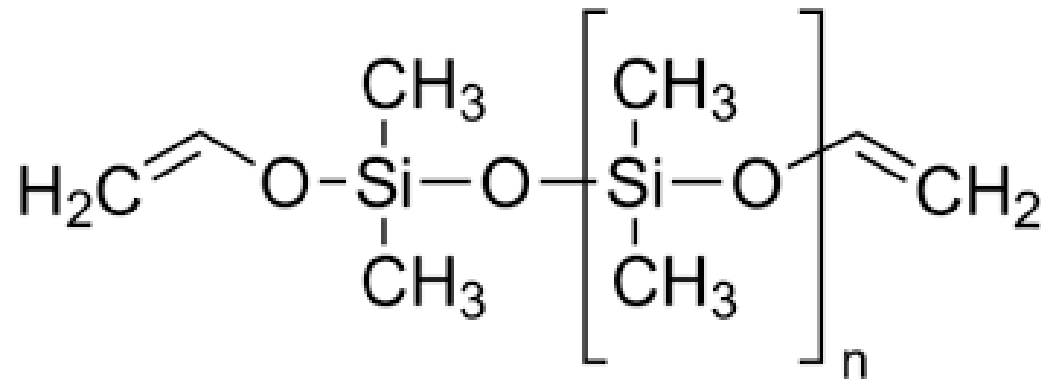
(Cross-linker.)
(HMS-301, Gelest)



(Catalyst.)
(SIP6831.2, Gelest)

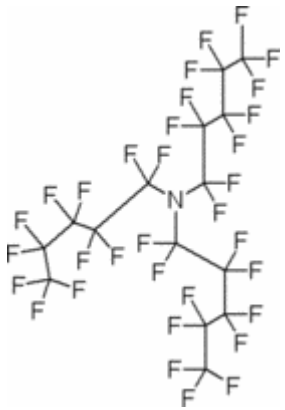
Sylgard

- Mixed if curing agents
- Degased
- Cured at 40–60°C for at least one week.



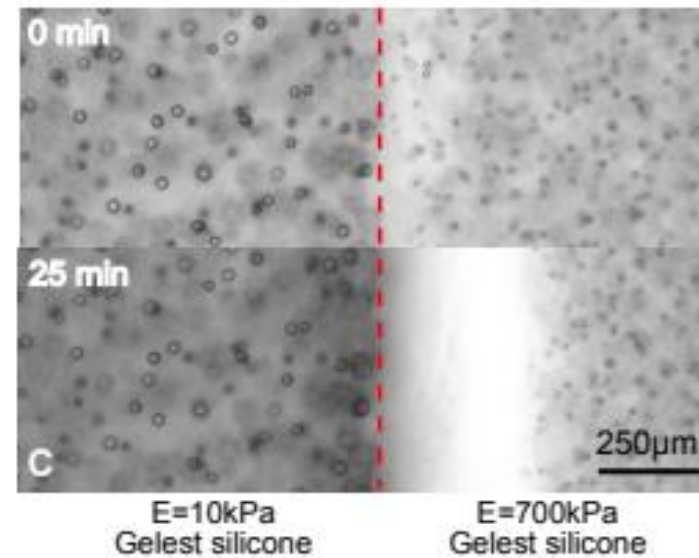
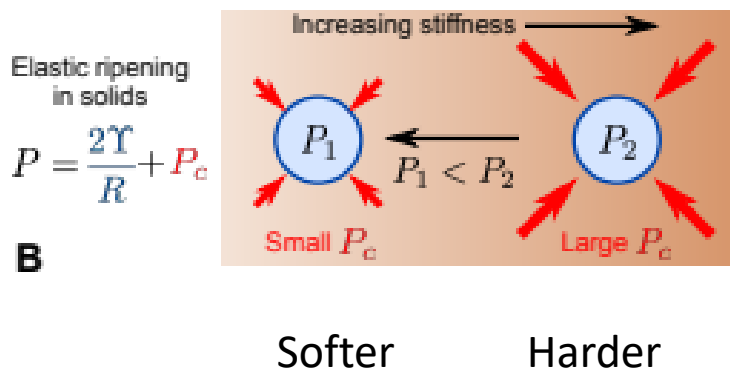
The Bubble Formation in the Gels

- Gels are saturated in Fluorinated oil (Fluorinert FC-770).
- Cooled passively to 22-23 °C.
- Grow by pushing open holes in the gel.
- First cure the stiffer silicone than the softer one.



Firts Results

After fast droplet formation, we observe slow evolution of the droplets near the interface.



The mechanisms in this process is different of the Ostwald ripening.

Comparison of the 2 Gels

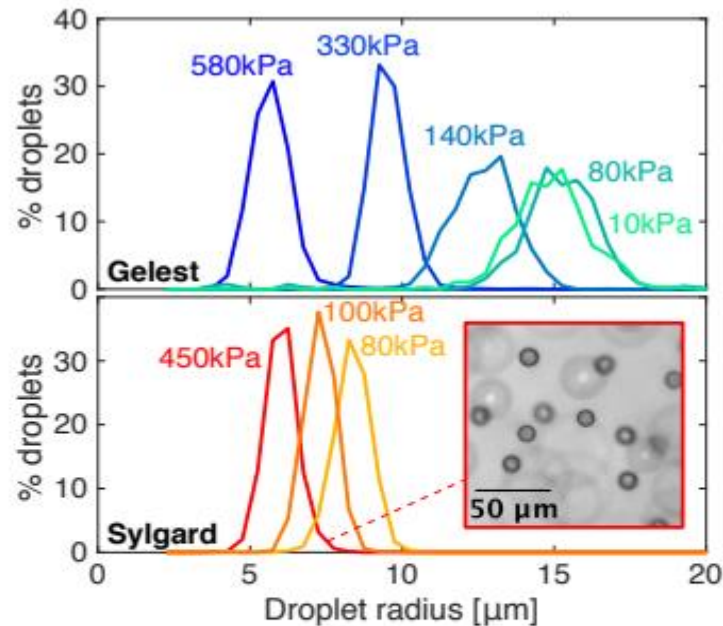


FIG. 2: *Droplets in Sylgard and Gelest silicones have different sizes.* The size distributions of droplets formed by phase separation in different stiffness silicones. For a given stiffness, droplets in Gelest silicones are typically larger than droplets in Sylgard silicones. The inset shows a typical image of droplets formed in Sylgard silicone with $E = 450\text{kPa}$.

Gelest

Stiffness: 10 to 580 kPa.

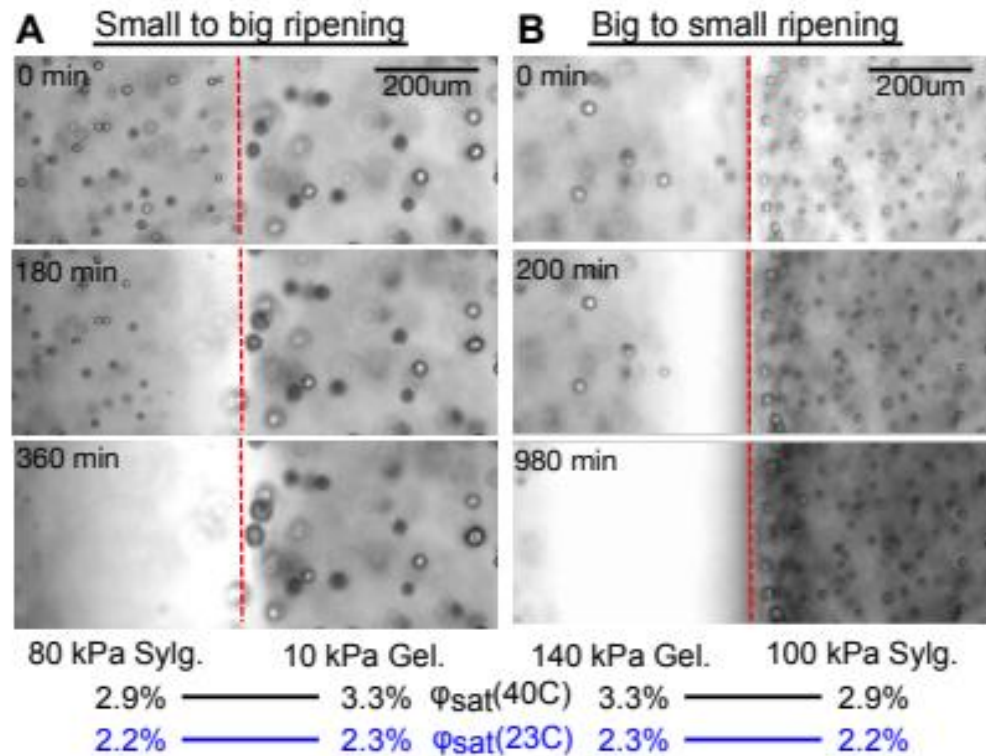
Mean droplet radius : 14.9 to 5.7 μm .

Sylgard

Stiffness: 80 to 450 kPa.

Mean droplet radius : 8.3 to 6.0 μm .

Experimental Results



- Samples made from only one of these silicone families, elastic ripening and Ostwald ripening proceed in the same direction.
- In A, smaller fluorinated oil droplets on the stiff side shrink while feeding the growth of larger droplets on the soft side.
- In B, larger droplets near the interface on the stiff side shrink while small droplets on the soft side grow.

A Complication

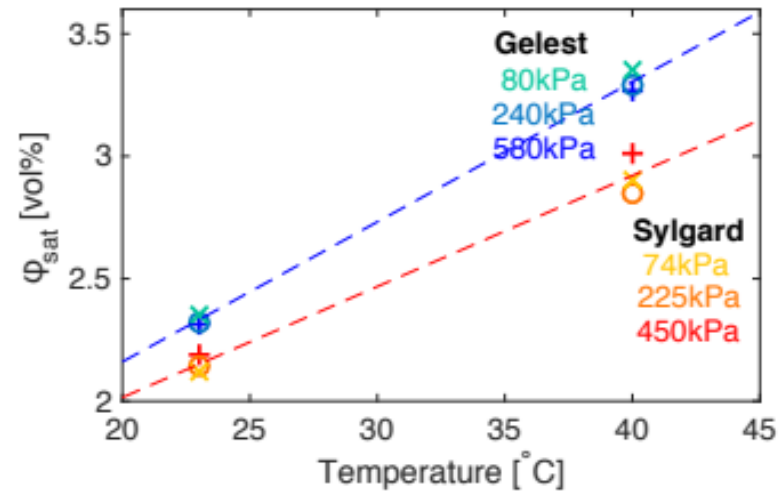


FIG. 4: *Sylgard and Gelest silicones have different saturations.* A plot of ϕ_{sat} as a function of temperature shows how fluorinated oil is more soluble in Gelest than in Sylgard silicones. The solubility is effectively independent of stiffness for the two different types of silicone.

- The saturation of the 2 gels increase if the T.
- The solubility of the fluorinated oil is diferente in the 2 gels.
- These factors is importante in the ripening behaviour.

Diffusion Process

Fick's Law

$$\vec{J} = -D\vec{\nabla}\phi$$

↓ Gels with a heterogeneous saturation.

$$\vec{J} = -\frac{\phi D}{k_B T} \vec{\nabla} \mu.$$

→ $\mu = k_B T \log(\phi/\phi_{sat}).$

$$\mu \approx P/n_L$$

Theoretical Result

$$P = \frac{2\Upsilon}{R} + P_c. \quad \xleftrightarrow{\text{Compressive stress.}} \quad P_c = \alpha E$$

Diference in pressure between two domains.

$$\Delta P = 2\Upsilon\Delta R/R^2 + \alpha\Delta E,$$

Elastic-dominated ripening when

$$\left(\frac{\Upsilon}{\Delta ER}\right) \left(\frac{\Delta R}{R}\right) \ll 1.$$

Since $\frac{\Delta R}{R} = O(1)$. We have $\left(\frac{\Upsilon}{\Delta ER}\right) \ll 1$

$$\Delta P \sim \Delta E$$

Simulation

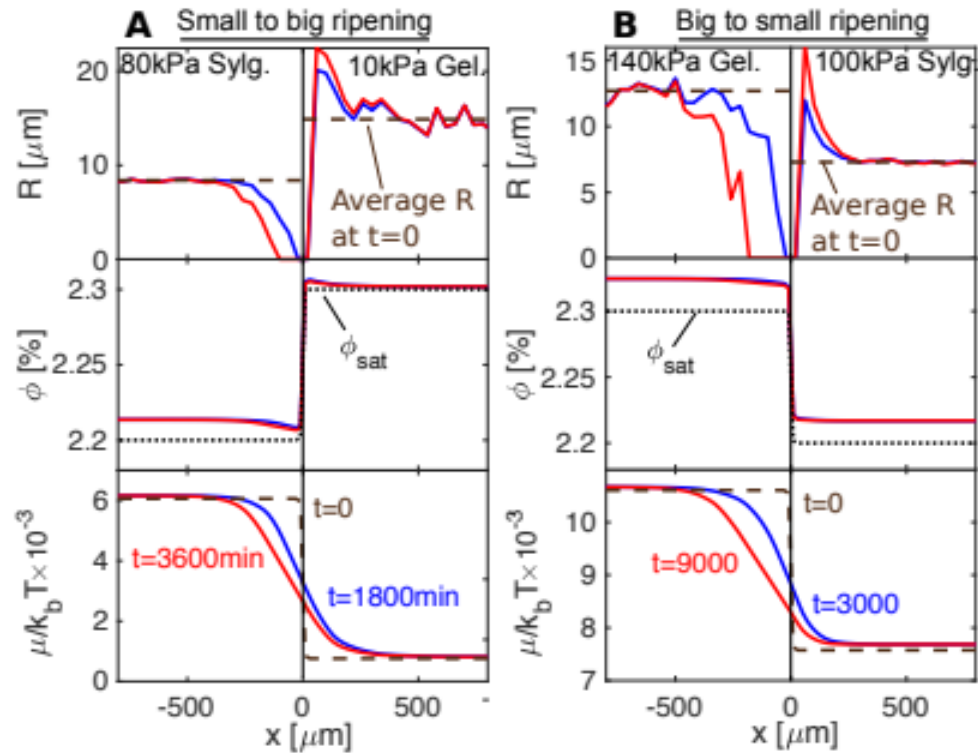


FIG. 5: Numerical simulations of the experimental setups presented in Figure 3. Top: Droplet radius. Middle: Concentration in the dilute phase, ϕ . Bottom: chemical potential, μ . A) For 80kPa Sylgard next to 10kPa Gelest, elastic ripening moves against concentration gradients. B) For 140kPa next to 100kPa Sylgard, elastic ripening goes against classical Ostwald ripening.

Conclusion

Droplets grown in a Polymer network have contribution from both surface tension and the Compressive network stress. In case of the reverse Ostwald ripening the former on dominated the process.

The experiments and theory are inspired by recent observations of phase separation in living cells that is a complex system. But the system on this work can be considered in near equilibrium. So these results should not be applied in living cells, but can be usefull in near equilibrium process like the formation of segregated ice during the processing of frozen foods, in cryopreservation, etc.

THANKS!